The reactivity of rare-earth metallocenes towards alkynes
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2. Rare-earth metalallocene propargyl/allenyls

2.1. Introduction

Organo rare-earth metal chemistry has witnessed a tremendous growth during the last two decades.\(^1\) This spectacular growth in research activities can be attributed to the fact that many of these compounds exhibit not only unique structural and physical properties, but are highly active catalysts in a variety of catalytic processes as well. Among the different classes of organo rare-earth metal complexes, the hydride and alkyl derivatives are the most studied, as they often display activities dramatically higher than that of comparable transition metal complexes. Other classes, such as alkynyl, aryl and allyl derivatives, have been investigated less extensively, but their preparation, molecular structure and properties are well-documented.

In contrast to allenyl and propargyl derivatives of transition metals, alkali metals and alkaline earth metals, which play an important role in organic synthesis,\(^2\) relatively little is known about the corresponding rare-earth metal congeners. \(\eta^1\)-Allenyl (I) and \(\eta^1\)-propargyl (III) metal complexes are known to exhibit interesting structural features and an unusual reactivity (Scheme 2-1).\(^3\) An aspect that has received much recent attention is their tautomeric behavior. Metal \(\eta^1\)-propargyls have been shown to undergo both reversible and irreversible tautomerization into metal \(\eta^1\)-allenyls. In addition, well-characterized delocalized \(\pi\)-bonded \(\eta^3\)-allenyl/propargyl complexes (II) are known as well.\(^4\)

To the best of our knowledge, the first report of rare-earth metal allenyl and propargyl derivatives is the reaction of Cp\(^*\)\(_2\)LuMe with allene and 2-butyne in the early 1980s.\(^5\) A facile 1,3-metal shift of the propargyl to yield the observed allenyl was put forward in a review article (Scheme 2-2), but no experimental data were given in the references. In 1990 Heeres et al. reported a series of spectroscopically characterized alkyl- and silyl-substituted lanthanidocene propargyls Cp\(^*\)\(_2\)LnCH\(_2\)CCR (Ln = La, Ce).\(^6\) The reactivity of these derivatives remained largely unexplored and the exact nature of the bonding was unknown, as structural data were lacking.

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**Scheme 2-1.** Structural isomerism in allenyl/propargyl metal complexes.

**Scheme 2-2.** Early examples of propargyl and allenyl lanthanides.
Since then, only three studies involving well-defined allenyl/propargyl lanthanide species have appeared in literature, including the spectroscopically characterized yttrium $\eta^1$-allenyl species A, which is reported to be in a rapid equilibrium with its $\eta^1$-propargyl isomer $A'$,\textsuperscript{7} the structurally characterized $\eta^3$-propargyl samarium half-sandwich complexes (e.g. B), incorporating a chelating allenyl/propargyl ligand system,\textsuperscript{8} and a divalent ytterbium $\eta^1$-propargyl (C) which has also been structurally characterized (Scheme 2-3).\textsuperscript{9} The only other reports regarding propargyl and/or allenyl rare-earth metal complexes are reactive intermediates in synthetic organic reactions, prepared \textit{in situ} via transmetalation reactions of organopalladium intermediates\textsuperscript{10} or Grignard reagents.\textsuperscript{11}

Lanthanide propargyl derivatives Cp*$_2$LnCH$_2$CCR have been proposed to be the active catalyst in the catalytic cyclodimerization of 1-methylalk-2-ynes CH$_3$CCR in the presence of Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = La, Ce) (Scheme 2-4).\textsuperscript{6} Motivated by the possibility to apply this reaction to bifunctional aromatic substrates and thereby prepare a novel class of polymers (Chapter 3), a study of the synthesis, structure and reactivity of rare-earth metallocene aryl-substituted propargyls was initiated. The investigations described in this chapter represent the first systematic study of allenyl/propargyl derivatives of group 3 and lanthanide metals and include the first crystallographic structure determination of these derivatives having the common trivalent oxidation state and non-chelating allenyl/propargyl ligands.

2.2. Synthesis of substrates

Introduction

In order to explore the scope of propargylic C-H activation of 1-methylalk-1-ynes by rare-earth metalloocene derivatives, a series of 1-aryl-1-propynes was prepared. \textit{Ortho}-substituted phenyl derivatives were prepared to study steric effects and a pentafluorophenyl derivative was prepared to address electronic effects.

1-(2-methylphenyl)-1-propyne (2)

The synthesis of 2-propynyltoluene (2) was straightforward and accomplished by palladium-catalyzed cross-coupling of the corresponding iodoarene and propynylzinc bromide (the Negishi reaction, Scheme 2-5).\textsuperscript{12} The zinc reagent was prepared \textit{in situ} from commercially available propynylmagnesium bromide, propyne gas and anhydrous zinc bromide.
The preparation of 2,6-dimethylpropynylbenzene (3) was achieved analogously to 2-propynyltoluene, but started with the aqueous iodode diazotization of 2,6-dimethylaniline, according to a published procedure.\textsuperscript{13} When 2,6-dimethyliodobenzene was cross-coupled via the Negishi protocol, the corresponding 1-aryl-1-propyne was obtained in high yield and purity.

\begin{scheme}
\begin{center}
\includegraphics[width=\textwidth]{Scheme_2-5}
\end{center}
\end{scheme}

\textit{Reaction conditions:} (i): CH\textsubscript{3}CCMgBr (1.2 equiv), ZnBr\textsubscript{2} (1.2 equiv), Pd(PPh\textsubscript{3})\textsubscript{4} (5 mol%), THF, 50 °C. (ii): (1) NaNO\textsubscript{2}, HCl; (2) KI.

\begin{scheme}
\begin{center}
\includegraphics[width=\textwidth]{Scheme_2-6}
\end{center}
\end{scheme}

\textit{Reaction conditions:} (i): HBF\textsubscript{4}, n-BuONO, 0 °C, EtOH/H\textsubscript{2}O; (ii): KI, I\textsubscript{2}, copper bronze, DMSO, 50 °C; (iii) n-BuONO, KI, I\textsubscript{2}, copper bronze, DMSO, 50-60 °C.

1-(2,6-diisopropylphenyl)-1-propyne (4)

Unfortunately, the application of a similar strategy in the preparation of 1-(2,6-diisopropylphenyl)-1-propyne (4) was not successful. When 2,6-diisopropylaniline was subjected to the standard iododediazotization methodology, a mixture was obtained which contained 2,6-diisopropylchlorobenzene (41%, GC), 2,6-diisopropylphenol (7%), 2,6-diisopropyliodobenzene (21%) and an unknown compound (m/z 352, 11%), according to GC-MS analysis.\textsuperscript{14} It was believed that the low solubility of 2,6-diisopropylaniline in aqueous solution allowed for the occurrence of competing reactions.\textsuperscript{15} The crude yield of the iodo compound (47%, GC) was increased by the addition of ethanol and the use of aqueous hydrogen iodide solution. Surprisingly, the use of copper(I) iodide or copper bronze was also found to increase the crude yield of the desired iodo compound (60-65%, GC).\textsuperscript{16} Subsequent column chromatography (silica, hexanes) and vacuum distillation (120-140 °C, 5 mmHg) furnished samples of desired aryl iodide in reasonable purity (95%, GC). Nonetheless, samples of the corresponding propynylarene (97% pure, GC), prepared via cross-coupling with propynylcopper (vide infra), were unsuitable for the present reactivity studies involving organo rare-earth metallocenes, presumably due to inseparable, unidentified impurities of the iododiazotization reaction.

It should be noted that the synthesis of 2,6-diisopropyliodobenzene (by aqueous iododiazotization of 2,6-diisopropylaniline) has been reported after preparation of this manuscript. In all of these cases, however, experimental details are lacking\textsuperscript{17} and/or the isolated yields are quite low (35%).\textsuperscript{18} The synthesis of 2,6-diisopropylbromobenzene is also documented in literature (albeit in low yields and purity either via the...
Sandmeyer reaction\textsuperscript{19} or via aprotic diazotization\textsuperscript{20}), but was not considered in this study, as iodides are generally more reactive than bromides and triflates in transition metal-catalyzed cross-coupling reactions with organometallics.\textsuperscript{21} In view of the low solubility of 2,6-diisopropylaniline in aqueous hydrogen halide solutions, continued efforts to prepare 2,6-diisopropyliodobenzene were directed along the lines of aprotic diazotization.\textsuperscript{22} Several reports involving the in situ aprotic diazotization of 2,6-diisopropylanilines (followed by chlorination\textsuperscript{23a} or cyanation\textsuperscript{23b}) and the preparation of substituted iodobenzenes\textsuperscript{24} (by in situ aprotic diazotization of the corresponding anilines in the presence of iodine) suggested that in situ aprotic iododiazotization of 2,6-diisopropylaniline should, in principle, be feasible, but initial attempts based on these protocols were unsuccessful.\textsuperscript{25} Based on experiments with 2,6-diisopropylbenzenediazonium tetrafluoroborate,\textsuperscript{26} it was possible to develop a convenient procedure in which 2,6-diisopropylaniline could directly be transformed into the corresponding iodide by treatment with $n$-butyllithium in the presence of iodine, potassium iodide and copper bronze under an inert atmosphere and using dry DMSO as a solvent (Scheme 2-6). The only by-product was 1,3-diisopropylbenzene ($<$1\%, GC/GC-MS) which could completely be separated by column chromatography (silica, hexanes) or vacuum distillation (120-140 °C, 5 mmHg).

In contrast to 2,6-dimethyliodobenzene, its diisopropyl analogue did not react with propynylmagnesium bromide and zinc bromide in the presence of Pd(PPh$_3$)$_4$, not even after a prolonged reaction time or after increasing the reaction temperature and catalyst loading.\textsuperscript{27} This lack of reactivity can plausibly be ascribed to the steric hindrance of the two ortho-isopropyl groups.\textsuperscript{28} Other attempts involving the cross-coupling of 2,6-diisopropyliodobenzene with a propynylboronic ester (the Suzuki-Miyaura reaction)\textsuperscript{30} and the use of 2,6-diisopropylphenyl triflate were equally disappointing.\textsuperscript{31}

An early report in which the substitution of 2,4,6-triisopropyliodobenzene was achieved by a copper(I) acetylide\textsuperscript{32}, albeit in low yield, prompted us to explore this reaction (the Castro reaction) in the present context.\textsuperscript{33} Motivated by the well-recognized highly explosive nature of copper(I) acetylides,\textsuperscript{34} attempts were undertaken to develop a convenient one-pot procedure.\textsuperscript{35} These attempts failed, however, and the Castro reaction had to be performed with isolated propynylcopper (prepared in ammonia from propyne gas, according to a modified published procedure\textsuperscript{36}). The potentially explosive copper compound was kept moist with ether after isolation and added directly in a large excess to a solution of the 2,6-diisopropyliodobenzene in dry pyridine. Heating the suspension at reflux under an inert nitrogen atmosphere for several days afforded the desired propynylarene (4) in good yield (Scheme 2-7). The only contaminants in the crude product mixture were 1,3-diisopropylbenzene (4\%, GC/GC-MS) and 2,6-diisopropyliodobenzene (5\%) which could be removed to a large extent after repeated column chromatography (silica, hexanes).\textsuperscript{37} The final sample of 4 contained small amounts of 1,3-diisopropylbenzene ($<$2\%, $^1$H NMR). As this compound was considered to be relatively inert towards the rare-earth metallocene derivatives in subsequent reactivity studies, no further attempts were undertaken to obtain a sample of higher purity.

1-Pentafluorophenyl-1-propyne (5)

In order to investigate electronic effects in the propynylaromatic substrates as well, it was decided to prepare pentafluoro-1-propynylbenzene (5). According to a modification of a general procedure, pentafluorophenylpropyne (5) was prepared in a low yield (24\%) from the reaction of propynyllithium with excess hexafluorobenzene in THF at low temperature (Scheme 2-8).\textsuperscript{38} Propynyllithium was generated in situ from propyne gas and $n$-butyllithium in THF at -70 °C. The product mixture was evaporated to dryness after

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**Scheme 2-7.** The synthesis of 1-(2,6-diisopropylbenzene)-1-propyne 4.

\[
\begin{align*}
\text{CuSO}_4 + \text{CH}_3\text{C} &= \text{CCH}_3 & \text{Cu} &= \text{C} \equiv \text{CCH}_3 \\
\text{Cu} &= \text{C} \equiv \text{CCH}_3 & \text{CuSO}_4 + \text{CH}_3\text{C} &= \text{CCH}_3
\end{align*}
\]

Reaction conditions: (i): NH$_2$OH·HCl, NH$_3$, RT (aq); (ii): pyridine, 110-120 °C.
which the product was conveniently isolated by sublimation. The major by-product of the reaction was identified as 1,4-dipropylnhexa-fluorobenzene.

2.3. Synthesis of propargyl/allenyls

2.3.1. Introduction

As synthetic routes in organo rare-earth metal chemistry starting from halide derivatives are known to be plagued by the undesired incorporation of alkali metal salts and solvents, the most straightforward synthetic strategy towards Cp*₂LnCH₂CCR complexes via salt metathesis reaction of a halide precursor and a propargylic metal salt was a priori considered to be problematic. Owing to this tendency to form “ate” complexes, Lewis-base free complexes are typically prepared from alkyl or hydride precursors in the organometallic chemistry of rare-earth metals.

The alkyl derivative of the type Cp*₂LnCH(SiMe₃)₂ represents the most commonly used and well-characterized entry into the synthetic and reactive chemistry of Lewis-base free, 14-electron lanthanidocenes. Attempts to prepare Lewis-base free, monomeric propargyl/allenyl rare-earth metal complexes started therefore with reactivity studies of Cp*₂LnCH(SiMe₃)₂ (6) and [Cp*₂Ln(µ-H)]₂ (7) (Ln = La, Y) towards 1-methylalkynes.

2.3.2. Reactions of alkyls with 1-aryl-1-propynes

1-Phenyl-1-propyne (1) and ortho-substituted 1-phenyl-1-propynes (2–4)

When an equimolar amount of 1-phenyl-1-propyne (1) and Cp*₂LaCH(SiMe₃)₂ (6a) was allowed to react in benzene-d₆, no reaction was observed by ¹H NMR spectroscopy after several days. The clean, but slow formation of the desired propargyl species Cp*₂LaCH₂CCPh (7a) was apparent upon warming the reaction mixture to 80 °C. For example, 2% of 6a was converted into 7a and CH₂(SiMe₃)₂ after 3 hours at 80 °C (Scheme 2-9). The rate of propargylic metalation was only moderately increased by increasing the reaction temperature. For example, 14% of 6a was converted into 7a and CH₂(SiMe₃)₂ after 20 hours at 100 °C. The use of an excess amount of substrate, on the other hand, resulted in a significant acceleration of propargylic metalation, accompanied by the formation of several organic products, as indicated by ¹H NMR spectroscopy and GC-MS analysis after quenching the reaction mixture with methanol-d₄ (Section 2.5.6). For example, the use of a 10-fold molar excess of substrate led to the complete conversion of 6a into 7a, CH₂(SiMe₃)₂, and several organic products after 2 hours at 100 °C.

Analogous reactions of Cp*₂YCH(SiMe₃)₂ (6b) with 1-phenyl-1-propyne (1) and Cp*₂LaCH(SiMe₃)₂ (6a) with CH₂CCC₆H₄Me-2 (2), CH₂CCC₆H₄Pr₂-2,6 (3) and CH₂CCC₆H₄Pr₂-2,6 (4) gave similar results, but the corresponding propargyl species Cp*₂LnCH₂CCAr (7-10) was formed at a considerably lower rate (Scheme 2-9). For example, a stoichiometric mixture of 6b and 1 gave 5% conversion of the alkyl derivative (6b) into the propargyl derivative (7b) after 2 days at 100 °C.

These reactions allowed for the spectroscopic characterization of the corresponding propargyls (7-10) by means of multinuclear 1D and 2D NMR spectroscopy. In all cases, the Cp* ligands were magnetically
equivalent and one CH$_2$ signal was observed in the $^1$H NMR spectrum, suggesting that the propargyls Cp*$_2$Ln($^1$-CH$_2$CCAr) in solution adopt either a static $^1$-propargyl structure or exist as a rapid equilibrium mixture of the $^1$-propargyl and $^1$-allenyl tautomers. Variable-temperature $^1$H and $^{13}$C NMR studies of Cp*$_2$LaCH$_2$CCPh (7a), Cp*$_2$YCH$_2$CCPh (7b) and Cp*$_2$LaCC$_6$H$_3$Me$_2$-2,6 (9a) in toluene-$d_8$ down to -80 °C and up to 120 °C indicated that these complexes are nonfluxional on the $^1$H and $^{13}$C NMR time scale in this temperature range. The details of NMR and infrared spectroscopic parameters are discussed in Section 2.4.

These initial reactivity studies demonstrated that the reactions of the alkyl derivatives Cp*$_2$LnCH(SiMe$_3$)$_2$ (6) with 1-aryl-1-propynes (1-4) proceed via slow and selective propargylic C-H activation of the 1-aryl-1-propynes, even at elevated temperatures. The slow rate of propargylic metalation renders the preparation of propargyl derivatives Cp*$_2$LnCH$_2$CCAr (7-10) via the reactions of 6 with 1-aryl-1-propynes inconvenient. Although the rate of reaction was considerably increased by the use of an excess amount of substrate, the concomitantly formed organic products impeded the isolation of 7 by fractional crystallization and extraction. As a consequence, the preparation of Cp*$_2$LnCH$_2$CCAr (7-10) from the reaction of 6 and 1-4 were found to be impractical and other routes towards these propargyls were explored.

1-Pentafluorophenyl-1-propyne (5)

In marked contrast to the reactions of Cp*$_2$LnCH(SiMe$_3$)$_2$ (6 (Ln = La, Y)) with phenylacetylene and ortho-substituted analogues, such as 2-ethyltoluene and (2,6-dimethylphenyl)acetylene, that proceed via rapid acetylenic metalation, even at low temperatures (Chapter 4), the present reactions of 6 with 1-phenyl-1-propyne and ortho-substituted analogues were found to proceed via slow propargylic metalation. It seems natural to ascribe the lower rate of propargylic C-H activation relative to acetylenic C-H activation to the lower (kinetic) acidity of the propargylic C-H bond. A study of the lithiation reactions of a series of 1-aryl-1-propynes revealed that the rate of propargylic lithiation of 1-methyl-1-alkynes increases with the electron-withdrawing capacity of the aromatic group. Accordingly, the reaction of 6 and 1-pentafluorophenyl-1-propyne (5) was conducted to investigate whether propargylic metalation by Cp*$_2$LnCH(SiMe$_3$)$_2$ (6) could be increased upon increasing the acidity of the propargylic C-H bond in this system. The electron-withdrawing and carbanion-stabilizing capacity of the pentafluorophenyl group is well established.

When a mixture of Cp*$_2$LaCH(SiMe$_3$)$_2$ (6a) and a stoichiometric amount of CH$_3$CCC$_6$F$_5$ (5) was heated in benzene-$d_6$ to 50 °C for 1 day, no reaction was observed by $^1$H NMR spectroscopy. The slow formation of the propargyl Cp*$_2$LaCC$_6$F$_5$(11a) and CH$_3$(SiMe$_3$)$_2$ was observed after heating the reaction mixture for several hours at 80 °C. For example, 12% of 6a was converted after 52 hours at 80 °C. Complete conversion of 6a into 11a and CH$_3$(SiMe$_3$)$_2$ was observed after heating the reaction mixture for 13 days at 80 °C, albeit less selectively as observed previously for 1-phenyl-1-propyne and its ortho-substituted analogues (vide supra). Although the reaction of Cp*$_2$LaCH(SiMe$_3$)$_2$ (6a) and CH$_3$CCC$_6$F$_5$ (5) yielded 11a as the major organometallic product, based on the presence of one major Cp* $^1$H NMR resonance at $\delta$ 1.80 ppm, the yield was only 47%, based on integration versus CH$_3$(SiMe$_3$)$_2$. 

\[ \text{Scheme 2-9. The reactions of 6 with 1-5.} \]

\[
\begin{align*}
\text{Cp*}_2\text{LnCH(SiMe}_3\text{)_2} + \text{CH}_3\text{CCCAr} & \xrightarrow{\Delta} \text{Cp*}_2\text{LnCH}_2\text{CCAr} + \text{CH}_3\text{(SiMe}_3)\text{)_2} \\
\text{Ln} &= \text{La (a), Y (b)}
\end{align*}
\]

Ar

CH$_3$CCAr

Cp*$_2$LnCH$_2$CCAr

1 2 3 4 5

6 7 8 9 10 11
Multinuclear NMR spectroscopy and GC/GC-MS analysis of the reaction mixture after quenching with H\textsubscript{2}O and D\textsubscript{2}O plausibly ruled out the occurrence of H/D scrambling at the Cp* methyl groups and C-F activation of 5, but failed to shed light on the identities of the formed organometallic by-products. Because quantitative 1H NMR analysis indicated that 0.90 equiv. of 5 was converted relative to CH\textsubscript{2}(SiMe\textsubscript{3})\textsubscript{2} after complete conversion of 6\textsubscript{a}, it is believed that the low yield of Cp*\textsubscript{2}LaCH\textsubscript{2}CCC\textsubscript{6}F\textsubscript{5} (11\textsubscript{a}) is the result of the limited thermal stability of 11\textsubscript{a}. Additional support for this view is provided by the observed lower yield of 11\textsubscript{a} (25%), when the analogous reaction was conducted at 100 °C.

The validity of the linear relationship between the rate of proton transfer from a carbon acid and the first-order carbon-hydrogen coupling constant of the corresponding carbon (\textit{J}\textsubscript{CH}) has been demonstrated by many studies.\textsuperscript{44} The rationale for this behavior is found in the relative amount of s-character of the hybrid orbital on the carbon atom. As the s-character increases, the hybrid orbital is more tightly bound to the carbon atom and the C-H bond becomes more polar, thereby increasing the acidity of the hydrogen atom. Conversely, the formed anion is the most stable in the orbital with the highest s-character. Hence, the following relative order of increasing kinetic acidity was found: 3 \approx 4 < 1 < 5, on the basis of the first-order carbon-hydrogen coupling constant of the propargylic methyl group (\textit{J}\textsubscript{CH}).\textsuperscript{45}

It seems that the anticipated rate increase of propargylic C-H activation is only modest upon increasing the kinetic acidity of the propargylic methyl group by substituting the phenyl group in 1-phenyl-1-propyne with a pentafluorophenyl group. In addition, experiments indicated that the corresponding propargyl Cp*\textsubscript{2}LaCH\textsubscript{2}CCC\textsubscript{6}F\textsubscript{5} (11\textsubscript{a}) was thermally less stable than its non-fluorinated analogues (7-10), decomposing into unidentified compounds after prolonged times at relatively high temperatures. Thus, both the relative slow rate and thermal instability limit the utility of the present reaction as a convenient preparative route towards propargyl derivatives of rare-earth metalloccenes.

2.3.3. Reactions of hydrides with 1-aryl-1-propynes

1-Phenyl-1-propyne (1)

Because the formation of the corresponding propargyl was slow from the reaction of alkyl derivatives Cp*\textsubscript{2}LnCH(SiMe\textsubscript{3})\textsubscript{2} (6) with 1-aryl-1-propynes (1-5), analogous reactions of [Cp*\textsubscript{2}Ln(µ-H)]\textsubscript{2} (12) were studied as a more convenient preparative route towards propargyl derivatives of rare-earth metalloccenes Cp*\textsubscript{2}LnCH\textsubscript{2}CCAr (7-10). When 0.5 equiv. of 1-phenyl-1-propyne was added to a solution of [Cp*\textsubscript{2}La(µ-H)]; (12\textsubscript{a}) in benzene-\textit{d}_{6}, a complex reaction mixture formed with a time-dependent composition, as indicated by in situ \textsuperscript{1}H NMR spectroscopy. After 5 min at room temperature, the hydride was converted completely into three major Cp*\textsubscript{2}La species (on the basis of Cp* \textsuperscript{1}H NMR resonances at δ 1.92, 1.90 and 1.88 ppm) of which the propargyl species Cp*\textsubscript{2}LaCH\textsubscript{2}CCPh (δ 1.92 ppm) constituted only 31% of the total intensity of the Cp* \textsuperscript{1}H NMR
resonances present. In addition, cis-1-phenylprop-1-ene was identified in the reaction mixture and its concentration increased slowly in time.

\[
\begin{align*}
\text{[Cp}^*\text{2La(µ-H)}]_2 + 2 \text{CH}_3\text{C}≡\text{CPh} & \quad \rightarrow \\
\text{12a} & \quad \text{12a} \\
\text{Cp}^*\text{2LaCH}_2\text{C}≡\text{CPh} & + \\
\text{7a} & + \\
\text{Cp}^*\text{2La} & + \\
\text{13a} & + \\
\text{LaCp}^* & + \\
\text{14a} & .
\end{align*}
\]

Interestingly, the propargyl derivative became the major organometallic product present (75%, \(^1\text{H NMR}\) after standing for 1 day at room temperature. GC/GC-MS and \(^1\text{H NMR}\) analysis of the major organic products in the reaction mixture after addition of methanol-\(d_4\) indicated the presence of cis-1-phenylprop-1-ene, cis-1-phenylprop-1-ene-\(d_1\), phenylallene-\(d_1\), and 1-phenyl-1-propyne-\(d_1\). The latter two compounds are formed from deuterolysis of \(\text{Cp}^*\text{2LaCH}_2\text{C}≡\text{CPh}\) (7a) (Section 2.5.2). The use of toluene-\(d_8\) as solvent gave similar results, thereby indicating that the reactions described above do not involve solvent molecules, as previously observed for lanthanide hydrides and alkyls in aromatic solvents.\(^{46}\)

These results can plausibly be rationalized by proposing three separate pathways by which a monomeric hydride derivative reacts with 1-phenyl-1-propyne (Scheme 2-10). Although no spectroscopic evidence for \(\text{Cp}^*\text{2LaH}\) was obtained in this study, ample evidence exist in literature that hydride derivatives of rare-earth metallocenes \([\text{Cp}^*\text{2Ln(µ-H)}]_2\) (12) are present in solution as an equilibrium between dimer and monomer.\(^{47}\) The formed monomeric hydride derivative may, in principle, undergo both alkyn insertion into the La-H bond and propargylic C-H activation. Propargylic metatation of 1-phenyl-1-propyne by \(\text{Cp}^*\text{2LaH}\) yields 7a and dihydrogen. The reversible nature of propargylic metatation was demonstrated by the independent reaction of 7a with excess dihydrogen (1 atm.). In this reaction, 7a was consumed within several hours, giving rise to phenylpropane and \([\text{Cp}^*\text{2La(µ-H)}]_2\) (12a) over the course of 1 day at room temperature. Although the relatively low rate of the reaction of 7a with excess \(\text{H}_2\) may suggest that reversible metatation of \(\text{Cp}^*\text{2LaH}\) by 1-phenyl-1-propyne is only of minor importance in the present system, efficient hydrogen capture is not without precedent.\(^{48}\)

Insertion of the carbon-carbon triple bond into the La-H bond of the monomeric hydride derivative may take place both in a 2,1- and 1,2-manner, affording the corresponding 1-phenylprop-1-en-1-yl 12a and 1-phenylprop-1-en-2-yl derivatives 13a, respectively. Clearly, the ratio of these insertion products is determined by

**Scheme 2-10.** The proposed reaction sequences in the reaction of 12a with 1.
the electronic and steric properties of the substituents at the carbon-carbon triple bond and those of the metal complex and is difficult to predict a priori. 1,2-Insertion may be favored under steric control, but 2,1-insertion of 1-arylalk-1ynes and 1-arylalk-1-enes is commonly observed in rare-earth metal chemistry (Chapter 4). It should also be noted that no evidence for reversible alkyne insertion was obtained in the reaction of [Cp*₂Ln(µ-H)]₂ with diphenylacetylene.

The transient alkenyl species Cp*₂LaC(Ph)=C(CH₃)H (13a) and Cp*₂LaC(CH₃)=C(Ph)H (14a) were inferred from the presence of cis-1-phenylprop-1-ene and the formation of cis-1-phenylprop-1-ene-d₁ upon quenching the reaction mixture with methanol-d₄. However, the relative preference for 2,1- or 1,2-insertion in this system could not be determined by means of NMR spectroscopy or GC-MS analysis. Attempts to spectroscopically identify the proposed 1-phenylprop-1-en-1-yl and 1-phenylprop-1-en-2-yl derivatives were hampered by the complexity of the 'H NMR spectrum and overlapping signals.

The reaction of the formed propenyl derivatives with 1-phenyl-1-propyne may give rise to the observed cis-1-phenylprop-1-ene via propargylic C-H activation. Evidence for this hypothesis was provided by the reaction of Cp*₂LaC(Ph)=C(Ph)H (15a) with 1-phenyl-1-propyne, affording Cp*₂LaCH₂CCPh (7a) and cis-diphenylethene (Scheme 2-11). This alkenyl derivative was conveniently prepared from [Cp*₂La(µ-H)]₂ and diphenylethyne. Another route towards the observed cis-1-phenylprop-1-ene may plausibly involve the reaction of the propenyl derivatives with dihydrogen formed from propargylic metalation of 1-phenyl-1-propyne, as implicated by the reaction of Cp*₂LaCH₂CCPh with excess dihydrogen, giving phenylpropane and [Cp*₂La(µ-H)]₂.

Because the reaction of the hydride [Cp*₂La(µ-H)]₂ (12a) and 1-phenyl-1-propyne (1) was not found to be clean at room temperature, it was decided to investigate whether the proposed competition between propargylic C-H activation and alkyne insertion could be influenced in the favor of propargylic C-H activation by lowering the reaction temperature. Thus, the reaction of 12a and 1 (2 equiv.) in toluene-d₈ at -60 °C was monitored with 'H NMR spectroscopy. The 'H NMR spectrum of the reaction mixture was more complex, however, exhibiting nine Cp* resonances of which the propargyl represented only 13% of the total Cp* 'H NMR resonance intensities. No significant changes in the composition were observed upon slowly warming to room temperature and further standing. The occurrence of insertion reactions of unsaturated substrates into La-C bonds is ruled out by the observed masses of the reaction products. These considerations suggest that alternative C-H activation sequences compete more effectively with propargylic C-H activation at lower reaction temperatures. Examples of lanthanidocene derivatives undergoing allylic, vinylic and aromatic C-H activation are well-documented.

The above reaction sequences imply that alkyne insertion is competitive with propargylic C-H activation due to reversible propargylic metalation in a closed atmosphere. Following this line of reasoning, it was put forward that the removal of dihydrogen gas may render propargylic metalation irreversible, thereby suppressing alkyne insertion under the above reaction conditions. This notion was confirmed by performing the reactions under dynamic vacuum, affording the propargyl in high yields (~90%, ¹H NMR). Even so, the presence of cis-1-phenyl-1-propene indicated that alkyne insertion was still competitive with propargylic C-H activation under these reaction conditions.

The desired propargyl Cp*₂LaCH₂CCPh (7a) was successfully prepared by performing the reaction of the hydride 12a in an aliphatic (e.g. pentane, hexane) or aromatic solvent at room temperature under dynamic vacuum. Also, the use of an excess amount of substrate was found to be necessary to compensate for the seemingly unavoidable hydrogenation of the substrate. A preparative more convenient method that avoids the
handling of the highly reactive hydride involves the in situ formation of the hydride \([\text{Cp}^* \text{2Ln(µ-H)}]_2\) from the alkyl \(\text{Cp}^* \text{2LnCH(SiMe}_3\text{)}_2\) (Scheme 2-12). \(\text{Cp}^* \text{2LaCH}_2\text{CCPh}\) (7a) is extremely soluble in alkane and aromatic solvents and was initially isolated as a red oil which did not easily form crystals.54,55 A crystalline solid was obtained after complete in vacuo removal of the organic compounds in the crude product mixture (e.g. cis-1-phenyl-1-propene, CH\(_2\)(SiMe\(_3\))\(_2\), unreacted 1-phenyl-1-propyne) and prolonged cooling at -80 °C. Recrystallization from toluene afforded single-crystals suitable for an X-ray crystallographic study in which 7a was identified as an \(\eta^3\)-propargyl/allenyl complex in the solid state. Structural data is discussed in more detail in Section 2.4.4. A similar methodology also afforded the yttrium analogue \(\text{Cp}^* \text{2YCH}_2\text{CCPh}\) (7b) in good isolated yields and single-crystals suitable for X-ray analysis were obtained analogously.

**Ortho-substituted 1-phenyl-1-propynes (3-4)**

When \([\text{Cp}^* \text{2La(µ-H)}]_2\) (12a) was allowed to react in benzene-\(\text{d}_6\) at room temperature with 2 equiv. of CH\(_3\)CCC\(_6\)H\(_4\)Me\(_2\)-2,6 (3), an instantaneous reaction was observed with 1H NMR spectroscopy. Although propargylic C-H activation was found to be the major pathway, forming the propargyl \(\text{Cp}^* \text{2LaCH}_2\text{CCC}\(_6\)\text{HMe}_2\)-2,6 (9a) quite selectively (>90%, 1H NMR), hydrogenation was still operative, as indicated by the presence of cis-1-(2,6-dimethylphenyl)-prop-1-ene (1H NMR, GC-MS) in the reaction mixture. When the reaction mixture was allowed to stand at room temperature for several days, no significant changes were observed with 1H NMR spectroscopy.

The complex \(\text{Cp}^* \text{2LaCH}_2\text{CCC}\(_6\)\text{HMe}_2\)-2,6 (9a) was isolated on a preparative scale by employing the above methodology consisting of the in situ preparation of the hydride derivative and the application of dynamic vacuum. However, the isolated yield was low (22%), most likely due incomplete removal of organic products from the reaction mixture, thereby hampering the crystallization of the propargyl. Unfortunately, attempts to obtain single-crystals suitable for X-ray analysis were unsuccessful.

The reaction of \([\text{Cp}^* \text{2La(µ-H)}]_2\) (12a) with 0.5 equiv of CH\(_3\)CCC\(_6\)H\(_2\)Pr\(_2\)-2,6 (4) in benzene-\(\text{d}_6\) gave two major \(\text{Cp}^*\) resonances (δ 2.22, 1.92) in the \(^1\)H NMR spectrum after 1 h at room temperature of which the propargyl was the major species (δ 1.92, 58%). Again, the substrate was partially hydrogenated, as indicated by the presence of cis-1-(2,6-diisopropylphenyl)-1-propene (\(^1\)H NMR, GC-MS) in the reaction mixture. After 2 days at room temperature both the concentration of the propargyl (74%) and hydrogenated substrate increased.

Unfortunately, no crystalline product could be isolated at a preparative scale from the reaction mixture of \(\text{Cp}^* \text{2LaCH(SiMe}_3\text{)}_2\) and 4, following the above procedure. The organic products were difficult to remove in vacuo and unidentified organometallic reaction products could not be separated by extraction with appropriate solvents.

**1-Pentafluorophenyl-1-propyne (5)**

When the prop-1-ynylpentafluorobenzene (5) (1.0 equiv per La) was added to a solution of 12a in benzene-\(\text{d}_6\), at room temperature, a complex time-dependent reaction mixture formed, as indicated by \(^1\)H NMR spectroscopy. After 10 min the \(^1\)H NMR resonances of the hydride and substrate had completely disappeared and four major \(\text{Cp}^*\) \(^1\)H NMR resonances were observed (δ 1.88, 1.84, 1.83 and 1.80 ppm) of which the propargyl \(\text{Cp}^* \text{2LaCH}_2\text{CCC}\(_6\)\text{F}_5\) (11a: δ 1.88) represented only 7% of the total \(\text{Cp}^*\) \(^1\)H NMR resonance intensities. Attempts to identify the major organometallic products by means of NMR spectroscopy failed. After two days standing at room temperature, the concentration of 11a increased to 14%, while more \(\text{Cp}^*\) \(^1\)H NMR resonances appeared concomitantly.

\(^1\)F NMR spectroscopy indicated the presence of at least four different pentafluorophenyl groups in a 0.4:1.0:0.3:0.3 ratio. When the reaction mixture was quenched with methanol-\(\text{d}_4\) after 2 days at room temperature, NMR and GC/GC-MS analysis indicated the presence of two major organic products that were plausibly identified as 1-pentafluorophenyl-1-propene-\(\text{d}_1\) and the monodeuterated coupling product C\(_6\)F\(_5\)C(\(\text{D})\)C(Me)C(C\(_6\)F\(_5\))=CHMe in a ratio of 1.00:0.33, respectively. The geometry of the double bonds in the latter double insertion product could not be determined unequivocally and the proposed structure is based on the
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Based on the inferred presence of the propenyl derivative, Cp*$_2$LaC(C$_6$F$_5$)=CH(CH$_3$) (16a) could be characterized with $^1$H and $^{19}$F NMR spectroscopy ($\delta$ 7.67, q, $J$ = 6.7 Hz, CH, 1 H; 1.84, s, Cp*, 30 H; 1.51, d, $J$ = 6.7 Hz, C$_3$H$_3$, 3 H). This assignment is further supported by the close resemblance of its $^1$H NMR spectral data with that of Cp*$_2$LaC(Ph)=CH(Ph) (i.e. the vinylic proton resonates at $\delta$ 7.69 ppm and the Cp* ligands appear as one singlet at $\delta$ 1.84 ppm) (vide supra). The complexity of the $^1$H NMR spectrum thwarted attempts to characterize Cp*$_2$LaC(C$_6$F$_5$)=C(CH$_3$)C(C$_6$F$_5$)=CH(CH$_3$) (17a) unambiguously.

2.4. Structural characterization of propargyl/allenyls

2.4.1. Introduction

The Cp*$_2$LnCH$_2$CCAr complexes exhibit equivalent Cp* and CH$_2$ resonances in the $^1$H and $^{13}$C NMR spectrum indicative of either a static $\eta^3$-propargyl structure or a rapid equilibrium mixture of the $\eta^1$-propargyl and $\eta^1$-allenyl species. Because no $^1$H and $^{13}$C NMR resonances attributable to distinct $\eta^1$-propargyl and $\eta^1$-allenyl derivatives of Cp*$_2$LaCH$_2$CCPh (7a), Cp*$_2$YCH$_2$CCPh (7b) and Cp*$_2$LaCC$_6$H$_3$Me$_2$-2,6 (9a) were observed at -80 °C, the former picture is presently favored. To investigate this issue further, these compounds were also characterized by $^{13}$C NMR and infrared spectroscopy and, in some cases, by X-ray crystallography.

Furthermore, spectroscopic parameters are likely to reflect structural changes in the present Cp*$_2$LnCH$_2$CCAr complexes resulting from differences in the steric and electronic properties of the aryl-substituted ligands employed in this study. If the Cp*$_2$LnCH$_2$CCAr complexes are static $\eta^3$-propargyls (E), it is believed that substitution at the ortho-positions of the phenyl ring will shift the $\eta^1$-propargyl structure closer to a more $\eta^1$-propargyl-like structure (D) in the continuum of canonical structures, due to the larger steric hindrance between the Cp* ligands and the ortho-substituent in the $\eta^1$-allenyl-like structure (F) (Scheme 2-14). Alternatively, if the Cp*$_2$LnCH$_2$CCAr complexes are engaged in a rapid equilibrium mixture between the $\eta^1$-
propargylic (D) and η1-allenyl tautomer (F), the formation of F is likely to be disfavored upon ortho-substitution and more D will be present in the equilibrium mixture.

2.4.2. Spectroscopic properties of the propargyl/allenyls

The 1H and 13C NMR resonances of the rare-earth metallocene propargyl derivatives Cp*2LnCH2CCAr are shown in Table 2-2. The CH2 proton resonances are observed between δ 3.08 and 2.71 ppm. These values suggest a considerable contribution from the propargylic structure, as η1-bound allenylic methylene protons typically resonate within the region of δ 3.9-4.3 ppm and those associated with the propargylic tautomer lie at higher field between δ 1.75 and 3.0 ppm (Table 2-3).3c The 13C NMR spectra exhibit downfield shifted CH2 propargyl carbon resonances (C-1, δ 47.7-57.8 ppm) relative to the neutral 1-phenyl-1-propyne ligand (δ 3.92 ppm, see Table 2-1). The chemical shifts are in the range of values observed for other substituted, sp3 α-carbons in rare-earth metallocenes, such as Cp*2Y[η3-CH(Ph)CH2Ph]δ (δ 56.40 ppm, JCH = 128 Hz), Cp*2La[η1-CH(Ph)CH2Ph]° (δ 49.20 ppm, JCH = 131 Hz) and Cp*2Y(CH2C6H3Me2-3,5 (δ 47.35 ppm, JCH = 133 Hz).57 The first-order carbon-hydrogen coupling constants 1JCH (156.7-162.5 Hz), on the other hand, are significantly larger than those observed in the above complexes and reveal that the C-H bonds of the propargylic carbon have considerably more s character. The values are close to that of a sp2 carbon (typically 156.4 Hz) and may be interpreted as to discard η1-propargyl bonding (sp3 hybridization is expected for the propargylic carbon in an η1-propargyl, Scheme 2-16). However, such an unambiguous interpretation is complicated by the fact that inductive/field effects originating from polar substituents influence 1JCH values to such an extent that the 1JCH values mostly do not reflect the true hybridization state of the carbon.58 The CH2CC central carbon resonances (C-2, δ 145.6-165.2 ppm) are closer to the central carbon atom of the neutral phenyllallene (δ 209.9 ppm) than that of 1-phenyl-1-propyne (δ 79.9 ppm), thereby suggesting a high degree of allenyl character for the central carbon. Also, the CH2CC carbon resonances (C-3, δ 100.3-112.8 ppm) are closer to that of the corresponding carbon atom of phenyllallene than to that of 1-phenyl-1-propyne (δ 85.9 ppm).

Table 2-2. Spectroscopic data of the Cp*2LnCH2CCAr complexes.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ln, Ar</th>
<th>CH2</th>
<th>Cp*</th>
<th>C-1 (JCH, JYC)</th>
<th>C-2</th>
<th>C-3 (JCH)</th>
<th>νC≡C (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Y, Ph</td>
<td>2.82</td>
<td>1.93</td>
<td>49.33</td>
<td>155.09</td>
<td>106.79</td>
<td>1920</td>
</tr>
<tr>
<td>(7b)</td>
<td></td>
<td></td>
<td></td>
<td>(159.1, 5.2)</td>
<td>(11.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>La, Ph</td>
<td>2.82</td>
<td>1.91</td>
<td>54.00</td>
<td>152.19</td>
<td>112.75</td>
<td>1944</td>
</tr>
<tr>
<td>(7a)</td>
<td></td>
<td></td>
<td></td>
<td>(158.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>La, C6HMe2-2,6</td>
<td>2.71</td>
<td>1.92</td>
<td>49.00</td>
<td>149.28</td>
<td>105.79</td>
<td>1975</td>
</tr>
<tr>
<td>(9a)</td>
<td></td>
<td></td>
<td></td>
<td>(156.9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>La, C6HPr2-2,6</td>
<td>2.68</td>
<td>1.92</td>
<td>47.69</td>
<td>145.61</td>
<td>100.31</td>
<td></td>
</tr>
<tr>
<td>(10a)</td>
<td></td>
<td></td>
<td></td>
<td>(156.7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>La, C6F3</td>
<td>3.08</td>
<td>1.88</td>
<td>55.77</td>
<td>165.24</td>
<td>108.76</td>
<td></td>
</tr>
<tr>
<td>(11a)</td>
<td></td>
<td></td>
<td></td>
<td>(162.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>CH3CCPh</td>
<td>-</td>
<td>-</td>
<td>24.9</td>
<td>79.9</td>
<td>85.9</td>
<td>2251</td>
</tr>
<tr>
<td>7b</td>
<td>CH2CCPh</td>
<td>-</td>
<td>-</td>
<td>78.9</td>
<td>209.9</td>
<td>94.1</td>
<td>1940</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a NMR measurements in C6D6 at 25 °C under a nitrogen atmosphere. The chemical shifts are reported in ppm and coupling constants in Hz. IR measurements under a nitrogen atmosphere. NMR measurements in CDCl3 at 25 °C for entries 6 and 7.° Data taken from Ref. 67.° Compounds not isolated.
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structure (Table 2-3). The observation that the $^{13}$C NMR chemical shifts are intermediate of those observed for η$^1$-CH$_2$CCPh and η$^1$-C(Ph)=C=CH$_2$ complexes is in accord with this view (Entries 8 and 9).

Infrared spectroscopy has been widely used as a diagnostic tool in determining the relative contribution of allenylic and propargylic structures. 2,59 In the 2250-1750 cm$^{-1}$ region of the infrared spectrum, strong absorptions at 1944 and 1920 cm$^{-1}$ are observed for Cp*$_2$LaCH$_2$CCPh (7a) and Cp*$_2$YCH$_2$CCPh (7b), respectively (Figure 2-8). Comparison with reported data indicates that these values are intermediate of those typically observed for σ-propargyl (2100-2215 cm$^{-1}$) and σ-allenyl metal complexes (1800-1920 cm$^{-1}$),60 thereby providing additional support to the view that the present rare-earth metallocene complexes adopt an η$^3$-propargyl/allenyl structure.

Remarkably, comparison with IR data of reported η$^3$-propargyl/allenyl complexes is difficult, because IR data of these compounds are rare in literature. 3d-f One of the few literature examples involves the crystallographically characterized Cp$_2$ZrMe(η$^3$-CH$_2$CCPh), which is reported to display two medium absorptions at 2176 and 1924 cm$^{-1}$.4b,61 These vibrations were not assigned and their understanding is not clear-cut, because a static η$^3$-bonding would be expected to lead to a single absorption in this region. The observation of two absorptions in the 1800-1920 and 2100-2215 cm$^{-1}$ range has, in fact, typically been interpreted in terms of an equilibrium between η$^1$-allenylic and η$^1$-propargylic organometallic species. 2 However, no fluxional behavior was observed in solution Cp$_2$ZrMe(η$^3$-CH$_2$CCPh) down to -40 °C and the authors did not comment on this ambiguity. The titanocene derivative Cp*$_2$Ti(CH$_2$CCPh) is reported to exhibit only one strong absorption at 1902 cm$^{-1}$ in this region and was assigned the η$^3$-hapticity by comparison with Cp$_2$ZrMe(η$^3$-CH$_2$CCPh).62 Following this line of reasoning, it seems that both NMR and IR spectroscopy are consistent with an η$^3$-propargyl/allenyl structure.

Yttrium has a nucleus with I = $\frac{1}{2}$ in a natural abundance of 100% and a coupling interaction in Cp*$_2$YCH$_2$CCPh (7b) is observed with the terminal carbons of the CH$_2$CC ligand (Table 2-2). These couplings are in agreement with the nature of metal CH$_2$CC bonding. According to several molecular orbital studies, the CH$_2$CCR ligand binds mainly through its terminal carbons, while the π-bond of the carbon-carbon triple bond does not interact significantly with the metal fragment.63 The observed yttrium-carbon coupling of the propargyl carbon (5.9 Hz) is notably smaller than that of other yttrocene-bonded methylene carbons, such as Cp*$_2$Y(η$^3$-CH$_2$C$_6$H$_3$Me-3,5) (35 Hz) and Cp*$_2$Y[η$^1$-CH(Ph)CH$_2$Ph] (12 Hz), but is comparable to that of the terminal allyl carbon in Cp*$_2$Y(η$^3$-CH$_2$CH=CH$_2$) (35 Hz) and the smallest coupling

Table 2-3. Selected NMR data for allenyl and propargyl complexes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>CH$<em>2$ C-1 ($^1$J$</em>{CH}$)</th>
<th>C-2</th>
<th>C-3</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(PPh$_3$)$_2$Pt(η$^3$-CH$_2$CCPh)]$^+$</td>
<td>2.74 48.3 (170)</td>
<td>97.3</td>
<td>102.1</td>
<td>[4f,e]</td>
</tr>
<tr>
<td>2</td>
<td>[(PPh$_3$)$_2$Pd(η$^3$-CH$_2$CCPh)]$^+$</td>
<td>3.19 50.9</td>
<td>94.2</td>
<td>105.4</td>
<td>[4g]</td>
</tr>
<tr>
<td>3</td>
<td>Cp$_2$ZrMe(η$^3$-CH$_2$CCPh)</td>
<td>3.37 55.5 (167)</td>
<td>120.5</td>
<td>114.1</td>
<td>[4b]</td>
</tr>
<tr>
<td>4</td>
<td>CpMo(η$^3$-CH$_2$CCPh)(η$^5$-CH$_2$CCPh)</td>
<td>3.90 41.6</td>
<td>142.3</td>
<td>124.8</td>
<td>[63b]</td>
</tr>
<tr>
<td>5</td>
<td>Cp$_2$Zr(CH$_2$CCPh)$_2$</td>
<td>2.80 30.7 (151)</td>
<td>128.4</td>
<td>103.5</td>
<td>[4b]</td>
</tr>
<tr>
<td>6</td>
<td>Cp*($^1$TBM)Zr(η$^3$-CH$_2$CCMe)</td>
<td>2.51 51.0</td>
<td>99.9</td>
<td>91.7</td>
<td>[4h]</td>
</tr>
<tr>
<td>7</td>
<td>[Cp*$_2$Zr(η$^3$-CH$_2$CCMe)$_2$]$^+$</td>
<td>2.93 61.7 (158)</td>
<td>128.4</td>
<td>103.5</td>
<td>[88]</td>
</tr>
<tr>
<td>8</td>
<td>[Pt(CO)(PPh$_3$)$_2$(η$^3$-CH$_2$CCPh)]$^+$</td>
<td>1.98 7.1</td>
<td>92.2</td>
<td>86.1</td>
<td>[4e]</td>
</tr>
<tr>
<td>9</td>
<td>[Pt(CO)(PPh$_3$)$_2$(η$^3$-CH$_2$CCMe)$_2$]$^+$</td>
<td>3.65 72.9</td>
<td>203.1</td>
<td>101.5</td>
<td>[4e]</td>
</tr>
</tbody>
</table>

*a Chemical shifts in ppm and coupling constants in Hz.
constant in the asymmetrically bridging formimidoyl carbon in \([\text{Cp}_2\text{Y}(\mu-\eta^1:\eta^1-\text{N,C-HC}=\text{NC}^t\text{Bu})]_2\) (1) \(\text{J}_{YC} = 5 \text{ Hz},\) \(\text{J}_{Y'C} = 35 \text{ Hz}\) (Scheme 2-15). 65 The yttrium-carbon coupling constant of the terminal carbon (11.9 Hz) in 7b is similar to that observed for the terminal acetylide carbon with the distant \(\text{Cp}^*\_2\text{Y}\) moiety in \([(\text{Cp}^*_2\text{Y})_2(\mu-\text{O,C}-\text{OCH}=\text{CHC}≡\text{C})]\) \(\text{J}_{YC} = 12 \text{ Hz},\) \(\text{J}_{Y'C} = 53 \text{ Hz}\) (Scheme 2-15). 66 These findings reveal that the observed yttrium-carbon coupling constants are consistent with the proposed delocalized metal \(\eta^3\)-CH\(_2\)CC bonding.

2.4.3. Ligand and metal ion size effects

The observed NMR spectral parameters of the propargyl derivatives \(\text{Cp}^*_2\text{LnCH}_2\text{CCAr}\) clearly indicate that the chemical shift of the propargylic CH\(_2\) protons varies with the nature of the aromatic group (δ 3.08-2.71 ppm), while that of the \(\text{Cp}^*_2\text{ ligand changes only little (δ 1.93-1.88 ppm) (Table 2.2). In fact, the CH\(_2\) proton resonances move upfield with increasing ortho-substitution in the \(\text{Cp}^*_2\text{LaCH}_2\text{CCC}_6\text{H}_3\text{R}_2\text{-2,6 (R = H 7a, Me 9a, iPr 10a)}\) series. In view of the relatively high field proton resonance of the allenyl CH\(_2\) group in phenylallene \(\delta 4.85 \text{ ppm}\) and \(\eta^3\)-allenyl metal complexes (e.g. entry 8, Table 2-3) as compared to the relatively low field proton resonance of the propargylic CH\(_2\) group in 1-phenyl-1-propyne (δ 1.65 ppm) and \(\eta^1\)-propargyl metal complexes (e.g. entry 9, Table 2-3), this finding suggests a shift to either a more propargyl-like \(\eta^3\)-propargyl structure or a shift towards the formation of the \(\eta^1\)-propargyl in an equilibrium mixture between a \(\eta^1\)-propargyl and a \(\eta^3\)-allenyl derivative.3c

Replacing the phenyl group by a pentafluorophenyl group seems to have the opposite effect, favoring either a more allenyl-like \(\eta^3\)-propargyl structure or the formation of the \(\eta^1\)-allenyl in the equilibrium mixture.68 It seems reasonable to ascribe this change in character to the \(\alpha\)-carbanion-stabilizing property of the pentafluorophenyl group.43 Electronic substituent effects in propargyl-allenyl equilibria of organoindium derivatives have been reported.69 For these compounds, both experimental and theoretical data revealed that the electron-donating nature of a methyl group at the terminal carbon destabilizes the sp\(^2\) carbanion in the allenyl structure relative to the propargylic structure, thereby favoring the formation of the \(\eta^1\)-propargyl species.32

The \(^{13}\text{C}\) NMR spectral data within the \(\text{Cp}^*_2\text{LaCH}_2\text{CCAr}\) series are in agreement with the trend observed with \(^1\text{H}\) NMR spectroscopy (Table 2-2). When the steric bulk at the \text{ortho}-positions of \(\text{Cp}^*_2\text{LaCH}_2\text{CCAr}\) is increased, the CH\(_2\) and CH\(_2\)CC resonances shift upfield and CH\(_2\)CC resonances shift downfield, consistent with the view that an increase of steric bulk at the \text{ortho}-positions increases the propargylic character of \(\text{Cp}^*_2\text{LaCH}_2\text{CCAr}\). When the phenyl group in \(\text{Cp}^*_2\text{LaCH}_2\text{CCPh}\) is replaced by a pentafluorophenyl group, the opposite change in character is observed with \(^{13}\text{C}\) NMR spectroscopy (i.e. the CH\(_2\) and CH\(_2\)CC resonances shift downfield and the CH\(_2\)CC shift upfield) which is in agreement with the proposed increase in allenyl character.
Another interesting feature of the NMR spectra data concerns the first-order carbon-hydrogen couplings of the propargylic carbon (C-1) in the Cp*₂LaCH₂CCAr series. It can be seen that these $^{1}J_{CH}$ values (in Hz) decrease in the same order as the order of increasing propargylic character based on the carbon chemical shifts, i.e. C₆F₅ (162.5) > C₆H₅ (158.3) > C₆H₃Me₂-2,6 (156.9) > C₆H₃iPr₂-2,6 (156.7). Although $^{1}J_{CH}$ couplings are well-known to correlate with the hybridization of the carbon atom in hydrocarbons, polar substituents have a much greater effect on $^{1}J_{CH}$ couplings and their presence renders these couplings unsuitable for estimating the $s$ character of the carbon bonding orbital in some cases. Assuming that the polar effects of the metal center are constant in the series Cp*₂LaCCAr, the decrease in $^{1}J_{CH}$ for the propargylic carbon arguably reflects a change in hybridization which can be interpreted as a change from a sp²-type carbon in H and I to a more sp³-type carbon in G (Scheme 2-16).

Additional evidence for the proposed changes in the bonding of the present Cp*₂LaCH₂CCAr complexes as a function of the steric and electronic properties of the ligand is supplied by comparing the spectral properties of the complexes with those of the corresponding neutral ligand. Based on both NMR spectroscopy, the relative $\sigma$-electron-withdrawing ability of the ligand CH₃CCAr was found to increase in the following order: 3 (C₆H₃Me₂-2,6, 131.0) ≈ 4 (C₆H₃iPr₂-2,6, 131.0) < 1 (Ph, 131.4) < 5 (C₆F₅, 133.0) (Table 2-1). It can be seen that several structurally diagnostic spectral parameters of the Cp*₂LaCH₂CCAr complexes, such as the proton chemical shift of the CH₂ group (Figure 2-1), the carbon chemical shifts of the C₃ ligand (Figure 2-2) and the first-order carbon-hydrogen coupling constant of the CH₂ group (Figure 2-3), correlate in a similar manner with the $\sigma$-electron withdrawing ability of the ligand. These spectral parameters indicate also that the propargylic character of Cp*₂LaCH₂CC₆H₃Me₂-2,6 is somewhat higher than that of Cp*₂LaCH₂CC₆H₃iPr₂-2,6, despite the fact that the $\sigma$-electron withdrawing ability of their aromatic substituents is similar. This minor discrepancy may plausibly be ascribed to the increased steric bulk of the 2,6-disopropylphenyl group relative to the 2,6-dimethylphenyl group. In summary, these findings strongly suggest that the bonding of Cp*₂LaCH₂CCAr becomes increasingly more propargylic in character upon increasing the steric bulk of the aromatic substituent.

Scheme 2-16. The hybridization of the terminal carbon atoms in the limiting structures of the prop-2-ynyl/allenyl anion.
and more allenic in character upon an increase in the \(\sigma\)-electron-withdrawing ability of the aromatic substituent.

When the lanthanum metal center is substituted by the smaller yttrium, the relative position of the \(\eta_3\)-allenyl/propargyl ligand in either an \(\eta_3\)-allenyl/propargyl continuum or an \(\eta_1\)-allenyl/\(\eta_1\)-propargyl equilibrium mixture is difficult to ascertain spectroscopically. A clear-cut interpretation of the observed spectral parameters is complicated by a difference in inductive/field effects of the metals. Also, the solid-state molecular structures of \(7a\) and \(7b\) did not provide additional insight into the influence of the metal ion size on the nature of bonding of the \(\eta_3\)-allenyl/propargyl ligand in \(7a\) and \(7b\) (Section 2.4.4).

### 2.4.4. The molecular structures of \(\text{Cp}^*\text{LnCH}_2\text{CCPh} (\text{Ln} = \text{La, Y})\)

In order to shed more light on the nature of the bonding in the present propargyl derivatives \(\text{Cp}^*\text{LnCH}_2\text{CCPh}\), X-ray crystallographic studies were performed on \(\text{Cp}^*\text{LaCH}_2\text{CCPh} (7a)\) and \(\text{Cp}^*\text{YCH}_2\text{CCPh} (7b)\). In both cases, single crystals were grown from toluene solutions at low temperature. Complexes \(7a\) and \(7b\) crystallize in the orthorhombic space groups \(Pna_21\) with \(Z = 4\) and \(Pca_21\) with \(Z = 4\), respectively. The crystal structures of \(7a\) and \(7b\) are shown in Figures 2-3 and 2-4, respectively, and selected bond distances and angles are given in Table 2-4. The bent metallocene in \(7a\) is similar to that in other lanthanum and lanthanide metallocenes. The \(137.1^\circ\ \text{Ct}_1\text{La-Ct}_2\) angle and the average 2.54 \(\text{La-Ct}_1\) and 2.51 \(\text{La-Ct}_2\) distances are normal. The \(\text{C}_5\text{Me}_5\) are in the usual staggered conformation with a twist angle of 28.9° compared to 36° for a perfectly staggered arrangement.

The phenyl-substituted propargyl/allenyl ligand is clearly bound in an \(\eta_3\)-mode. The \(\text{La-C(propargyl)}\) distances for \(\text{La-C21, La-C22 and La-C23}\) are 2.811(6), 2.695(7) and 2.740(7) \(\text{Å}\), respectively. At first glance, the main interaction of the metal center with the \(\text{C}_3\) ligand center would seem to take place on \(\text{C22}\). However, theoretical studies have shown that the metal bonding with an \(\eta_3\)-propargyl/allenyl ligand occurs through the terminal carbon atoms. In agreement with delocalized \(\eta^1\)-bonding, the observed \(\text{La-C21 and La-C22 distances}\) are longer than that of reported \(\text{La-C \(\sigma\)-bond lengths}\), such as 2.537(5) and 2.588(4) \(\text{Å}\) in \(\text{Cp}^*\text{La(CH(SiMe}_3)_2}\) and 2.651(8) and 2.627(10) \(\text{Å}\) in \(\text{Cp}^*\text{La(CH(SiMe}_3)_2}(\text{THF})\).

The backbone of the \(\eta_3\)-propargyl/allenyl ligand is virtually coplanar with \(\text{La}\) (atom displacements from the least squares plane: \(\text{La 0.000, C21 0.001, C22 0.003, C23 0.002 Å}\)). Such coplanar rearrangements have also been reported for other \(\eta_3\)-propargyl/allenyl complexes and this structural feature is believed to be characteristic of \(\eta_3\)-propargyl/allenyl complexes. The atoms \(\text{La, C21, C22 and C23}\) all lie in the mirror plane that reflects the two \(\text{Cp}\) ligands of \(7a\). This symmetry, obviously, results in the observed magnetic equivalence of the two hydrogen atoms bonded to \(\text{C21}\) and the \(\text{Cp}\) ligands in the \(^1H\) and \(^{13}C\) NMR spectrum of \(7a\) (Section 2.4.2). The crystallographic \(\text{C21-C22 and C22-C23 bond distances}\) of 1.36(1) and 1.23(1) \(\text{Å}\), respectively, are
intermediate between those generally accepted for C-C single (1.45 Å) and double (1.31 Å) and double and triple (1.20 Å) bonds, respectively, and the C₁ ligand backbone is thus consistent with resonance between propargyl and allenyl structures. The relatively large difference of 0.13(1) Å between the two C-C bond lengths suggests that the propargylic contribution to the bonding description of 7a is relatively more important than the allenylic contribution. Although both of the resonance forms of the η³-propargyl/allenyl ligand would be expected to lead to a linear geometry at the central carbon atom, the bond angle C21-C22-C23 of 159.3(7)° indicates a considerable deviation from linearity. This structural feature appears to be another characteristic of η³-propargyl/allenyl complexes, as angles of 145-155° have been reported for other (phenyl-substituted) η³-propargyl/allenyl complexes (Table 2-4).³⁴

The overall geometry of Cp*₂YCH₂CCPh (7b) is similar to that of its lanthanum congener 7a. The Y-C bond distances are smaller and reflect the differences in Y³⁺ (1.019 Å) and La³⁺ (1.160 Å) ionic radii for eight-coordination.⁷¹ The metrical parameters corresponding to the Cp*₂-Y fragment of 7b are not exceptional, as

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**Figure 2-4.** The molecular structure of 7a with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

**Figure 2-5.** The molecular structure of 7b with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.
values for the C1-Y-C2 angle (139.3°) and the average Y-C(Cp) distances (2.36 Å) are normal. The C5Me5 ligands are in a staggered conformation with a twist angle of 24.1°. The Y-C(propargyl) bond lengths of 2.653(3), 2.529(3) and 2.560(3) Å are longer than that of reported Y-Cσ bonds, such as 2.44(2) Å in Cp*2YMe(THF)78a, 2.468(7) Å in Cp*2YCH(SiMe3)2.78b. It is interesting to note that the smaller bond distance of Y-C23 (2.560(3) Å) relative to Y-C21 (2.653(3) Å) is reflected by the smaller yttrium-carbon coupling constant of the propargylic carbon (JCH = 5.2 Hz) relative to that of the terminal carbon (JCH = 11.9 Hz).

Similar to Cp*2LaCH2CCPh (7a), Cp*2YCH2CCPh (7b) exhibits a nearly coplanar rearrangement of the C3 propargyl carbons and the metal center, albeit slightly more distorted (atom displacements from the least squares plane: Y 0.001, C21 0.005, C22 0.009, C23 0.005 Å). Most of the observed differences corresponding to the propargyl/allenyl ligand of 7a and 7b are within experimental error, but there are two exceptions. Firstly, the C21-C22-C23 angle of 155.9(3)° indicates that the C3 ligand is more bent the yttrium derivative. It seems natural to ascribe this to the smaller size of yttrium. Secondly, the phenyl group is almost coplanar with the plane defined by the C3 ligand and the metal in 7b, whereas the phenyl group is virtually perpendicular to the same plane in 7a. This difference may also be the result of the smaller size of the metal center, as the more proximate Cp* ligands are likely to force the phenyl group more into the equatorial girdle, but other effects resulting from

| Table 2-5. Selected bond lengths (Å) and angles (°) in Cp*2LnCH2CCPh (Ln = La, Y) complexes.4 |
|---------------------------------|---------------------------------|
| Ln = La (7a)                   | Ln = Y (7b)                     |
| **Bond lengths**               | **Bond lengths**               |
| C21-C22                        | 1.362(10)                      |
| C22-C23                        | 1.234(10)                      |
| C23-C24                        | 1.465(9)                       |
| La-C21                         | 2.811(6)                       |
| La-C22                         | 2.695(7)                       |
| La-C23                         | 2.740(7)                       |
| av. La-C(Cp*)                  | 2.806(16)                      |
| av. Y-C(Cp*)                   | 2.535(3)                       |
| C21-C22                        | 1.366(4)                       |
| C22-C23                        | 1.268(4)                       |
| C23-C24                        | 1.462(4)                       |
| Y-C21                          | 2.653(3)                       |
| Y-C22                          | 2.529(3)                       |
| Y-C23                          | 2.560(3)                       |
| av. Y-C(Cp*)                   | 2.654(4)                       |
| av. Y-C21-C22-C23              | 2.362                          |
| av. Y-C22-C23-C24              | 2.362                          |
| **Bond angles**                | **Bond angles**                |
| C11-La-C12                     | 137.1(1)                       |
| C21-C22-C23-C24                | 159.3(7)                       |
| C22-C23-C24-C25                | 141.2(7)                       |
| C23-C24-C25-C26                | 141.5(3)                       |
| C21-La-C21-C22                 | 159.3(7)                       |
| C22-La-C22-C23                 | 141.2(7)                       |
| C23-La-C23-C24                 | 141.5(3)                       |
| C21-C22-C23-C24                | 77.9(14)                       |
| C21-C22-C23-C24                | 77.9(14)                       |
| C21-C22-C23-C24                | 177.0(16)                      |
| C21-C22-C23-C24                | 172.9(6)                       |
| **Torsion angles**             | **Torsion angles**             |
| C22-C23-C24-C25                 | 77.9(14)                       |
| C21-C22-C23-C24                 | 177.0(16)                      |
| C22-C23-C24-C25                 | 172.9(6)                       |
| α                               | 159.3(7)                       |
| α                               | 155.9(3)                       |
| α                               | 155.4(3)                       |
| α                               | 146.1(6)                       |
| α                               | 152.2(9)                       |
| α                               | 159.3(7)                       |
| α                               | 155.9(3)                       |
| α                               | 155.4(3)                       |
| α                               | 146.1(6)                       |
| α                               | 152.2(9)                       |
| α                               | 155.9(3)                       |
| α                               | 155.4(3)                       |
| α                               | 146.1(6)                       |
| α                               | 152.2(9)                       |
| α                               | 155.9(3)                       |
| α                               | 155.4(3)                       |
| α                               | 146.1(6)                       |
| α                               | 152.2(9)                       |

Values for the C1-Y-C2 angle (139.3°) and the average Y-C(Cp) distances (2.36 Å) are normal. The C5Me5 ligands are in a staggered conformation with a twist angle of 24.1°. The Y-C(propargyl) bond lengths of 2.653(3), 2.529(3) and 2.560(3) Å are longer than that of reported Y-Cσ bond lengths, such as 2.44(2) Å in Cp*2YMe(THF)78a, 2.468(7) Å in Cp*2YCH(SiMe3)2.78b. It is interesting to note that the smaller bond distance of Y-C23 (2.560(3) Å) relative to Y-C21 (2.653(3) Å) is reflected by the smaller yttrium-carbon coupling constant of the propargylic carbon (JCH = 5.2 Hz) relative to that of the terminal carbon (JCH = 11.9 Hz).

Similar to Cp*2LaCH2CCPh (7a), Cp*2YCH2CCPh (7b) exhibits a nearly coplanar rearrangement of the C3 propargyl carbons and the metal center, albeit slightly more distorted (atom displacements from the least squares plane: Y 0.001, C21 0.005, C22 0.009, C23 0.005 Å). Most of the observed differences corresponding to the propargyl/allenyl ligand of 7a and 7b are within experimental error, but there are two exceptions. Firstly, the C21-C22-C23 angle of 155.9(3)° indicates that the C3 ligand is more bent the yttrium derivative. It seems natural to ascribe this to the smaller size of yttrium. Secondly, the phenyl group is almost coplanar with the plane defined by the C3 ligand and the metal in 7b, whereas the phenyl group is virtually perpendicular to the same plane in 7a. This difference may also be the result of the smaller size of the metal center, as the more proximate Cp* ligands are likely to force the phenyl group more into the equatorial girdle, but other effects resulting from

| Table 2-4. Selected bond distances (Å) and angles (°) for 7a and 7b and related compounds CpZr(Me)(η3-CH2CCPh)4b (D), Cp*Zr(TBM)(η3-CH2CCMMe)3b (E), CpMo(η2-MeCCPh)(η3-CH2CCPh)63b (F) and [(PPh3)2Pt(η3-CH2CCPh)]OTf 4f (G). |
|---------------------------------|---------------------------------|
| Complex                         | 7a                               |
|                                 | 7b                               |
|                                 | D                                |
|                                 | E                                |
|                                 | F                                |
|                                 | G                                |
| C1-C2                           | 1.362(10)                        |
| C2-C3                           | 1.234(10)                        |
| C3-C4                           | 1.268(4)                        |
| C4-C5                           | 1.259(4)                        |
| C5-C6                           | 1.218(7)                        |
| C6-C7                           | 1.284(13)                       |
| C7-C8                           | 1.218(7)                        |
| C8-C9                           | 1.227(13)                       |
| M-C1                            | 1.362(10)                        |
| M-C2                            | 1.234(10)                        |
| M-C3                            | 1.268(4)                        |
| M-C4                            | 1.259(4)                        |
| M-C5                            | 1.218(7)                        |
| M-C6                            | 1.284(13)                       |
| M-C7                            | 1.218(7)                        |
| M-C8                            | 1.227(13)                       |
| a                               | 159.3(7)                        |
| b                               | 155.9(3)                        |
| c                               | 155.4(3)                        |
| d                               | 146.1(6)                        |
| e                               | 152.2(9)                        |
conjugation and solid-state packing cannot be excluded.

When comparing the structural data of 7a and 7b with that of other (phenyl-substituted) propargyl/allenyl complexes reported in literature (Table 2-4), it can be seen that they have similar structures. In all cases, the metal propargylic carbon (C1) distance is larger than the metal internal carbon (C2) distance. The M-C1 distance is larger than the M-C3 distance for CpZr(Me)(η\(^3\)-CH\(_2\)CCPh), Cp*Zr(TBM)(η\(^3\)-CH\(_2\)CCMe), CpMo(η\(^3\)-MeCCPh)(η\(^3\)-CH\(_2\)CCPh) and smaller for [(PPh\(_3\))\(_2\)Pt(η\(^3\)-CH\(_2\)CCPh)]OTf. This observation may be related to the relative contribution of the allenyl or propargyl resonance structure in the η\(^3\)-propargyl/allenyl complexes, but classification of the present η\(^3\)-propargyl/allenyl rare-earth metal complexes in either of these two groups is hampered by the observed experimental error. The carbon-carbon distances in the η\(^3\)-propargyl/allenyl ligand are similar for all complexes, the C1-C2 distance being larger than the C2-C3 distance in all complexes, and the angle α varies from 145 to 160°, seemingly both as a function of metal radius and the coordination environment.

2.5. Reactivity of propargyl/allenyls

2.5.1. Introduction

Spectroscopic and structural analysis of the lanthanidocene propargyls has provided evidence for static η\(^3\)-propargyl/allenyl structures. Further insight into the properties of this largely unexplored class of rare-earth metallocenes was obtained by exploring their reactivity towards a variety of substrates. The documented reactivity of η\(^3\)-propargyl/allenyl transition-metal complexes is dominated by the addition of nucleophiles to cationic complexes and the reported reactions may be classified as nucleophilic additions to the metal or the nucleophilic, regiospecific additions to the central carbon of the η\(^3\)-propargyl/allenyl ligand (Scheme 2-17). When the nucleophile adds to the metal, η\(^1\)-propargyl or η\(^1\)-allenyl complexes are formed, depending on the nature of the nucleophile. These η\(^3\)-propargyl and η\(^1\)-allenyl complexes may display further reactivity, such as insertion of unsaturated reagents into the M-CH\(_2\) bond and the addition of electrophiles to the ligand.

If the η\(^1\)-tautomers are kinetically accessible, the reactive chemistry of present η\(^3\)-propargyl/allenyl complexes will most likely involve reactions of η\(^1\)-propargyl and η\(^1\)-allenyl derivatives, depending on their relative importance. It seems reasonable to expect that the η\(^1\)-propargylic and η\(^1\)-allenyllic tautomer exhibit each distinct C-H activation and insertion reaction sequences, in analogy to rare-earth metallocene η\(^1\)-alkyl and η\(^1\)-hydride derivatives. Examples of rare-earth metal complexes containing ligands undergoing a conversion from η\(^3\)- to η\(^1\)-bonding include allyl Cp\(^*\)\(_2\)Lu(n(η\(^1\)-CH\(_2\)CH=CHR) and tris(pentamethylcyclopentadienyl) derivatives Cp\(^*\)\(_2\)Ln. Permethyllanthanidocene allyls undergo insertion reactions with ethylene, CO and CO\(_2\) and the bonding of the allyl ligand is fluxional in solution. Although these findings indicate that access to an η\(^1\) form is facile in solution, the crystallographic studies obtained so far have shown that the allyl ligands adopt η\(^3\) structures in the solid state. Similarly, the observed reactivity of Cp\(^*\)Sm with ethylene, H\(_2\), CO, PhCN and PhCNO is in agreement with that of an η\(^1\)-alkyl, but no spectroscopic or structural evidence for a Cp\(^*\)Sm(η\(^3\)-C\(_2\)Me\(_2\)) species has been observed in solution or in the solid state.
2.5.2. The reactivity towards protic acids

Methanol

When Cp*₂YCH₂CCPh (7b), Cp*₂LaCH₂CCPh (7a) and Cp*₂LaCH₂CCC₆H₃Me₂-2,6 (8a) were allowed to reacted with an excess of methanol-d₄ (5-10-fold molar excess) in benzene-d₆, the orange solutions turned yellow instantaneously. On the basis of NMR and GC-MS analysis, the organic reaction products were identified as the corresponding acetylenic ArCCCH₂D and allenic ArCD=C=CH₂ deuterolysis products (Ar = Ph, C₆H₃Me₂-2,6) (Scheme 2-18). Because the relative amount of allenic and acetylenic quenchings products is expected to reflect the relative importance of the η¹-propargylic and η¹-allenyl tautomers in the present η³-allenyl/propargyl complexes, analogous reactions with methanol were conducted for Cp*₂LnCH₂CCAr. The ratios of acetylenic and allenic products were determined by in situ ¹H NMR spectroscopy (using appropriate long pulse delays to avoid signal saturation under the present anaerobic conditions and long experiment times to allow for reliable signal-to-noise ratios) and are shown in Table 2-6.

NMR spectroscopy indicated the following order of increasing propargylic character within the lanthanum series: Cp*₂LaCH₂CCC₆F₅ (10a) < Cp*₂LaCH₂CCPh (7a) < Cp*₂LaCH₂CCC₆H₃Me₂-2,6 (8a) < Cp*₂LaCH₂CCPr₂-2,6 (9a) (Section 2.4.3). Surprisingly, the relative amount of acetylenic quenching product did not increase with the degree of propargylic bonding in the above η³-propargyl/allene complexes Cp*₂LnCH₂CCAr. Instead, the relative amount of acetylenic quenching product was found to decrease with the steric size of the substituent of the η³-propargyl/allenyl ligand. Moreover, the higher relative amount of acetylenic quenching product for 7a as compared to 7b suggests that the formation of acetylenic quenching products increases with the coordination space around the metal center under the assumption that the bonding in Cp*₂LaCH₂CCPh (7a) and Cp*₂YCH₂CCPh (7b) have a similar degree of propargylic character (Section 2.4.3).

These results can plausibly be rationalized as proceeding via initial Lewis base coordination of methanol (Scheme 2-19). Nucleophilic attack at the metal center may take place at the substituted side or at the unsubstituted side of the η³-propargyl/allenyl ligand. Obviously, the latter mode of nucleophilic attack is sterically favored. The formation of the Lewis-base adducts is followed by the electrophilic attack of the

Table 2-6. Allene/alkyne ratios for the reaction of Cp*₂LnCH₂CCAr with methanol.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ln, Ar</th>
<th>alkyne:allene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Y, C₆H₅ (7b)</td>
<td>1.00:1.00</td>
</tr>
<tr>
<td>2</td>
<td>La, C₆H₅ (7a)</td>
<td>1.11:1.00</td>
</tr>
<tr>
<td>3</td>
<td>La, C₆H₃Me₂-2,6 (8a)</td>
<td>1.06:1.00</td>
</tr>
<tr>
<td>4</td>
<td>La, C₆H₃Pr₂-2,6 (9a)</td>
<td>0.58:1.00</td>
</tr>
<tr>
<td>5</td>
<td>La, C₆F₅ (10a)</td>
<td>1.17:1.00</td>
</tr>
</tbody>
</table>

* Reactions in benzene-d₆ at room temperature. The ratios were determined by in situ ¹H NMR spectroscopy.
Scheme 2-19. The proposed mechanism for the reactions of the Cp*₂Ln(η³-CH₂CCAr) complexes with methanol-d₄.

The above results revealed that Lewis base coordination of methanol at the unsubstituted side is only moderately favored over Lewis base coordination at the phenyl-substituted side of the η³-propargyl/allenyl ligand in Cp*₂La(CH₂CCPh) (7a) and Cp*₂Y(CH₂CCPh) (7b). This finding suggests that electronic effects are more important than steric effects in determining the side of nucleophilic attack at the metal center in the propargyl complexes Cp*₂LnCH₂CCPh. In this light, it was decided to study the effect of another Brønsted acid having different Lewis basic properties. The choice of phenylacetylene was based on the relatively high acidity of the acetylenic proton and the soft Lewis basic character of both the carbon-carbon triple bond and the phenyl group. Methanol, in contrast, is typically classified as a hard Lewis base, according to Pearson’s hard-soft-acid-base (HSAB) principle.

Reactions of Cp*₂La(η³-CH₂CCPh) (7a) with phenylacetylene were performed in benzene-d₆ at room temperature and their progress was monitored by in situ ¹H NMR spectroscopy, using hexamethyldisiloxane (HMDSO) as an internal standard. When a stoichiometric amount of phenylacetylene was added to a benzene-d₆ solution of 7a at room temperature, the light-orange solution turned immediately dark red and only 57% of the propargyl was converted upon complete consumption of phenylacetylene. The propargyl derivative (7a) was
converted into two new organometallic products that were identified as the butatrienediy1 \(18a\) (24%) and the but-1-en-3-yn-1-yl derivative \(19a\) (9%), on the basis of NMR spectroscopy (Chapter 4). The major organic products in the reaction mixture were identified as the protonated \(\eta^3\)-propargyl/allenyl ligand (phenylallene and 1-phenyl-1-propyne in a 1.00:0.20 ratio, respectively) and \(\text{trans-1,4-diphenylbut-1-en-3-yne}\) (eq. 2.2).

Upon standing at room temperature the amount of phenylallene and \(19a\) decreased under the formation of two unidentified lanthanocene species having Cp* 1H NMR resonances at \(\delta 1.97\) and \(1.92\) ppm, while the amount of \(18a\) and \(7a\) did not change significantly. When \(7a\) was allowed to react with a two- and ten-fold molar excess of phenylacetylene, 80% and 88% of \(7a\) was converted, respectively, upon complete consumption of phenylacetylene. In both cases, phenylacetylene was converted into phenylallene, 1-phenyl-1-propyne, \((E)\)-1,4-diphenylbut-1-en-3-yne and traces of 2,4-diphenylbut-1-en-3-yne, according to NMR and GC-MS analysis.

The formation of phenylacetylene dimers and the observation of lanthanocene derivatives, previously observed in the lanthanocene-catalyzed oligomerization reaction of phenylacetylene, strongly suggest that the reaction of \(7a\) with phenylacetylene gives rise to the monomeric, alkynyl derivative \(\text{Cp*}_2\text{LaCCPh}\) which has been implicated as the active catalyst in the permethyllanthanocene-catalyzed oligomerization reaction of phenylacetylene (Chapter 4). Mononmeric, permethyllanthanidoocene alkynyl derivatives \(\text{Cp*}_2\text{LnCCR}\) are unstable and dimerize into dinuclear, \(\mu\)-alkynyl derivatives \([\text{Cp*}_2\text{Ln}(\mu\text{-CCR})]_2\). In some cases, these dimeric, alkynyl derivatives undergo subsequent C-C coupling to form butatrienediy1 derivatives \([\text{Cp*}_2\text{Ln}](\mu\text{-RC=C=C=CR})_2\)\(^5\). Examples of the latter two types of dinuclear compounds have been isolated and characterized, but no spectroscopic or structural evidence for monomeric, lanthanidocene alkynyl derivatives have been reported in literature. The present results reveal that \(\text{Cp*}_2\text{LaCCPh}\) reacts faster with phenylacetylene than \(\text{Cp*}_2\text{La}(\eta^3\text{-CH}_2\text{CCPh})\)(\(7a\), thereby accounting for the incomplete conversion of \(7a\) in the reaction with excess phenylacetylene.

Another feature of the reaction of \(7a\) with phenylacetylene concerns the reactivity of \(\text{Cp*}_2\text{LaC(Ph)=C(H)CCPh}\) (\(19a\)) with phenylallene. The reactivity of allenes and alkynyl metal derivatives is relatively unexplored in organo rare-earth metal chemistry.\(^b\) Even so, both C-H activation and insertion reactions are plausible processes, in analogy to the well-documented reactive chemistry of rare-earth metalloocene \(\eta^1\)-alkyl and \(\eta^1\)-hydride derivatives.\(^5\) Reactions of \(19a\) with phenylallene, proceeding via insertion into the La-C bond, yield organic compounds \(\text{C}_8\text{H}_{12}\) after protonolysis. GC-MS analysis did not supply evidence for the presence of such organic compounds after quenching reaction mixtures with \(\text{H}_2\text{O}\), thereby excluding the possibility that \(19a\) reacts with phenylallene via insertion reactions.\(^c\)

Nonregioselective C-H activation of phenylallene by \(\text{Cp*}_2\text{LaC(Ph)=C(H)CCPh}\) (\(19a\)) yields, in principle, two new allenyl lanthanocene species and \(\text{Cp*}_2\text{La}(\eta^1\text{-CH}_2\text{CCPh})\) (Scheme 2-21). This scenario accounts for the observation of two new lanthanocene species, having \(\text{Cp*}_2\) NMR resonances at \(\delta 1.97\) and \(1.92\) ppm \((\text{vide supra})\). Unfortunately, the complexity of the reaction mixtures thwarted attempts to identify these
proposed allenyl derivatives unequivocally and quenching experiments with H$_2$O and D$_2$O did provide experimental evidence to support this hypothesis. For the sake of convenience, these allenylic derivatives will be referred to as Cp*$_2$LaX ($\delta$ 1.92 ppm) and Cp*$_2$LaY ($\delta$ 1.97 ppm) in the proceeding discussion. Nonselective reactivity of allenylic substrates towards alkyl d$^0$ metal complexes has also been observed for isolectronic group 4 metallocene cations.$^{88}$

In an effort to obtain additional evidence for the above proposed reaction sequences, reactions of Cp*$_2$La(\(\eta^3\)-CH$_2$CCPh) (7a) with phenylacetylene were performed in toluene-$d_8$ at low temperatures and monitored by normalized, \textit{in situ} $^1$H NMR spectroscopy. Phenylacetylene (1.1 equiv.) was condensed onto a toluene-$d_8$ solution of 7a at -196 °C and allowed to warm up to -60 °C in the probe of the spectrometer. $^1$H NMR spectroscopy indicated quantitative conversion of 7a into the dimeric, bridged alkynyl derivative [Cp*$_2$La(\(\mu\)-CCPh)]$_2$ (20a) (one singlet for Cp* at $\delta$ 2.21 ppm, see Figure 2-6) and Cp*$_2$LaC(Ph)=C(H)CCPh (19a) (one singlet for Cp* at $\delta$ 2.01 ppm), accompanied by the formation of phenyllallene and 1-phenyl-1-propyne (in a 1.00:0.08 ratio, respectively).

Slowly warming the reaction mixture to room temperature resulted in the conversion of the dimeric alkynyl derivative [Cp*$_2$La(\(\mu\)-CCPh)]$_2$ (20a) into the butatrienediyl species ([Cp*$_2$La]$_2$(\(\mu\)-\(\eta^3\):\(\eta^3\)-PhC=C=C=Ph)] (18a) (one singlet for Cp* at $\delta$ 2.04 ppm which overlaps at low temperatures with the solvent, see Figure 2-6).
Chapter 2

and the reformation of 7a (one singlet for Cp* at δ 1.90 ppm). The C-C coupling reaction of 20a to yield 17a has been studied in more detail for reactions of Cp* 2LaCH(SiMe3)2 and [Cp* 2La(µ-H)]2 with phenylacetylene (Chapter 4). At higher temperature, the complete conversion of phenylallene was observed, accompanied by the conversion of 19a (one singlet for Cp* at δ 1.97 ppm) into Cp* 2LaX (δ 1.92 ppm) and Cp* 2LaY (δ 1.97 ppm). Finally, the slow formation of a new lanthanocene derivative having a Cp* 1H NMR resonance at δ 2.01 ppm was also observed. This derivative was also formed as a minor product in the low-temperature reactions of Cp* 2LaCH(SiMe3)2 and [Cp* 2La(µ-H)]2 with phenylacetylene and was tentatively assigned to an alkynyl derivative of unknown structure (Chapter 4).

The rapid and quantitative conversion of Cp* 2La(η^3-CH2CCPh) (7a) at low temperature followed by its reformation at higher temperature was unexpected and studied in more detail by a quantitative analysis.

**Scheme 2-22.** The reaction sequences proposed to account for the observed reactivity of phenylallene during the reaction of 7a with phenylacetylene at low temperature and subsequent warming to room temperature.
Kinetic profiles of the reaction products were obtained by monitoring their concentration in time by means of normalized, in situ H NMR spectroscopy using an internal reference (hexamethyldisiloxane) and appropriate long pulse delays (Figure 2-7). The rapid and quantitative protonolysis of Cp*₂La(η³-CH₂CCPh) (7a) by phenylacetylene affords Cp*₂LaCCPh which dimerizes into 20a. The experimental data indicate that the formed dimeric bridged alkyn derivative 20a reacts via two distinct processes at -30 °C. The reaction of 20a with phenyllallene competes with intramolecular C-C coupling of 20a to yield 17a. The kinetic profiles indicate also that the reaction of 20a with phenyllallene affords 7a, selectively. The concomitant increase in concentration of 19a undubitably originates from the reaction of Cp*₂LaCCPh and phenylacetylene, both formed from the reaction of of 20a with phenyllallene (Scheme 2-22).

In accord with previous results, the present results also indicated that Cp*₂LaC(Ph)=C(H)CCPh (19a) reacts with phenyllallene at 0 °C, forming mainly Cp*₂La(η³-CH₂CCPh) (7a), but at higher temperature also Cp*₂LaX (δ 1.92 ppm). At room temperature, both 19a and phenyllallene were completely consumed within several hours, to yield among others trans-1,4-diphenylbut-1-en-yne and Cp*₂LaY (δ 1.97 ppm).

Concluding remarks

The reactions of Cp*₂La(η³-CH₂CCPh) (7a) with phenylacetylene and methanol revealed that the relative amounts of propargyl and allenylic quenching products depend on the nature of the Lewis basic, Bronsted acid (i.e. methanol gave an allene-to-alkyne ratio of 1:0.01:11, while phenylacetylene resulted in a ratio of 1:0.00:20). Under the assumption that the reaction of 7a with phenylacetylene proceeds via initial alkyne coordination, the present data provide evidence that the tendency for Lewis base coordination at the sterically most hindered side of the η³-propargyl/allenylic ligand in 7a increases with the softness of the Lewis base. Circumstantial evidence for initial Lewis base coordination in the reactions of 7a with phenylacetylene is supplied by the observation of the Lewis base adduct Cp*₂LaCCPh(PbCCH) in the permethyllanthanocene-catalyzed oligomerization of phenylacetylene (Chapter 4), coordination equilibria of alkynes and divalent lanthanoidocenes Cp*₂Ln (Ln = Sm, Eu, Yb) in benzene-d₆ solution and alkene coordination prior to insertion into Ln-alkyl bonds. Based on the linear, rod-shape structure of phenylacetylene, it seems reasonable to assume that the steric requirements for Lewis base coordination of phenylacetylene are either similar or larger than that of methanol in 7a. In this light, the higher relative amount of allenylic quenching product for the reaction of 7a with phenylacetylene as compared to the reaction of 7a with methanol suggests that the side of nucleophilic attack is mainly determined by electronic factors rather than steric factors in the reaction of 7a with nucleophiles.

The above results indicate that the relative amount of propargyl and allenylic quenching products is influenced by the reaction temperature as well (i.e. at room temperature the reaction of 7a with phenylacetylene produced an allene-to-alkyne ratio of 1.00:0.20, but at -60 °C a ratio of 1.00:0.08 was found). If alkyne coordination takes place prior to protonolysis, it seems that the formation of the sterically most hindered Lewis base adduct, the η³-allenyl-like derivative of Cp*₂La(η³-CH₂CCPh) (7a), is favored by relatively low reaction temperatures. The η³-allenyl-like derivative of 7a may therefore represent the kinetic product, while the η³-propargyl-like derivative of 7a represents the thermodynamic product of the reaction of 7a with phenylacetylene.

2.5.3. Thermolysis

Prior to further reactivity studies, it was considered insightful to investigate the thermal stability of the present Cp*₂LaCH₂CCAr complexes. Thus, a toluene-d₆ solution of Cp*₂LaCH₂CCPh (7a) was heated to 120 °C. After two days, small signals appeared in the Cp* (δ 2.05, 2.01, 1.99, 1.83 ppm) and aliphatic region (δ 0.59, 0.45 ppm) which increased in intensity upon further heating. Also, a color change from light yellow to bright orange was observed after heating several days at 120 °C. The propargyl NMR signals disappeared almost completely after 10 days. Attempts to identify the thermolysis products were unsuccessful due to the high reactivity and instability of the products. The reaction mixture was quenched with methanol-d₆ after complete conversion of 7a. Subsequent GC/GC-MS analysis indicated the presence of Cp*H-d₆ and two oligodeuterated isomers of Cp*H-d₆, corresponding to the dimers of the phenyl-substituted propargyl ligand.

The above results revealed that 7a is thermally quite robust. It seems natural to ascribe the observed thermal stability to the delocalized η³-bonding of the propargyl/allenylic ligand, providing the electrophilic metal center with both steric and electronic saturation. Several studies of the thermal stability of Cp*₂LaCH(SiMe₃)₂ (6a) have been reported in literature. The decomposition of 6a in cyclohexane-d₂ at 120 °C was found to be relatively rapid (quantitative within 2 h) at 120 °C via intramolecular methyl C-H activation, yielding highly
The decomposition of 6a in toluene-$d_8$ at 112 °C produced the benzyl derivative Cp*$_2$LaCD$_2$C$_6$D$_5$ and CH$_2$(SiMe$_3$)$_2$ within several hours ($t_{1/2} = 3$ h), both selectively and quantitatively. Evidence was presented that solvent metalation is preceded by the intramolecular C-H activation of the Cp* methyl group, affording the fulvene derivative Cp*(C$_5$Me$_4$CH$_2$-$\eta^3$:$\eta^2$)La. The reversible nature of inter- and intramolecular C-H activation was put forward to account for the observed H/D exchange between solvent and Cp* ligand.

Accordingly, thermal decomposition of 7a can be envisioned to occur by intramolecular metalation, forming the fulvene derivative Cp*(C$_5$Me$_4$CH$_2$-$\eta^3$:$\eta^2$)La and the protonated $\eta^3$-propargyl/allenyl ligand, possibly both 1-phenyl-1-propyne and phenylallene (Scheme 2-23). Subsequent, reversible solvent metalation accounts for the observed deuteration of the Cp* ligand. The formation of the observed dimers of the $\eta^3$-propargyl/allenyl ligand can be explained by insertion of 1-phenyl-1-propyne and/or phenylallene into the La-C bond of 7a. The observation of only two isomers points to the regiorandom insertion of 1-phenyl-1-propyne into the La-CH$_2$ bond of the $\eta^3$-propargyl/allenyl derivative, however. Evidence for this view is supplied by the observed tendency of phenylallene to undergo C-H activation rather than insertion reactions with Cp*$_2$LnR complexes (Section 2.5.2) and catalytic reactions of 7a with excess 1-phenyl-1-propyne. A detailed study of the latter process demonstrated that insertion of 1-phenyl-1-propyne into the La-CH$_2$ bond of 7a represents the major reactive pathway under the present reaction conditions (Chapter 3). The fact that the dimers of the $\eta^3$-propargyl/allenyl ligand are oligodeuterated implies that the protonated $\eta^3$-propargyl/allenyl ligand undergoes reversible transmetalation with the benzyl derivative Cp*$_2$LaCD$_2$C$_6$D$_5$ before insertion. Due to the complexity of the $^1$H NMR spectrum, only Cp*$_2$La($\eta^3$-CD$_3$C$_6$D$_5$)$_2$ was identified spectroscopically, based on its reported Cp* $^1$H NMR resonance at δ 1.82 ppm. The observation of $^1$H NMR resonances at δ 0.59 and 0.45 ppm are, furthermore, consistent with the presence of $\alpha$-metalated methyl groups.

Heating mixtures of 7a and 7b for several days to 120 °C in benzene-$d_6$ gave similar organic products as observed for 7a in toluene (i.e. only the presence of oligodeuterated Cp*H and isomeric dimers of the protonated $\eta^3$-propargyl ligand was indicated by GC-MS analysis after treating the reaction mixture with methanol). Quantitative $^1$H NMR analysis of the decrease of the propargylic CH$_2$ proton resonance normalized against hexamethyldisiloxane (4.5 mM) in benzene-$d_6$ solution indicated that the thermolysis of 7a was first-order in 7a for at least 4 half-lives, as was evident from a linear plot of ln[7a]$_0$/[7a], versus time ($R^2 = 0.9889, t_{1/2} = 47.1$ h).
2.5.4. The reactivity towards Lewis bases

Tetrahydrofuran

The reactions of Lewis base with \( \eta^1 \)-propargyl/allenyl transition-metal complexes are known to give the Lewis base adduct of \( \eta^1 \)-propargyl or \( \eta^1 \)-allenyl derivatives, depending on the nature of the Lewis base.\(^{39,40} \)

To investigate whether the present \( \text{Cp}^* \text{LnCH}_2 \text{CCPh} \) complexes exhibit an analogous reactivity, the reaction of \( \text{Cp}^* \text{LaCH}_2 \text{CCPh} \) (7a) with an equimolar amount of tetrahydrofuran (THF) was conducted in benzene-\( d_6 \) at room temperature. No color change was observed and \(^1H \) NMR spectroscopy revealed a rapid and clean reaction. The upfield shifts of the THF \(^1H \) and \(^{13}C \) NMR resonances (e.g. \( \Delta \delta \) -0.55 and -0.04 ppm for the \( \alpha \)- and \( \beta \)-carbon, respectively, in the \(^{13}C \) NMR spectrum) are consistent with the coordination to the electrophilic metal center. The interpretation of the shifted propargyl NMR resonances is somewhat ambiguous, however. An increase in allenyl character is suggested by the downfield shift of the \( \text{CH}_2 \) proton resonance (\( \Delta \delta +0.13 \) ppm), whereas the upfield shift of its \( \text{CH}_2 \) carbon resonance (\( \Delta \delta d_6 \) ppm) points to an increase in propargylic character (Table 2-7). In spite of this contradiction, an \( \eta^3 \)-propargyl/allenyl structure is presently favored, based on the similarity of the NMR spectral parameters with the crystallographically characterized \([\text{Cp}^* \text{La} \eta^3 \text{-CH}_2 \text{CCPh}](\text{C}_5 \text{H}_5 \text{N})] \) (7a·py) (Section 2.5.5).

The complex 7a·THF is stable in benzene-\( d_6 \) solution at room temperature, as no changes were observed in the \(^1H \) NMR spectrum after standing for two days. When the reaction mixture was heated to 50 °C, the intensity of the NMR signals of the base adduct 7a·THF slowly decreased, giving rise to small vinylic \(^1H \) NMR resonances and several unidentified proton resonances in the \( \text{Cp}^* \) region. After 24 h, no resonances attributable to 7a·THF were observed and the reaction mixture was quenched with methanol-\( d_4 \). Subsequent GC-MS analysis indicated the presence of \( \text{Cp}^* \text{D} \), THF and one unidentified dimer \( \text{C}_9 \text{H}_{16} \) of the protonated phenyl-substituted propargyl ligand (identical to \( \text{C}_9 \text{H}_{16} \) found in the thermolysis reaction of 7a, Section 2.5.3).

The thermal lability of 7a·THF relative to the parent compound 7a is striking. The exact reason for this difference in stability is unknown at present. One possibility is that the additional ligand provides extra steric and electronic saturation to the metal center, thereby stabilizing the formation of an \( \eta^1 \)-propargyl (or \( \eta^1 \)-allenyl) structure in 7a. Addition of THF has, in fact, been found to facilitate the rapid \( \eta^3 \)-\( \text{C}_3 \text{H}_5 \) to \( \eta^1 \)-\( \text{C}_3 \text{H}_5 \) interconversion in \( \text{Cp}^* \text{Nd}(\text{C}_3 \text{H}_5) \) and \( \text{Cp}^* \text{Sm}(\text{C}_3 \text{H}_5) \).\(^{40} \) If a transient \( \eta^1 \)-propargyl or \( \eta^1 \)-allenyl species is formed, it may undergo intramolecular C-H activation with the C-H bond \( \alpha \) to the oxygen atom, with or without the intermediacy of \( \text{Cp}^* \text{FvLa} \) (THF), forming \( \text{Cp}^* \text{La} \eta^1 \text{-2-CH}_2 \text{O} \) and \( \text{CH}_3 \text{CCPh} \). The former process has been observed for \( \text{Cp}^* \text{YMe}(\text{THF}) \) and several ether adducts of lanthanocene hydrides, \( \text{Cp}^* \text{LnH}(\text{OR}) \) (\( \text{Ln} = \text{Lu}^{95}, \text{Y}^{96}, \text{Ce}^{96}, \text{La}^{96} \)), while the reaction of the samarium derivative \( \text{Cp}^* \text{SmMe}(\text{THF}) \) with benzene-\( d_6 \) and toluene-\( d_8 \) is reported to proceed via intramolecular \( \text{Cp}^* \text{C}-\text{H} \) activation.\(^{97} \) Although a temperature effect cannot be ruled out, this rationalization also accounts for the observation of only one of the two previously observed dimers \( \text{C}_9 \text{H}_{16} \) of the \( \eta^1 \)-propargyl/allenyl ligand in the thermolysis reaction of 7a (Section 2.5.3).\(^{98} \) Apparently, the formation of one tautomer is kinetically much facile. The observed mixture of products is probably the result of several types of C-O activation processes, such as reported for \( \text{Cp}^* \text{Y}(\text{THF}) \) and \( \text{(C}_3 \text{H}_4 \text{R}) \text{YCH}_2 \text{SiMe}_3 \) \( (\text{R} = \text{H}, \text{Me}) \).\(^{99} \) Nonetheless, no spectroscopic evidence for typical C-O cleavage products such as \( \text{Cp}^* \text{LaO} \text{Bu} \) or \( \text{[Cp}^* \text{La}(\mu-\text{OCH}-\text{CH}_3)] \) was obtained by comparison with reported NMR data.\(^{99} \)

Scheme 2-24. The reactions of 7a and 7b with Lewis bases.
A clean and quantitative reaction was also observed for the reaction of Cp* 2LaCH2CCPh (7a) with 1 equivalent of pyridine. The formation of the corresponding adduct (7a·py) is indicated by the upfield shifts of the propargyl proton (\(\Delta \delta -0.12, -0.17\) and -0.19 ppm for \(\alpha-, \beta-, \) and \(\gamma-\text{CH}\), respectively) and carbon resonances (\(\Delta \delta -0.55, -0.30\) and +1.77 ppm for \(\alpha-, \beta-, \) and \(\gamma-\text{CH}\), respectively) upon metal coordination. The changes of the propargyl 1H and 13C NMR resonances are similar as observed previously for 7a·THF, albeit slightly larger (Table 2-7). Again, the downfield shift of the CH2 proton resonance (+0.34 ppm) suggests an increase in allenylic character, while the upfield shift of its carbon resonance (\(\Delta \delta -2.93\) ppm) and the increase in 1JCH imply, conversely, an increase in propargylic character. An increase in propargylic character is also indicated by IR spectroscopy, revealing a shift of the symmetrical C≡C stretch from 1944 cm\(^{-1}\) to 1973 cm\(^{-1}\) (Figure 2-8). A single-crystal X-ray analysis study of 7a·py established unambiguously that the bonding of the propargyl/allenyl ligand in 7a·py is still tri-hapto, despite pyridine coordination (Section 2.5.5).

The Lewis base adduct Cp* 2LaCH2CCPh(C5H5N) (7a·py) was obtained on a preparative scale by the reaction of Cp* 2LaCH2CCPh (7a) with a small excess of pyridine (1.1 equiv) in a pentane solution at room temperature. Cooling a pentane solution of 7a·py afforded yellow crystals in a high isolated yield (83%). The complex 7a·py was found to be indefinitely stable in the solid state at room temperature, while 1H NMR spectroscopy indicated that benzene-d6 solutions of 7a·py remained unchanged at room temperature for at least seven days, but slowly underwent decomposition at 50 °C.

Thermal decomposition of 7a·py in benzene-d6 solution at 50 °C was accompanied by a color change from light-yellow to brown. The intensity of the pyridine and Cp* proton resonances decreased significantly within seven days at 50 °C, but only one new signal at 3.20 ppm formed concomitantly. Subsequent heating to 80 °C led to the formation of small vinylic signals and the complete disappearance of NMR signals due to 7a·py within two days. Addition of methanol-d6, followed by GC/GC-MS analysis indicated the presence of 2,2'-bipyridine as the major organic product. Compounds with m/z 197-198 (a mixture of C10H12N and C11H14ND), 234 (two isomers of C10H12D), and 333 were formed as minor products.

The above results indicate that thermal decomposition of 7a·py is complex and that the nature of the quenched decomposition products differ from that observed for the analogous reactions of 7a and 7a·THF. The masses of the observed quenching products provide evidence for the occurrence of variety of C-C coupling processes. The broad 1H NMR resonance at 3.20 ppm and the presence of 2,2'-bipyridine point to the formation of the paramagnetic species Cp*-La(72-2,2'-bipyridyl) which is reported to be formed from Cp*-La(72-2,2'-bipyridyl) upon heating at 50 °C.100 However, the complexes Cp*-La(72-2,2'-bipyridyl) or Cp*-La(72-2,2'-bipyridyl) are not observed spectroscopically by comparison with reported 1H NMR data.

To investigate the effect of metal size on the bonding mode of the C≡C coupling upon Lewis base coordination, the reaction of Cp* 2LaCH2CCPh (7b) with pyridine in benzene-d6 was also studied. NMR spectroscopy indicated that the addition of 1 equiv. of pyridine to 7b led to the rapid and clean formation of the corresponding Lewis base adduct 7b·py. The upfield shifts of the CH2CC carbon resonances are larger than previously observed for 7a·py (Table 2-7). The observed yttrium-carbon coupling of the propargyl and terminal carbon resonances indicate that the propargyl/allenyl ligand is still bound in an η1-fashion.

### Table 2-7. IR and NMR spectral parameters of Lewis base adducts.

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<tr>
<th>Compound</th>
<th>7a</th>
<th>7a·THF</th>
<th>7a·py</th>
<th>7b</th>
<th>7b·py</th>
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<td>2.95</td>
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<table>
<thead>
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<th>Parameter</th>
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<th>1H NMR</th>
<th>13C NMR</th>
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</thead>
<tbody>
<tr>
<td>ν (cm(^{-1}))</td>
<td>1944</td>
<td>1973</td>
<td>2148</td>
</tr>
</tbody>
</table>

a NMR spectra measured in C6D6 at 25 °C. Chemical shifts in ppm and 1JCH and 1JCC coupling constants in Hz. IR spectra measured as Nujol mulls. b Not observed. c Complex not isolated.
Rare-earth metalloocene propargyl/allenyls

the CH$_2$ $^1$H NMR resonance moved upfield ($\Delta \delta$ -0.19 ppm) rather than downfield as observed for 7a upon coordination of THF and pyridine. IR spectroscopy indicates a substantial increase of propargylic character, as evidenced by a shift of the C≡C stretch from 1923 cm$^{-1}$ to 2148 cm$^{-1}$ (Figure 2-8).

The Lewis base adduct Cp$_{\ast}$YCH$_2$CCPh(C$_5$H$_5$N) (7bpy) was prepared analogously to Cp$_{\ast}$LaCH$_2$CCPh(C$_5$H$_5$N) (7aphy) and isolated in reasonable yields (63%) as an off-white thermolabile solid. Attempts to obtain single-crystals of 7bpy suitable for X-ray analysis failed. Freshly prepared 7bpy turned dark red within hours upon standing at room temperature. NMR and GC/GC-MS analysis indicated the formation of a multitude of decomposition products that defied characterization. In a closed atmosphere, 7bpy was found to be stable in benzene-$d_6$ solution at room temperature for 7 days. Heating to 50 °C, however, resulted in slow decomposition in a manner similar to that observed for 7aphy. The same organic compounds were found with GC-MS analysis after quenching the reaction mixture with methanol-$d_4$, while the formation a broad signal in the $^1$H NMR spectrum at $\delta$ 4.20 ppm, accompanied by slowly disappearing signals due to 7aphy, are consistent with the formation of the paramagnetic derivative Cp$_{\ast}$Y(η$^2$-2,2'-bipyridyl)).

Many examples are reported in literature involving the reaction of rare-earth metalloocene derivatives Cp$_{\ast}$LnR (e.g. Ln = Lu$^{3+}$, R = H, Me; Ln = Sc$^{3+}$, R = Me, CH$_3$C$_6$H$_5$, C$_6$H$_5$; Ln = Y$^{3+}$, R = CH(SiMe$_3$)$_3$; Ln = Y$^{3+}$, R = η$^1$-2-C$_5$H$_4$O, η$^1$-2-C$_5$H$_4$S) with pyridine. These reactions proceed via the initial formation of the corresponding Lewis base adduct, followed by transmetalation, forming Cp$_{\ast}$Ln(η$^2$-2-C$_5$H$_4$N) and RH. However, no spectroscopic evidence for the (transient) formation of Cp$_{\ast}$Y(η$^2$-2-C$_5$H$_4$N) or Cp$_{\ast}$Y(η$^2$-2-C$_5$H$_4$N)(C$_6$H$_5$N)

Figure 2-8. Infrared spectra of 7a (upper spectrum, black line), 7aphy (upper, grey), 7b (lower, black) and 7bpy (lower, grey) as nujol mulls.
Chapter 2

was found by comparison with reported $^1$H NMR data. The formation of unidentified material, accompanied by gradual coloration of the reaction mixture to deep red, has previously been noted for rare-earth metal pyridyl and phenyl complexes.

2.5.5. The molecular structure of Cp*$_2$La($\eta^3$-CH$_2$CCPh)(py)

Complex 7a·py crystallized in the triclinic space group $P_1\overline{1}$ with $Z = 4$. The solid-state molecular structure is depicted in Figure 2-9 and selected bond distances and angles are given in Table 2-8. The Cp*$_2$La moiety of 7a·py is similar to that of reported bent permethyllanthanocenes Cp*$_2$La(X)(Y) complexes, having a Ct1-La-Ct2 angle (134.2°) and average La-Ct1 (2.57 Å) and La-Ct2 (2.58 Å) distances. Crystallographically characterized formally nine-coordinated bent lanthanidocenes (C$_5$R$_5$)$_2$LnL$_3$ are relatively scarce in literature and the only other example is – to the best of our knowledge – represented by [Cp*$_2$La(NCCH$_3$)(DME)]$\text{[BPh}_4\text{]}$. Although the geometry of 7a·py may seem reminiscent of a bent metallocone with three equatorial ligands or a highly distorted trigonal bipyramid, neither description is entirely accurate. In fact, irregular geometries are common in the structural chemistry of lanthanide complexes, as ligand field effects are practically absent in lanthanide metals.

The Cp* ligands are in an unusual eclipsed conformation with a twist angle of 2.85°. It has been suggested that the presence of eclipsed Cp* ligands is the result of steric crowding, but examples of structures with eclipsed rings in which steric crowding is not so obvious have been reported as well. The steric crowding in 7a·py is evidenced by the La-N distance of 2.743(2) Å which is considerably longer than those reported for [Cp*$_2$La(NCCH$_3$)(DME)]$\text{[BPh}_4\text{]}$ (2.60(2) Å), [Cp*$_2$La(NHMe)(NH$_2$Me)]$^{186}$ (2.70(1) Å) and [1,2,4-(Me$_3$Si)$_3$C$_5$H$_2$]$_2$LaI(C$_5$H$_5$N)$^{187}$ (2.643(1) Å). Steric crowding in [Cp*$_2$La(NCCH$_3$)(DME)]$\text{[BPh}_4\text{]}$ was indicated by nonequivalent La-N distances. The observed La-N distance of in 7a·py is not exceptional, however, as it falls in the 2.70-2.80 Å range, reported for nonmetallocene lanthanum complexes. Comparing the crystal structures of 7a and 7a·py reveals several changes upon pyridine coordination. Firstly, a distortion of the coplanar rearrangement of the metal center with the $\eta^3$-propargyl/allenyl carbon backbone is observed (atom displacements from the least squares plane relative to 7a·py: La $\Delta +0.002$, C26 $\Delta +0.010$, C27 $\Delta +0.018$, C28 $\Delta -0.010$ Å). An apparent shift towards a more propargyl-like structure is also observed, as evidenced by the increased distances between lanthanum and the terminal carbon (Δ 0.08(1) Å). This change is also reflected by the upfield shift of the CH$_2$CC$^\text{13}$C NMR resonance (Δδ ~2.93 ppm), but is in contradiction with the observed downfield shift of the CH$_2$CC$^\text{1H}$ NMR resonance (Δδ +0.34 ppm). These findings suggest that the propargylic carbon resonance is a more reliable structural indicator for the relative contribution of propargyl- and allenyl structures than the corresponding proton resonance. In order to accommodate pyridine at the metal center, the average La-Ct1 (Δ 0.04(2) Å) and La-Ct2 distances (Δ 0.07(2) Å)

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>7a</th>
<th>7a·py</th>
</tr>
</thead>
<tbody>
<tr>
<td>C21-C22</td>
<td>1.362(10)</td>
<td>C26-C27</td>
</tr>
<tr>
<td>C22-C23</td>
<td>1.234(10)</td>
<td>C27-C28</td>
</tr>
<tr>
<td>C23-C24</td>
<td>1.465(9)</td>
<td>C28-C29</td>
</tr>
<tr>
<td>La-C21</td>
<td>2.811(6)</td>
<td>La-C26</td>
</tr>
<tr>
<td>La-C22</td>
<td>2.695(7)</td>
<td>La-C27</td>
</tr>
<tr>
<td>La-C23</td>
<td>2.740(7)</td>
<td>La-C28</td>
</tr>
<tr>
<td>av. La-C(Cp*)</td>
<td>2.806(16)</td>
<td>av. La-C(Cp*)</td>
</tr>
<tr>
<td>av. La-C(Cp*)</td>
<td>2.780(16)</td>
<td>av. La-C(Cp*)</td>
</tr>
<tr>
<td>La-Ct1</td>
<td>2.535(3)</td>
<td>La-Ct1</td>
</tr>
<tr>
<td>La-Ct2</td>
<td>2.509(4)</td>
<td>La-Ct2</td>
</tr>
<tr>
<td>av. La-C(Cp*)</td>
<td>2.571</td>
<td>2.584</td>
</tr>
<tr>
<td>av. La-C(Cp*)</td>
<td>2.743(2)</td>
<td>2.743(2)</td>
</tr>
</tbody>
</table>

Table 2-8. Selected bond lengths (Å) and angles (°) in Cp*$_2$LaCH$_2$CCPh (7a) and Cp*$_2$LaCH$_2$CCPh(C$_5$H$_5$N) (7a·py).

2.5.5. The molecular structure of Cp*$_2$La($\eta^3$-CH$_2$CCPh)(py)
have increased relative to 7a, together with the C1-La-C2 angle (Δ 2.9(1)°), as is expected for an increase in coordination number and concomitant steric crowding.

Another interesting feature of the crystallographic structure of 7a·py is the position of the pyridine ligand which is cis relative to the phenyl group and approximately coplanar with lanthanum and the carbons of the C1 backbone (atom displacements from the least squares plane: La -0.044, N -0.032, C26 -0.066, C27 0.054 Å). Such a coplanar and cis rearrangement seems sterically unfavorable and may point to an electronic origin.

In principle, quantum chemical investigations lend themselves as a valuable complement to experiments in order to understand the structure and reactivity of metal complexes. However, the presence of the large number of electrons in s, p, and f shells renders the quantum chemical calculations of lanthanide metal complexes less straightforward. Even so, several theoretical studies have shown the atomic 4f shell of the lanthanide atom is strongly stabilized and does not contribute significantly to the chemical bonding. The [Cp2Ln]+ frontier orbitals may therefore assumed to involve mostly 5d metal orbitals.

The electronic structure of Cp2MLn complexes has been thoroughly analyzed in terms of interaction of the bent CpM moiety with the n ligands L. In C2v symmetry, the CpM fragment has three low-lying orbitals 1a1, b2 and 2a1 and two high-lying orbitals b1 and a2. The b1 and a2 orbitals are destabilized by strong interaction with the π orbitals of the Cp rings. Only the three low-lying orbitals are capable of bonding with additional ligands L. The a1 orbital is mainly s, z in character, 1b2 mainly y2 and y and 2a1 mainly y2-z2, but the exact contribution of the atomic orbitals to the CpM molecular orbitals varies with the metal and the Cp(centroid)-M-Cp(centroid) angle. Interestingly, Lauher and Hoffmann predicted coordination of carbon monoxide along the line perpendicular to the Cp(centroid)-M-Cp(centroid) plane for d0 Cp2MR2 complexes,
because this lateral approach was considered to provide good overlap between the lowest unoccupied molecular orbital (LUMO), approximately of a $z^2$ type, and the carbon lone pair of CO (Scheme 2-25).\textsuperscript{112a} Nucleophilic attack from lateral positions in the carbonylation reaction of zirconocenes was later corroborated experimentally.\textsuperscript{113}

To determine the possible coordination site(s) of the Cp*$_2$Ln($\eta^3$-CH$_2$CCPh) complexes, a molecular orbital calculation was performed on the model complex Cp$_2$Y($\eta^3$-CH$_2$CCPh) in a geometry modeled after the crystal structure of Cp*$_2$Y($\eta^3$-CH$_2$CCPh) (7b). Computational simplifications involving the replacement of lanthanide metals with yttrium and permethylated Cp* ligands with unsubstituted cyclopentadienyl ligands are well-established.\textsuperscript{114,112} The former simplification is justified by a large body of experimental work that demonstrates that yttrium behaves very similarly to most lanthanides.\textsuperscript{1} The electronic properties of the ligand, on the other hand, are believed to be only of importance in reactions involving a change of oxidation state.\textsuperscript{115} The calculations were carried out with the Turbomole program at the bp86/RIDFT level using the Turbomole SV(P) basis set on all atoms (small-core pseudopotential on Y).\textsuperscript{116} Electron donating reactants are expected to interact with the unoccupied molecular orbitals of 7b. The calculated lowest and second lowest unoccupied molecular orbital (SLUMO) are depicted in Figure 2-10.

The position of the coordinated pyridine in the solid-state molecular structure of 7a·py corresponds well with the spatial extension of the calculated LUMO and reveals that Lewis bases may coordinate in a trans (to the phenyl group) and coplanar rearrangement as well. The latter coordination mode seems actually less sterically hindered. These results provide additional support for the formation of $\eta^3$-propargyl-like and $\eta^3$-allenyl-like Lewis bases, the proposed intermediates in the reaction of 7a with methanol and phenylacetylene (Section 2.5.2). It can be anticipated that Lewis base coordination of these proic acids at the position cis to the phenyl group results in the formation of the propargylic quenching product, while coordination trans to the phenyl group leads to the allenyl quenching product (Scheme 2-19). Following this line of reasoning, the regioselectivity of the protonolysis reaction of 7a appears to be related to the preferential nucleophilic attack at either the cis or trans lobe of the LUMO, but more experimental data is needed to support this hypothesis. Interestingly, a similar picture was also put forward to rationalize the reactions of [(PPh$_3$)$_2$Pt($\eta^3$-CH$_2$CCPh)] with nucleophiles.\textsuperscript{63c} In this case, a theoretical study indicated that the nucleophile addition reactions of simple donor nucleophiles to the platinum metal center proceed via a frontier-orbital controlled nucleophilic attack that utilizes a LUMO which is largely composed of the Pt 6p$_z$ atomic orbital.

2.5.6. The reactivity towards unsaturated substrates

Ethylene

Attempted ethylene polymerization reactions with Cp*$_2$La($\eta^3$-CH$_2$CCPh) (7a) and Cp*$_2$Y($\eta^3$-CH$_2$CCPh) (7b) in toluene (1.6 mM) indicated that these complexes did not exhibit any reactivity towards ethylene (7.5 atm) after 0.2 h at 80 °C. The reaction mixtures remained solutions without precipitation of polymer and only the expected quenching products (i.e. Cp*H, phenylallene and 1-phenyl-1-propyne) were observed with GC-MS after addition of methanol.
1-Hexene

In accord with above results involving ethylene, no reaction was observed with $^1$H NMR spectroscopy after heating a reaction mixture of $7a$ and $7b$ (20 mM) and excess 1-hexene (100-150 equiv.) for 4 days at 100 °C in benzene-$d_6$. When the reaction temperature was increased to 120 °C, slow substrate conversion was observed for $7a$, but not for $7b$. The reaction mixture of $7a$ and 1-hexene (145 equiv.) was monitored with $^1$H NMR spectroscopy for 74 days at which point 64% of the substrate was converted and quenched with methanol. GC-MS analysis indicated the presence of cis- and trans-hex-2-ene, hexane and derivatives of 1-hexene dimers (e.g. methyl-substituted undecenes and undecanes), trimers ($m/z$ 250) and tetramers ($m/z$ 334). Unidentified organic compounds having masses consistent with derivatives from the cross-coupled product between 1-phenyl-1-propyne and 1-hexene were also found.

The absence of substituted derivatives of the pentamethylcyclopentadiene ligand argues against the involvement of fulvene derivatives, while the formation of 1-hexene isomers, hexane and both saturated and unsaturated 1-hexene oligomers strongly suggest that a lanthanum hydride species is formed. The monomeric hydride derivative Cp*$_2$LaH is a well-known and highly active catalyst for alkene hydrogenation.$^{53b,d}$ Because these reactions are kinetically very facile, the generation of such a hydride derivative in the present reaction mixture must be very slow. A plausible route towards Cp*$_2$LaH involves $\beta$-H elimination after 1,2- or 2,1-insertion of 1-hexene into the metal-carbon bond of the $\eta^3$-allenyl/propargyl derivative. Unfortunately, the present experimental data do not allow differentiation between insertion into the propargylic La-CH$_2$ bond or the allenyl La-CPh bond of $7a$. Because the insertion of 1-phenyl-1-propyne into the propargylic La-CH$_2$ bond represents the major pathway in the reaction of $7a$ with 1-phenyl-1-propyne (vide infra), the former insertion reaction is presently favored (Scheme 2-26). In view of the well-documented high reactivity of Cp*$_2$LaH and the observed slow consumption of 1-hexene, either insertion of 1-hexene or $\beta$-H elimination must be rate-limiting.

As NMR resonances of $7a$ were still present after several days and no major organometallic intermediates were observed with NMR spectroscopy, slow insertion is presently favored.

In spite of the higher degree of propargylic bonding in Cp*$_2$La($\eta^3$-CH$_2$CCPh) ($7a$) as compared to Cp*$_2$LaCH$_2$CCPh ($7a$) (Section 2.4.3), the behavior of $9a$ towards 1-hexene was similar to that of $7a$. Slow conversion of 1-hexene into analogous compounds was observed after heating a benzene-$d_6$ solution of $9a$ in the presence of an excess of 1-hexene for several days at 100 °C.

1-Phenyl-1-propyne

When a reaction mixture of Cp*$_2$La($\eta^3$-CH$_2$CCPh) ($7a$) was heated to 80 °C in the presence of an excess of 1-phenyl-1-propyne (10-25 equiv) slow consumption of 1-phenyl-1-propyne was observed. NMR analysis of the reaction mixture pointed to the catalytic cyclodimerization reaction of 1-phenyl-1-propyne into mainly (E)-3-benzylidene-2-methyl-1-phenylcyclobutene (eq. 2.3). Catalytic cyclodimerization of alkyl- and silyl-substituted methyacetylenes was previously observed for Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = La, Ce), while a catalytic cycle based on a kinetic and mechanistic study is given in Chapter 3. The reaction mixtures obtained with $7a$ were identical to those observed for the reaction of Cp*$_2$LaCH(SiMe$_3$)$_2$ (6a) and [Cp*$_2$La(μ-H)$_2$] (12a) with excess 1-phenyl-1-propyne (Section 2.3.2). Interestingly, the major products were found to originate from
substrate insertion into the propargylic La-CH$_2$ bond of 7a, while the minor products originated from substrate insertion into the allenyllic La-CH(Ph) bond.

\[ \text{(2.3)} \]

\[
\begin{align*}
\text{Ph} & \quad \text{Cp*}_2\text{LaR} \quad 5 \text{ mol}\% \\
\text{C}_6\text{D}_6 & \quad 100 \ ^\circ\text{C}
\end{align*}
\]

\[ R = \text{CH(SiMe}_3)_2, \text{ CH}_2\text{CCPh, H} \]

Aspects concerning the influence of the reaction temperature, the lanthanide metal and the catalyst structure on the rate and selectivity of the catalytic cyclodimerization reaction are discussed in Chapter 3. It should be noted that no catalytic cyclodimerization of 1-phenyl-1-propyne was observed with Cp*$_2$YCH$_2$CCPh (7b).

\[ \text{(2.4)} \]

\[
\begin{align*}
\text{Cp*}_2\text{LaCH}_2\text{CCPh} & \quad 5 \text{ mol}\% \\
\text{C}_6\text{D}_6 & \quad 100 \ ^\circ\text{C}
\end{align*}
\]

1-(2-Methylphenyl)-1-propyne

Catalytic cyclodimerization was also observed for 1-(2-methylphenyl)-1-propyne, when a mixture of Cp*$_2$LaCH$_2$CCPh (7a) was heated to 100 °C in the presence of an excess of 1-(2-methylphenyl)-1-propyne (10-25 equiv) (eq. 2.4). The rate of substrate consumption was considerably lower and the reaction products were also formed less selectively as observed for the reactions of 7a with 1-phenyl-1-propyne, however. Further details are discussed in Chapter 3.

\[ \text{(2.5)} \]

\[
\begin{align*}
\text{Cp}^*_2\text{La} & \quad \text{7a} \\
\text{3} & \quad \text{Cp}^*_2\text{La} \quad \text{9a}
\end{align*}
\]

1-(2,6-dimethylphenyl)-1-propyne

In contrast to the reaction of Cp*$_2$La(η$_3$-CH$_2$CCC$_6$H$_5$) (7a) with 1-(2-methylphenyl)-1-propyne, NMR spectroscopy did not indicate the formation of oligomers of 1-(2,6-dimethylphenyl)-1-propyne (3) upon heating a benzene-$_d_6$ solution of 7a to 100 °C in the presence of 3 (20 equiv.). Instead, transmetalation of 7a with 3 took place, as evidenced by the formation of Cp*$_2$La(η$_3$-CH$_2$CCC$_6$H$_3$Me$_2$-2,6) (9a) and 1-phenyl-1-propylene (Eq. 2.5). Upon further heating, both 1-phenyl-1-propylene and 7a were completely converted into (E)-3-benzylidene-2-phenyl-1-methylcyclobutene and 9a, respectively. The reaction mixture was quenched after 10 days with methanol-$_d_4$ and GC-MS analysis indicated the presence of trace amounts of cross-coupling products of 3 and 1-
Rare-earth metallocene propargyl/allenyls

phenyl-1-propyne (m/z 260) and coupling products of 3 (m/z 288), besides the expected organic compounds formed upon deuterolysis (i.e. Cp*D, 1,2,6-dimethylphenyl-1-propyne-d₈, 2,6-dimethylphenyl-propadiene-d₂, and isomers of (E)-3-benzylidene-2-phenyl-1-methylocyclobutene).

The formation of (E)-3-benzylidene-2-phenyl-1-methylocyclobutene reveals that insertion of 1-phenyl-1-propyne into the propargylic La-CH₂ bond of 7a took place, forming the cyclodimer after subsequent intramolecular alkyne insertion and protonolysis by 1-phenyl-1-propyne or 1-(2,6-dimethylphenyl)-1-propyne (3), as previously proposed for the lanthanocene-catalyzed cyclodimerization reaction of 1-phenyl-1-propyne (Chapter 3). Because the electronic properties of 1-phenyl-1-propyne and 3 are comparable (Section 2.3.2), the above results suggest that the insertion of 3 into 7a is inhibited for sterical reasons. The large amount of (E)-3-benzylidene-2-phenyl-1-methylocyclobutene relative to the cross-coupling product of 1-phenyl-1-propyne and 3 reveals, in addition, that the insertion of 1-phenyl-1-propyne into 7a is rapid relative to the insertion of 1-phenyl-1-propyne into 9a. This observation may be attributed to slow transmetalation of 7a with 3, producing only a small amount of 9a relative to 7a, and/or slow insertion of 1-phenyl-1-propyne into 9a. To discriminate between both possibilities, analogous reactions with 9a were conducted.

NMR spectroscopy provided evidence that the bonding in Cp*₂LaCH₂CC(C₆H₃Me₂-2,6) (9a) displayed a higher degree of propargylic character than that in Cp*₂LaCH₂CCPh (7a). To determine whether an increased propargylic character results in a higher tendency to undergo insertion reactions for the present aryl-substituted η³-propargyl/allenyl complexes Cp*₂LaCH₂CCAr, the reactivity of 9a was investigated towards 1-phenyl-1-propyne and 1-(2,6-dimethylphenyl)-1-propyne (3). When a benzene-d₆ solution of 9a was allowed to react in the presence of a 20-fold molar excess of 3, no reactivity was observed after heating several days at 100 °C by 'H NMR spectroscopy. The addition of 1-phenyl-1-propyne (1 equiv.), followed by subsequent heating to 100 °C, led to its slow conversion into (E)-3-benzylidene-2-phenyl-1-methylocyclobutene (Scheme 2-27). Upon complete conversion of 1-phenyl-1-propyne, the reaction mixture was quenched with methanol-d₄. Subsequent GC-MS analysis indicated among others the presence of trace amounts of homo- and cross-coupling products of 3 (m/z 288 and 260).

These findings indicate that that insertion of both 1-phenyl-1-propyne and 1-(2,6-dimethylphenyl)-1-propyne (3) into Cp*₂LaCH₂CC(C₆H₃Me₂-2,6) (9a) does not take place. Apparently, the steric constraints posed by the additional 2,6-dimethyl groups in the phenyl-substituted propargyl impede insertion. Similarly, 2,6-dimethyl substitution at the phenyl group of the substrate seems to hinder substrate insertion into 7a as well. Thus, catalytic cycldimerization of 1-arylalk-2ynes is found to be quite sensitive towards ortho substitution of the simple 1-phenyl-1-propyne system. No insertion chemistry was observed upon substituting the phenyl group of either the η³-propargyl/allenyl ligand or the substrate with two ortho-methyl groups.

1-Pentafluorophenyl-1-propyne

When Cp*₂La(η³-CH₃CCPh) (7a) was heated to 80 °C in benzene-d₆ in the presence of a 20-fold molar excess of 1-pentafluorophenyl-1-propyne (5) and monitored with 'H NMR spectroscopy, no significant consumption of 5 was observed after 20 days. Instead, slow conversion of Cp*₂La(η³-CH₃CCPh) into Cp*₂La(η³-C₆F₅CCF₃) (11a) took place. This conversion was complete within 48 h at 80 °C during which new Cp* proton resonances appeared, accompanied by the formation of several vinylic and aliphatic proton resonances. Further heating led to the decomposition of 11a, as observed previously for the reaction of Cp*₂LaCH(SiMe)₃ (6a) and 5 (Section 2.3.2). Quenching the mixture with methanol-d₆, followed by GC-MS analysis, indicated the presence of 1-pentafluorophenyl-1-propyne-d₈, pentafluorophenylpropadiene-d₁, Cp*D, 1-
phenyl-1-propyne and small amounts of several organic compounds of which the major products were identified as C_{18}H_{5}DF_{10} (m/z 413), consistent with the mass of a dimer of 5, and four isomers of C_{27}H_{13}DF_{10} (m/z 529), consistent with a trimer composed of two 5 units and one 1 unit. Heating a similar mixture to 120 °C resulted in a more rapid decomposition of 11a, while C_{18}H_{5}DF_{10} was the only coupling product observed with GC-MS.

These results can be rationalized by the reaction sequences depicted in Scheme 2-28. Rather than insertion into the La-C bond of 7a as observed for 1-phenyl-1-propyne (1), 1-pentafluorophenyl-1-propyne (5) undergoes transmetalation with 7a. The four observed isomers of C_{27}H_{13}DF_{10} can be explained by regiorandom insertion of 5 and 1 into 11a. The observation of only one isomer of C_{18}H_{5}DF_{10} suggests that insertion of 5 into 11a is more rapid than insertion of 1-phenyl-1-propyne into 11a. This observation implies as well that one of the two regioisomeric products formed upon insertion of 5 into 11a is more reactive towards 1-phenyl-1-propyne than the other and that the more reactive regioisomeric product is completely converted by 1-phenyl-1-propyne. Because the structure of the products could not be determined unequivocally by NMR spectroscopy, it is not known which of the two regioisomeric insertion products of 5 into 11a is the least reactive towards 1-phenyl-1-propyne and produces C_{18}H_{5}DF_{10} upon deuterolysis.

The exact reason for the reluctance of 5 to undergo insertion reactions with 7a as compared to 1 is unknown at present. The similar steric requirements of the pentafluorophenyl group as compared to the phenyl group argue for electronic reasons, however.\textsuperscript{117} Also, the absence of intramolecular alkyn insertion of the insertion product of 11a and 5 is not understood presently, mainly because the precise effect of the increased electron-withdrawing nature of the alkyn substituent (C_{6}F_{5} versus C_{6}H_{5}) on the stability of the alk-1-ene-4-yn-1-yl species is difficult to assess \textit{a priori}.\textsuperscript{118}

**Diphenylethylene**

As 1-phenyl-1-propyne was found to undergo insertion into the metal-carbon bond of Cp*-LaCH_{2}CCPh (7a), it was considered interesting to explore the reactivity of 7a towards diphenylethylene as well. Because the steric size of the methyl group is smaller than that of the phenyl group,\textsuperscript{116} the steric requirements for insertion of diphenylethylene into 7a are somewhat higher than that of 1-phenyl-1-propyne, though.

---

**Scheme 2-28.** The proposed reaction sequences to account for the products observed for the reaction of 7a with 5.
A benzene-$d_6$ solution of $7a$ and diphenylethyne (1.2 equiv) was heated for several days to 100 °C and the progress of reaction was monitored with $^1$H NMR spectroscopy. As the resonances of $7a$ slowly disappeared, resonances previously observed in the thermolysis of $7a$ in benzene-$d_6$ solution appeared, while the total amount of proton intensities in the aliphatic and vinylic region decreased as well. Analogous to the thermolysis reaction, the light-yellow solution changed into red-orange during heating. The reaction mixture was quenched with methanol after 20 days and GC/GC-MS analysis indicated the presence of small amounts of 1-phenylprop-1-ene-$d_n$ and phenylallene-$d_n$, pentamethylcyclopentadiene-$d_n$ and several isomeric and oligodeuterated compounds (e.g. m/z 232, 261 and 429) of which trans-diphenylethene and an unknown compound (m/z 429) were identified as the major products.

Although the details of the formation of the observed products are not known presently, the masses of the observed organic products are inconsistent with products originating from insertion of diphenylethyne into $7a$. It is believed that the observed products are the result of reactions involving a fulvene Cp*(C$_5$Me$_4$CH$_2$-$\eta^3$)La or phenyl derivative Cp*$_2$LaC$_6$D$_5$ both formed upon thermolysis of $7a$ (Section 2.5.3). Evidence for this view comes from the multitudinous incorporation of deuterium atoms in the observed quenching products, indicating extensive H/D scrambling.

To investigate the possibility of a cross-coupling reaction between 1-phenyl-1-propyne and diphenylethyne, a reaction mixture of $7a$ with a 20-fold molar excess of both diphenylethyne and 1-phenyl-1-propyne was heated for several days at 100 °C. NMR spectroscopy indicated that diphenylethyne was not consumed and that products from catalytic cyclodimerization of 1-phenyl-1-propyne formed exclusively.

Carbon monoxide

Many examples of facile carbon monoxide insertion into the metal-carbon bond of rare-earth metalloocene $\eta^1$-alkyl derivatives exist in literature.\(^{119}\) The fact that CO insertion was also observed for $\eta^n$-bound (n > 1) rare-earth metal complexes, such as allyl Cp*$_2$Ln($\eta^3$-CH$_2$CHCH$_3$),\(^{119}\) ortho-pyridyl Cp*$_2$Y($\eta^2$-C$_6$H$_4$N)\(^{120}\) and tris(pentamethyl-cyclopentadienyl) derivatives Cp*$_3$Ln,\(^{121}\) encouraged us to explore the reactivity of the present $\eta^3$-propargyl/allenyl derivatives Cp*$_2$LaC$_6$D$_5$ towards carbon monoxide as well.

When an excess of carbon monoxide (1 atm.) was applied to a benzene-$d_6$ solution of Cp*$_2$La($\eta^3$-CH$_2$CCPh) ($7a$), no reactivity was observed with $^1$H NMR spectroscopy after 5 days at room temperature. A multitude of Cp* $^3$H NMR resonances formed slowly upon heating to 100 °C, accompanied by a color change from light-yellow to red-orange. After 7 days at 100 °C, only ~5% of $7a$ was converted. No evidence for CO insertion into $7a$ was obtained by means of NMR spectroscopy and GC/GC-MS after quenching the mixture with methanol, however. Similar results were also obtained for analogous reactions of Cp*$_2$Y($\eta^3$-CH$_2$CCPh) ($7b$).

It appears that the $\eta^3$-propargyl/allenyl bonding of both $7a$ and $7b$ is too strong to allow insertion of CO into the metal-carbon bond at room temperature. Nonselective reactivity was observed upon increasing the reaction temperature, but the details of these reactions are unknown at present.

As $7a$ was found to react only slowly with excess CO, even at high temperatures, the possibility of trapping an intermediate of the catalytic cyclodimerization reaction of 1-phenyl-1-propyne was investigated. The intermediates proposed are alkynyl derivatives (Chapter 3) whose (reported) reactivity is relatively unexplored in organolanthanide chemistry.\(^{121}\) The application of CO (1 atm) to a reaction mixture containing $7a$ and 1-phenyl-1-propyne (20 equiv.) led after heating to 100 °C to the decomposition of $7a$ into several unidentified species, as evidenced by the decrease of the $7a$ proton resonances and the concomitant increase of numerous proton...
resonances in the Cp* region. Complete conversion of 7a was observed within 3 days at 100 ºC. No evidence for CO insertion was found with 1H/13C NMR and GC/GC-MS after quenching the mixture with methanol.

2.6. Conclusions

Novel rare-earth metallocene η₃-propargyl/allenyl derivatives have been prepared via the reactions of the alkyl derivatives Cp*₂LnCH(SiMe₃)₂ with the corresponding 1-aryl-1-propynes CH₃CCAr. The synthetic utility of this route towards the Cp*₂LnCH₂CCAr complexes is limited by the slow rate of propargylic metallation. The reactions of the hydride derivatives [Cp*₂Ln(µ-H)]₂ with 1-aryl-1-propynes CH₃CCAr also afforded the desired Cp*₂LnCH₂CCAr complexes in most cases. However, these reactions were less selectively and the high solubility of Cp*₂LnCH₂CCAr complexes hindered their isolation from the reaction mixtures in some cases.

Spectral and structural analysis provided evidence for a static η₃-bonding description of the propargylic/allenyl ligand in Cp*₂LnCH₂CCAr (Ln = La, Y), but a shift towards more η₁-propargylic and more η₁-allenyl bonding was observed for Cp*₂LaCH₂CCAr complexes, depending on the aromatic substituent of the η₃-propargyl/allenyl ligand. The former shift was favored by more sterically hindered substituents, while the latter shift was promoted by more σ-electron-withdrawing substituents.

The reactivity of the present η₃-propargyl/allenyl complexes Cp*₂LnCH₂CCAr was found to involve the formation of Lewis base adducts, C-H activation reactions with Brønsted acids and insertion reactions of unsaturated substrates. The reactions of Cp*₂LaCH₂CCPh (Ln = La, Y) with Lewis bases, such as THF and pyridine, yielded the corresponding Lewis base adduct, both rapidly and selectively, in which the propargyl/allenyl ligand was still bound in a η₃-fashion. Reactions of the Cp*₂LaCH₂CCAr complexes with Brønsted acids furnished both acetylenic (CH₃CCAr) and allenylic (CH₂=C=CHAr) protonolysis products. The insertion reactivity of Cp*₂LaCH₂CCPh towards unsaturated substrates was severely limited by the strong η₃-bonding of the propargylic/allenyl ligand. Even so, insertion of 1-phenyl-1-propyne into Cp*₂LaCH₂CCAr was implicated by its catalytic conversion into cyclodimers, as observed for the reaction of Cp*₂LaCH₂CCAr (or its catalyst precursors) with 1-phenyl-1-propyne. Catalytic cyclodimerization seems to be confined to reactions of Cp*₂LnR (R = CH(SiMe₃)₂, H, η₃-CH₂CCPh) complexes having relatively large metal centers (Ln = La, Ce) in combination with substrates having sterically relatively unhindered carbon-carbon triple bonds (Ar = Ph, C₆H₄Me-2).

2.7. Experimental Section

General considerations. All reactions and manipulations of air and moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk, vacuum line and glovebox techniques. Deuterated solvents were dried over Na/K alloy prior to use. Other solvents were dried by percolation over columns of aluminum oxide, BASF R3-11 supported Cu oxygen scavenger, and molecular sieves (4Å) (pentane), or by distillation from Na/K alloy (THF, cyclohexane). The compounds Cp*₂LnCH(SiMe₃)₂ (Ln = La₁₂², Y₁₂³), [(Cp*₂La(µ-H)]₂, 2,6-dimethyliodobenzene, n-butyl nitrite, copper bronze, copper(I) iodide, propynyllithium, and Pd(PPh₃)₂Cl₂ were prepared according to literature procedures. Reagents were purchased from Aldrich, Acros Chimica, Strem, Merck or Fluka and were used as received unless stated otherwise. 1-Phenyl-1-propyne (Aldrich) was dried over CaH₂ before use (vide infra). Diphenylethylene (Aldrich) was sublimed before use. Dimethyl sulfoxide was dried at least three times on freshly activated 4-Å molecular sieves.

Physical and analytical measurements. NMR spectra were recorded on a Varian VXR-300 (FT, 300 MHz, ¹H, 75 MHz, ¹³C), Varian XL-400 (FT, 400 MHz, ¹H; 100 MHz, ¹³C) or a Varian Inova 500 (FT, 500 MHz, ¹H, 125.7 MHz, ¹³C) spectrometers. NMR experiments on air-sensitive samples were conducted in flame-sealable tubes or tubes equipped with a Teflon valve (Young). The ³H NMR spectra were referenced to resonances of residual protons in deuterated solvents and reported in ppm relative to tetramethylsilane (δ 0.00 ppm). The ¹³C NMR spectra were referenced to carbon resonances of deuterated solvents. ¹⁹F NMR spectra were referenced externally to hexafluorobenzene in CDCl₃ (δ -163.0 ppm). IR spectra of pure compounds, KBr pellets or nujol solutions of the samples were recorded on a Mattson 4020 Galaxy FT-IR spectrophotometer. The
elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr, and the Microanalytical Department of the University of Groningen. GC analyses were performed on a HP 6890 instrument with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC-MS spectra were recorded at 70 eV using a HP 5973 mass-selective detector attached to a HP 6890 GC as described above.

**General drying procedure for 1-methylalk-2-yynes.** The liquids obtained after synthesis or received after purchase were brought in a flask containing freshly ground CaH₂ and allowed to react for at least one day at 50 °C under nitrogen. Vacuum transfer afforded colorless oils which were stored at -30 °C and under nitrogen.

### 2-Propynyltoluene (2)

A 1-L, three-neck, round-bottom flask, equipped with stir bar and gas-inlet adaptor, was charged with THF (200 mL) and degassed by freeze-thaw-pump cycles. A 3-L flask was connected to a lecture bottle of propyne and filled with an appropriate amount of propyne gas (~122 mmol) by adjusting the pressure. From this flask, the gas was allowed to condense into the reaction vessel which was cooled to -100 °C with a liquid nitrogen-ethanol bath. The 1-L flask was brought under nitrogen, connected to a cooler and drop funnel, while still maintaining the temperature of the bath at ca. -100 °C. Then n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

After addition of an excess of n-BuLi (5.2 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

1,3-Dimethyl-2-(prop-1-ynyl)benzene (3)

A 250-mL Schlenk flask was charged with 13.0 mL (32.5 mmol) of n-BuLi (2.5 M in hexanes) and 30 mL of THF. A 3-L flask was connected to a lecture bottle of propyne and filled with an appropriate amount of propyne gas (40 mmol) by adjusting the pressure. From this flask, propyne was allowed to condense into the Schlenk flask which was cooled to -100 °C with a liquid nitrogen-ethanol bath. After 15 min of stirring a solution of 7.70 g (34.2 mmol) of anhydrous ZnBr₂ in 20 mL of THF was added dropwise to the reaction mixture at -78 °C during 30 min while stirring. After addition the cooling bath was removed and the reaction mixture was allowed to warm up to room temperature. Then, 2-iodotoluene (8.6 mL, 67 mmol) and Pd(PPh₃)₄Cl₂ (2.3 g, 3.3 mmol) were added and the suspension was stirred for 14 h at room temperature. The reaction mixture was quenched with 200 mL of brine and filtered. The organic layer was extracted with petroleum ether (40-60 °C) and dried over MgSO₄. Rotatory evaporation afforded an orange oil which was purified by means of column chromatography (silica, 230-400 mesh, 60 Å) with petroleum ether. The volatiles were removed by means of rotatory evaporation and vacuum distillation using a 20-cm Vigreux column. Drying over CaH₂ and subsequent vacuum transfer afforded a light yellow liquid. Yield: 7.34 g (85%).

**1H NMR (300 MHz, CDCl₃, 25 °C): δ 2.15 (s, CCH₂, 3 H), 2.43 (s, CH₂, 6 H), 6.9-7.2 (m, CH, 3 H).**

**13C NMR (75 MHz, CDCl₃, 25 °C): δ 4.46 (CCCH₃), 21.03 (CCH₂), 77.24 (CH₂), 94.03 (ArC), 121.74 (i-C₆H₅), 126.48 (m-C₆H₅), 126.82 (p-C₆H₅), 140.04 (o-C₆H₅).** GC-MS, m/z (relative intensity): 131 (11), 130 (M⁻, 100), 129 (M⁻ - H, 61), 128 (62), 127 (28), 116 (5), 115 (M⁻ - CH₃, 78), 102 (8), 89 (6), 77 (8), 75 (4), 74 (5), 64 (8), 63 (11), 62 (4), 51 (11), 50 (5), 39 (5). IR (neat, [cm⁻¹]): 3066 (m), 3022 (m), 2917 (s), 2852 (m), 2733 (m), 2242 (m), 2047 (w), 1928 (m), 1579 (m), 1487 (m), 1456 (m), 1377 (m), 116 (m), 1045 (m), 765 (s), 493 (s). Anal. Calcd. for C₁₀H₁₀: C, 92.26%; H, 7.74%. Found: C, 92.12%; H, 7.63%.

2-Propynyltoluene (2)

A 1-L, three-neck, round-bottom flask, equipped with stir bar and gas-inlet adaptor, was charged with THF (200 mL) and degassed by freeze-thaw-pump cycles. A 3-L flask was connected to a lecture bottle of propyne and filled with an appropriate amount of propyne gas (~122 mmol) by adjusting the pressure. From this flask, the gas was allowed to condense into the reaction vessel which was cooled to -100 °C with a liquid nitrogen-ethanol bath. The 1-L flask was brought under nitrogen, connected to a cooler and drop funnel, while still maintaining the temperature of the bath at ca. -100 °C. Then n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

After addition of an excess of n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

2-Propynyltoluene (2)

A 1-L, three-neck, round-bottom flask, equipped with stir bar and gas-inlet adaptor, was charged with THF (200 mL) and degassed by freeze-thaw-pump cycles. A 3-L flask was connected to a lecture bottle of propyne and filled with an appropriate amount of propyne gas (~122 mmol) by adjusting the pressure. From this flask, the gas was allowed to condense into the reaction vessel which was cooled to -100 °C with a liquid nitrogen-ethanol bath. The 1-L flask was brought under nitrogen, connected to a cooler and drop funnel, while still maintaining the temperature of the bath at ca. -100 °C. Then n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

After addition of an excess of n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

2-Propynyltoluene (2)

A 1-L, three-neck, round-bottom flask, equipped with stir bar and gas-inlet adaptor, was charged with THF (200 mL) and degassed by freeze-thaw-pump cycles. A 3-L flask was connected to a lecture bottle of propyne and filled with an appropriate amount of propyne gas (~122 mmol) by adjusting the pressure. From this flask, the gas was allowed to condense into the reaction vessel which was cooled to -100 °C with a liquid nitrogen-ethanol bath. The 1-L flask was brought under nitrogen, connected to a cooler and drop funnel, while still maintaining the temperature of the bath at ca. -100 °C. Then n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

After addition of an excess of n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

2-Propynyltoluene (2)

A 1-L, three-neck, round-bottom flask, equipped with stir bar and gas-inlet adaptor, was charged with THF (200 mL) and degassed by freeze-thaw-pump cycles. A 3-L flask was connected to a lecture bottle of propyne and filled with an appropriate amount of propyne gas (~122 mmol) by adjusting the pressure. From this flask, the gas was allowed to condense into the reaction vessel which was cooled to -100 °C with a liquid nitrogen-ethanol bath. The 1-L flask was brought under nitrogen, connected to a cooler and drop funnel, while still maintaining the temperature of the bath at ca. -100 °C. Then n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).

After addition of an excess of n-BuLi (42.0 mL, 105 mmol, 2.5 M in hexanes) was added dropwise under stirring over a period of 1 h after which the temperature of the bath was allowed to warm up to -78 °C. A solution of ZnBr₂ (22.6 g, 100 mmol, flame-dried (85%).
Addition of cold diethyl ether and storage at -30 °C led to the precipitation of a white powder. The powder was subsequently washed on a glass filter with cold diethyl ether and light petroleum ether and kept moist prior to use. The explosive nature upon drying impeded the determination of the (crude) yield.

1H NMR (300 MHz, CDCl3, 25 °C): δ 7.62 (d, J_{HH} = 8.9 Hz, CH2), 7.40 (d, J_{HH} = 8.9 Hz, m-C6H4), 7.15 (m, m-C6H4), 2.16 (s, 3CH3). 13C NMR (75 MHz, CDCl3, 25 °C): δ 153.55, 129.87, 128.79, 127.79, 127.43, 126.87, 126.53, 123.00, 121.03, 21.37.

Propynylium copper (9). 25.0 g (100 mmol) of CuSO4·5H2O was dissolved in 100 mL of concentrated aqueous ammonia in a 500-mL Schlenk flask, equipped with a Teflon-coated stir bar. After stirring at 0 °C for 15 min 200 mL of water was added, followed by the slow addition of 13.9 g (200 mmol) of HONH2·HCl. Subsequently, propyne gas was bubbled through the solution for 24 h during which a yellow solid precipitated. The suspension was filtered under vacuum and the yellow powder was washed with water, ethanol and ether yellow powder. CAUTION: The yellow powder is explosive when dry and was kept moist with ether. (Crude wet yield): 8.6 g (84%).

1.3-Disopropyl-2-(prop-1-ynyl)benzene (4). 8.6 g (84 mmol) of freshly prepared copper(I) propynyl is brought in a 400-mL Schlenk flask, equipped with a Teflon-coated stir bar, and evacuated. After addition of 240 mL of dry pyridine and 3.0 g (10 mmol) of 2,6-diisopropyliodobenzene the reaction mixture was heated on reflux at 120 °C for 10 days. The mixture was quenched with water. Addition of petroleum ether (40-60), filtration, extraction of the organic layer with petroleum ether (40-60), drying over MgSO4 and rotary evaporation afforded a yellow oil which was purified by means of column chromatography (neutral alumina) with petroleum ether. Yield: 1.58 g (76%) of a colorless oil.

1H NMR (500 MHz, CDCl3, 25 °C): δ 1.20 (d, J_{HH} = 7.1 Hz, CH2), 7.40 (d, J_{HH} = 8.9 Hz, m-C6H4), 2.16 (s, 3CH3). 13C NMR (125.7 MHz, CDCl3, 25 °C): δ 144.03, 136.84, 132.33, 128.16, 127.68, 126.82, 125.29, 124.06, 122.41, 121.74, 21.74.

Pentfluoro(prop-1-ynyl)benzene (5). The following procedure represents a modified version of previously published ones. Propyne gas (ca. 60 mmol) was condensed in vacuo in THF (80 mL) which was cooled at -196 °C in a single-bulbed, 250-mL Schlenk flask, equipped with stir bar. The flask was brought under a nitrogen atmosphere and allowed to warm up to -80 °C. Dropwise addition of n-butyl lithium (21.0 mL, 52.5 mol, 2.5 M in hexanes) under stirring after which the solution was allowed to warm up to -30 °C, forming a white suspension. The mixture was cooled to -60 °C and a solution of hexafluorobenzene (8.74 g, 47.0 mmol) in THF (50 mL) was slowly added to the reaction mixture under vigorous stirring. After addition the reaction mixture was allowed to slowly warm up to room temperature and stirred overnight. Addition of water (100 mL),
extraction with diethyl ether, drying over MgSO₄ and rotatory evaporation (50 °C, 100 mbar) provided a white crystalline solid. Yield: 2.32 g (24%).

1H NMR (400 MHz, CDCl₃, 25 °C): δ 2.13 (s, CH₂, 3 H). 13C{¹H} NMR (100 MHz, CDCl₃, 25 °C): 137.55 (s, 1 C), 128.31 (d, 1 C), 126.32 (s, 1 C), 117.78 (m, 1 C). IR (nujol, cm⁻¹): 2924 (s), 2853 (s), 2725 (w), 1786 (m), 1666 (w), 1566 (w), 1400 (m), 1385 (m), 1295 (w), 1225 (w), 1127 (m), 1056 (s), 976 (w), 853 (m), 849 (s). GC-MS, m/z (relative intensity): 207 (10), 206 (M⁺, 100), 205 (M⁺ - H, 73), 188 (7), 187 (69), 186 (5), 180 (6), 179 (9), 167 (7), 161 (8), 156 (28), 155 (5), 117 (7), 105 (6), 104 (4), 103 (4), 93 (8). Anal. Calcd for C₉H₆F:C; C, 52.45%; H, 1.47%. Found: C, 52.25%; H, 1.38%.

Cp⁺⁻YCH=CPh (7b). Hydrogenation at a pressure of 1 bar was supplied to a solution of Cp⁺⁻YCH(SiMe₃)₂ (0.58 g, 1.12 mmol) in hexanes (5 mL). Stirring for 3 h at room temperature produced a light-yellow suspension. The hydrogen atmosphere was replaced by nitrogen and 1-phenyl-1-propyne (0.2 mL, 1.60 mmol) was added. Immediately, a red suspension formed. The suspension was stirred for 30 min at room temperature during which it was degassed several times. The solid was separated by decantation and filtration. Subsequent in vacuo removal of the solvent yielded a red crystalline material (0.49 g, 49% yield). Crystals suitable for X-ray analysis were obtained by recrystallization in toluene at low temperature.

1H NMR (500 MHz, CD₂Cl₂, 25 °C): δ 1.93 (s, CH₃, 3 H), 7.09 (d, JCH = 7.5 Hz, m-H, 2 H), 7.19 (d, JCH = 7.8 Hz, m-Ph, 2 H). 13C NMR (125.7 MHz, CD₂Cl₂, 25 °C): 111.22 (q, J,C = 125.6 Hz, CH(SiMe₃)₂), 138.31 (d, J,C = 5.2 Hz, CH= C, 1 C), 130.84 (dtd, 1 C), 126.32 (s, 1 C), 117.78 (m, 1 C). IR (nujol, cm⁻¹): 2924 (m), 2856 (w), 2727 (m), 1923 (m), 1592 (m), 1544 (m), 1455 (m), 1378 (m), 1269 (m), 1154 (m), 1065 (m), 1021 (m), 916 (w), 846 (w), 768 (m), 698 (m), 627 (m), 482 (s). Anal. Calcd for C₂₉H₃₇La: C, 66.24%; H, 7.12%.

Cp⁺⁻LaCH=CCPh (7a). Hydrogenation at a pressure of 1 bar was supplied to a solution of Cp⁺⁻LaCH(SiMe₃)₂ (0.82 g, 1.42 mmol) in pentane (5 mL). Stirring for 2 h at room temperature produced a yellow suspension. The hydrogen atmosphere was replaced by hydrogen and 1-phenyl-1-propyne (0.4 mmol, 3.2 mmol) was added. Immediately, a deep red suspension formed. The suspension is stirred for 1 h at room temperature during which it was degassed several times. The solid was separated by decantation and filtration. Subsequent in vacuo removal of the solvent yielded a red crystalline material (0.68 g, 91% yield). Crystals suitable for X-ray analysis were obtained by recrystallization in toluene at low temperature.

1H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 1.92 (s, Cp⁺⁻CH₃, 3 H), 7.09 (d, JCH = 7.2 Hz, m-H, 2 H), 7.12 (dd, JCH = 7.2 Hz, JCH = 7.3 Hz, m-Ph, 2 H), 7.24 (d, JCH = 7.2 Hz, m-Ph, 2 H). 13C NMR (125.7 MHz, CD₂Cl₂, 25 °C): 136.33 (q, J,C = 124.5 Hz, C(CH₃)₂), 150.79 (d, J,C = 159.9 Hz, C=CH₂, 1 C). IR (nujol, cm⁻¹): 2920 (m), 2850 (m), 1585 (m), 1387 (m), 1455 (s), 1380 (m), 1256 (w), 1090 (w), 1065 (w), 1020 (m), 900 (w), 760 (s), 690 (m), 600 (s), 450 (m). Anal. Calcd for C₂₉H₂₉La: C, 73.41; H, 7.86. Found: C, 73.24% H, 7.89.

Cp⁺⁻LaCH=CH(C₆H₅)CH=CH₂ (9a). Hydrogenation (1 bar) was applied to a solution of Cp⁺⁻LaCH(SiMe₃)₂ (0.56 g, 1.12 mmol) in hexanes (5 mL). Stirring for 3 h at room temperature produced a light-yellow suspension. The hydrogen atmosphere was replaced by nitrogen and 1-(2,6-dimethylphenyl)-1-propyne (0.21 g, 1.46 mmol) was added. Immediately, a red suspension formed. The suspension was stirred for 30 min at room temperature during which it was degassed several times. The solid was separated by decantation and filtration. Subsequent in vacuo removal of the solvent yielded a red crystalline material (0.49 g, 49% yield). Crystals suitable for X-ray analysis were obtained by recrystallization in toluene at low temperature.

1H NMR (400 MHz, CDCl₃, 25 °C): δ 2.13 (s, CH₃, 3 H), 7.09 (d, JCH = 7.2 Hz, m-H, 1 H), 7.12 (dd, JCH = 7.2 Hz, JCH = 7.3 Hz, m-Ph, 2 H), 7.24 (d, JCH = 7.2 Hz, m-Ph, 2 H). 13C NMR (125.7 MHz, CDCl₃, 25 °C): 136.33 (q, J,C = 124.5 Hz, C(CH₃)₂), 150.79 (d, J,C = 159.9 Hz, C=CH₂, 1 C). IR (nujol, cm⁻¹): 2920 (m), 2850 (m), 1585 (m), 1387 (m), 1455 (s), 1380 (m), 1256 (w), 1090 (w), 1065 (w), 1020 (m), 900 (w), 760 (s), 690 (m), 600 (s), 450 (m). Anal. Calcd for C₈H₁₆La: C, 66.41; H, 7.11. Found: C, 66.24% H, 7.00.

Rare-earth metalloocene propargyl/allenyls
2 F). GC-MS, m/z (relative intensity): 118 (6), 117 (72), 116 (100), 115 (15), 90 (8), 89 (6), 64 (6), 63 (8), 51 (7).

Reaction of Cp*2LaCH(SiMe3)2 with CH3CCPh. NMR Scale. Cp*2LaCH(SiMe3)2 (12.3 mg, 21.4 µmol) was dissolved in C6D6 and CH2CCPh (3.0 µL, 24 µmol) was added with a microsyringe in the glovebox. No changes were observed with 1H NMR spectroscopy after 24 h at room temperature. Also, when the sample is heated to 50 °C for 12 h, no changes were observed. After heating the sample to 80 °C for 3 h, the formation of Cp*LaCH2CCPh was observed and the yellow solution turned slowly deep red upon further heating. After 17 days at 80 °C the reaction mixture was quenched with CD3OD. The presence of CH2(SiMe3)2, Cp*D, 1-phenyl-1-propyne-d1 and phenyllallene-d1 was indicated by 1H NMR and GC-MS.

1-Phenyl-1-propyne-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 1.65 (s, CH2D, 2H), 2.05, 2.05, 2.05, 2.05. GC-MS, m/z (relative intensity): 118 (6), 117 (72), 116 (100), 115 (15), 90 (8), 89 (6), 64 (6), 63 (8), 51 (7).

Phenylpropa-1,2-diene-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 4.85 (s, CH2, 2H). GC-MS, m/z (relative intensity): 118 (7), 117 (76), 116 (100), 90 (6), 63 (9).

Analogous reactions of Cp*LaCH(SiMe3)2 with CH2CCCH2Me2, CH2CCCH2CH2-2,6 and CH2CCH2Pr2-2,6 and Cp*YCH(SiMe3)2 with CH3CCPh in C6D6 gave similar results.

Reaction of Cp*2La(CH(SiMe3)2) with CH3CCPh. NMR Scale. Cp*2La(CH(SiMe3)2)2 (15 mg, 26 µmol) was dissolved in C6D6 and CH2CCCH2 (5.5 mg, 27 µmol) was added in the glovebox. No changes were observed with 1H NMR spectroscopy after 24 h at room temperature. Also, when the sample is heated to 50 °C for 12 h, no changes were observed. After heating the sample to 80 °C for 3 h, the formation of Cp*LaCH2CCPh was observed and the yellow solution turned slowly deep red upon further heating. After 17 days at 80 °C the reaction mixture was quenched with CD3OD. The presence of CH2(SiMe3)2, Cp*D, 1-phenyl-1-propyne-d1 and phenyllallene-d1 was indicated by 1H NMR and GC-MS.

1-Phenyl-1-propyne-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 1.65 (s, CH2D, 2H), 2.05, 2.05, 2.05, 2.05. GC-MS, m/z (relative intensity): 118 (6), 117 (72), 116 (100), 115 (15), 90 (8), 89 (6), 64 (6), 63 (8), 51 (7).

Phenylpropa-1,2-diene-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 4.85 (s, CH2, 2H). GC-MS, m/z (relative intensity): 118 (7), 117 (76), 116 (100), 90 (6), 63 (9).

Analogous reactions of Cp*LaCH(SiMe3)2 with CH2CCCH2Me2, CH2CCCH2CH2-2,6 and CH2CCH2Pr2-2,6 and Cp*YCH(SiMe3)2 with CH3CCPh in C6D6 gave similar results.

Reaction of Cp*2La(CH(SiMe3)2) with CH3CCPh. NMR Scale. Cp*2La(CH(SiMe3)2)2 (15 mg, 26 µmol) was dissolved in C6D6 and CH2CCCH2 (5.5 mg, 27 µmol) was added in the glovebox. No changes were observed with 1H NMR spectroscopy after 24 h at room temperature. Also, when the sample is heated to 50 °C for 12 h, no changes were observed. After heating the sample to 80 °C for 3 h, the formation of Cp*LaCH2CCPh was observed and the yellow solution turned slowly deep red upon further heating. After 17 days at 80 °C the reaction mixture was quenched with CD3OD. The presence of CH2(SiMe3)2, Cp*D, 1-phenyl-1-propyne-d1 and phenyllallene-d1 was indicated by 1H NMR and GC-MS.

1-Phenyl-1-propyne-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 1.65 (s, CH2D, 2H), 2.05, 2.05, 2.05, 2.05. GC-MS, m/z (relative intensity): 118 (6), 117 (72), 116 (100), 115 (15), 90 (8), 89 (6), 64 (6), 63 (8), 51 (7).

Phenylpropa-1,2-diene-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 4.85 (s, CH2, 2H). GC-MS, m/z (relative intensity): 118 (7), 117 (76), 116 (100), 90 (6), 63 (9).

Analogous reactions of Cp*LaCH(SiMe3)2 with CH2CCCH2Me2, CH2CCCH2CH2-2,6 and CH2CCH2Pr2-2,6 and Cp*YCH(SiMe3)2 with CH3CCPh in C6D6 gave similar results.

Reaction of Cp*2La(CH(SiMe3)2) with CH3CCPh. NMR Scale. Cp*2La(CH(SiMe3)2)2 (15 mg, 26 µmol) was dissolved in C6D6 and CH2CCCH2 (5.5 mg, 27 µmol) was added in the glovebox. No changes were observed with 1H NMR spectroscopy after 24 h at room temperature. Also, when the sample is heated to 50 °C for 12 h, no changes were observed. After heating the sample to 80 °C for 3 h, the formation of Cp*LaCH2CCPh was observed and the yellow solution turned slowly deep red upon further heating. After 17 days at 80 °C the reaction mixture was quenched with CD3OD. The presence of CH2(SiMe3)2, Cp*D, 1-phenyl-1-propyne-d1 and phenyllallene-d1 was indicated by 1H NMR and GC-MS.

1-Phenyl-1-propyne-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 1.65 (s, CH2D, 2H), 2.05, 2.05, 2.05, 2.05. GC-MS, m/z (relative intensity): 118 (6), 117 (72), 116 (100), 115 (15), 90 (8), 89 (6), 64 (6), 63 (8), 51 (7).

Phenylpropa-1,2-diene-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 4.85 (s, CH2, 2H). GC-MS, m/z (relative intensity): 118 (7), 117 (76), 116 (100), 90 (6), 63 (9).

Analogous reactions of Cp*LaCH(SiMe3)2 with CH2CCCH2Me2, CH2CCCH2CH2-2,6 and CH2CCH2Pr2-2,6 and Cp*YCH(SiMe3)2 with CH3CCPh in C6D6 gave similar results.

Reaction of Cp*2La(CH(SiMe3)2) with CH3CCPh. NMR Scale. Cp*2La(CH(SiMe3)2)2 (15 mg, 26 µmol) was dissolved in C6D6 and CH2CCCH2 (5.5 mg, 27 µmol) was added in the glovebox. No changes were observed with 1H NMR spectroscopy after 24 h at room temperature. Also, when the sample is heated to 50 °C for 12 h, no changes were observed. After heating the sample to 80 °C for 3 h, the formation of Cp*LaCH2CCPh was observed and the yellow solution turned slowly deep red upon further heating. After 17 days at 80 °C the reaction mixture was quenched with CD3OD. The presence of CH2(SiMe3)2, Cp*D, 1-phenyl-1-propyne-d1 and phenyllallene-d1 was indicated by 1H NMR and GC-MS.

1-Phenyl-1-propyne-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 1.65 (s, CH2D, 2H), 2.05, 2.05, 2.05, 2.05. GC-MS, m/z (relative intensity): 118 (6), 117 (72), 116 (100), 115 (15), 90 (8), 89 (6), 64 (6), 63 (8), 51 (7).

Phenylpropa-1,2-diene-d1; 1H NMR (C6D6, 25 °C, 300 MHz): δ 4.85 (s, CH2, 2H). GC-MS, m/z (relative intensity): 118 (7), 117 (76), 116 (100), 90 (6), 63 (9).

Analogous reactions of Cp*LaCH(SiMe3)2 with CH2CCCH2Me2, CH2CCCH2CH2-2,6 and CH2CCH2Pr2-2,6 and Cp*YCH(SiMe3)2 with CH3CCPh in C6D6 gave similar results.
resonances were observed (i.e. δ 2.04, 2.01, 1.99, 1.97, 1.96, 1.91, 1.88, 1.87, 1.84 ppm) of which the propargyl (δ 1.91 ppm, 13%) constituted only a small amount. No changes were observed with 1H NMR spectroscopy after 24 h at room temperature and the reaction mixture was quenched with CD3OD producing a mixture containing Cp*Di, cis-1-phenyl/prop-1-ene-dl, 1-phenyl-1-propyne-dl and phenylallene-dl, as indicated by 1H NMR and GC-MS.

Cis-1-phenyl-prop-1-ene-dl: 1H NMR (C6D6, 25 °C, 500 MHz): δ 6.41 (dq, JNH = 1.7 Hz, JNH = 11.5 Hz, δ=CH, 1 H), 5.63 (dq, JNH = 11.5 Hz, JNH = 7.3 Hz, δ=CH, 1 H), 1.69 (dd, JNH = 1.7 Hz, H, 3 H).

Reaction of [Cp*La(µ-H)]2 with PhCCPh and CH3CCPh. NMR Scale. [Cp*La(µ-H)]; (5.0 mg, 6.1 µmol) was dissolved in C6D6 and PhCCPh (2.4 mg, 14 µmol) was added in the glovebox. The light-yellow solution turned immediately orange. A clean reaction forming the alkenyl derivative Cp*LaC(Ph)=CH(Ph) was observed (vide infra). No changes in the 1H NMR spectrum were observed after standing for 5 days at room temperature. Upon addition of 1-phenyl-1-propyne (3.5 mg, 30 µmol) the alkyl derivative was completely converted into the propargyl derivative Cp*La(µ-H) within 24 h at room temperature, giving rise to cis-diphenylethenes. The reaction mixture was quenched with CD3OD. GC/MS and 1H NMR analysis indicated the presence of Cp*D, 1-phenyl-1-propyne-dl, 1-phenyl-1-propyne, phenylallene-dl and cis-diphenylethene.

Scheme 2-30. Numbering scheme of Cp*LaC(Ph)=CH(Ph) (15a).

Cp*LaC(Ph)=CH(Ph) (15a): 1H NMR (C6D6, 25 °C, 500 MHz): δ 7.69 (s, CH, 1 H), 7.29 (m, CH, 2 H), 7.12 (m, CH, 2 H), 7.04 (m, CH, 1 H), 6.99 (m, CH, 1 H), 1.84 (s, Cp*, 30 H). 13C NMR (125.7 MHz, C6D6, 25 °C): δ 10.95 (q, JC=C = 125.2 Hz, C6Me6), 120.74 (m, C6Me6), 123.44 (dt, JC=C = 152.6 Hz, JC=C = 7.1 Hz, C6Me6), 124.70 (dd, JC=C = 159.4 Hz, JC=C = 7.6 Hz, m-CH), 125.57 (dm, JC=C = 154.1 Hz, p-CH), 126.59 (dt, JC=C = 163.2 Hz, JC=C = 7.1 Hz, m-CH), 129.89 (dd, JC=C = 153.7 Hz, JC=C = 1.4 Hz, JC=C = 7.9 Hz, p-CH), 130.83 (dd, JC=C = 152.6 Hz, JC=C = 152.6 Hz, p-CH), 134.28 (dt, JC=C = 147.2 Hz, JC=C = 4.0 Hz, JC=C = 7(C=PH)), 146.25 (s, i-C), 151.08 (s, i-C). The signal corresponding to LaC was not observed.

Cis-diphenylethene: 1H NMR (C6D6, 25 °C, 500 MHz): δ 6.46 (s, α=CH, 2 H). The aromatic proton signals overlapped with others. GC/MS, m/z (relative intensity): 180 (99), 179 (100), 178 (66), 177 (9), 176 (12), 166 (9), 165 (51), 152 (15), 151 (8), 102 (9), 89 (19), 76 (14), 63 (7), 51 (9). GC-MS, m/z (calc., found): 182 (1, 1.7), 181 (18.4, 15.3), 180 (100.0, 100.0).

Cp*LaC(Ph)=CH(Ph) (15a). To a suspension of [Cp*La(µ-H)]; (35.0 mg, 42.6 µmol) in cyclohexane (5 mL) was added diphenylacetylene (15.2 mg, 85.3 µmol). The light-yellow solution turned into an orange solution immediately. Removal of the solvent in vacuo gave a yellow solid in quantitative yield. Isolated yield: 49.2 mg (98%).

1H NMR (500 MHz, C6D6, 25 °C): δ 7.40 (s, D), 7.22 (t, JNH = 7.7 Hz, G), 7.20 (t, JNH = 7.7 Hz, A), 7.07 (tq, JNH = 7.1 Hz, JNH = 7.4 Hz, F), 6.95 (tq, JNH = 7.4 Hz, JNH = 1.1 Hz, B), 6.91 (d, JNH = 7.1 Hz, E), 6.73 (dq, JNH = 7.1 Hz, JNH = 7.1 Hz, C), 1.77 (s, Cp*, 30 H). 13C NMR (125.7 MHz, C6D6, 25 °C): δ 10.51 (q, JC=C = 125.4 Hz, C6Me6), 120.60 (s, C6Me6), 122.97 (dt, JC=C = 148.6 Hz, JC=C = 7.1 Hz, 3), 124.25 (d, overlap hampered determination of coupling constants, 2), 125.53 (dd, JC=C = 153.5 Hz, JC=C = 6.2 Hz, JC=C = 6.2 Hz, 8), 126.18 (dt, JC=C = 162.2 Hz, JC=C = 7.3 Hz, 9), 129.58 (dd, JC=C = 156.1 Hz, JC=C = 7.9 Hz, 1), 130.83 (dd, JC=C = 156.1 Hz, JC=C = 7.9 Hz, 10), 133.72 (dt, JC=C = 147.5 Hz, JC=C = 4.1 Hz, 6), 146.25 (q, JC=C = 6.6, 7), 150.83 (q, JC=C = 7.5 Hz, 4), 217.47 (s, 5). 1H-13C gHSQC (500.0 MHz, 125.7 MHz, C6D6, 25 °C): A, B, C, D, E, F, G, H. 1H-13C gHMBC (500.0 MHz, 125.7 MHz, C6D6, 25 °C): A δ24, B δ25, C δ25, D δ25, E δ21, F δ20, G δ20. Analytical Calcd. for C25H27La (588.61): C, 69.38%; H, 7.02%. Found: C, 69.51%; H, 6.90%.

Reaction of [Cp*LaCH2CCPh with excess of H2. NMR Scale. Hydrogen gas was applied (1 atm.) onto a solution of Cp*LaCH2CCPh (9.6 mg, 18.2 µmol) in 0.50 mL of benzene-d6. Within several minutes the yellow solution turned red and became darker in color upon standing. 1H NMR spectroscopy indicated the instantaneous formation of [(Cp*La(µ-H)]. Two other unidentified lanthanocene derivatives formed concomitantly, based on the presence of new Cp* 1H NMR resonances at δ 1.95 and 1.71 ppm. The reaction mixture was allowed to stand at room temperature for 1 day during which the progress of reaction was monitored.
periodically with 1H NMR spectroscopy. Upon standing, more [(Cp*2La)(µ-H)]2 formed at the expense of Cp*LaCH2C6H5. After 12 h, Cp*LaCH2C6H5 was completely consumed, while the intensities of the Cp*H NMR resonances at δ 1.95 and 1.71 ppm started to decrease. After 18 h, Cp*LaCH2C6H5 and n-propylbenzene were the only compounds present in the product mixture, as indicated by NMR spectroscopy and GC/MS analysis upon quenching with methanol.

**Reaction of [Cp*2La(µ-H)]2 with CH3CCC6H3Me2-2,6. NMR Scale.** [Cp*2La(µ-H)]2 (7.8 mg, 9.5 µmol) was dissolved in C6D6 and CH3CCC6H3Me2-2,6 (3 mg, 20.8 µmol) was added with a microsyringe in the glovebox. The light-yellow solution turned darker and became light-orange within several minutes at room temperature. Within 10 min 1H NMR resonances of the hydride and substrate disappeared and Cp*LaCH2CCC6H5Me2-2,6 and cis-1-(2,6-dimethylphenyl)prop-1-ene were observed. After 1 day at room temperature the reaction mixture did not change and was quenched with CD3OD forming Cp*D, cis-1-(2,6-dimethylphenyl)-1-propyne-d1 and (2,6-dimethylphenyl)allene-d1 as indicated by 1H NMR and GC-MS.

**Cis-1-(2,6-dimethylphenyl)prop-1-ene:** 1H NMR (C6D6, 25 °C, 300 MHz): δ 6.21 (dm, JCH = 11.4 Hz, =CH, 1 H), 5.64 (dq, JCH = 11.4 Hz, JHM = 6.9 Hz, =CH, 1 H), 2.15 (s, CH3, 6 H). 1H NMR analysis upon quenching with methanol.

**Relative concentration.** The relative concentration of the propargyl (74%) had increased. The reaction mixture was subsequently quenched with methanol forming a mixture containing Cp*H, cis-1-(2,6-dimethylphenyl)prop-1-ene, 1-(2,6-dimethylphenyl)allene as indicated by 1H NMR analysis. Also cis-1-(2,6-diisopropyl-phenyl)-1-propene was observed. After 2 days at room temperature, the relative concentration of the propargyl (74%) had increased. The reaction mixture was subsequently quenched with methanol forming a mixture containing Cp*H, cis-1-(2,6-diisopropylphenyl)prop-1-ene, 1-(2,6-diisopropylphenyl)allene and the unknown species (12%, 1.88 (propargyl, 14%) and 1.84 (assigned to the alkenyl species Cp*2LaC(C6F5)=C(CH3)H, 12%). 19F NMR analysis points to at least four major different pentafluorophenyl moieties (in a 0.4:1.0:0.3:0.3 ratio). No changes were observed with 1H NMR spectroscopy after 2 days at room temperature and CD3OD is added. NMR
and GC/GC-MS analysis pointed to the presence of 1-(pentafluorophenyl)prop-1-ene-1,3-diol monitored with 1H NMR spectroscopy. After completion the mixture was quenched with methanol and GC/GC-MS, m/z (relative intensity): 210 (4), 209 (M' - H, 84), 190 (M' - H - F, 26), 188 (M' - F - 2H or M' - F - D, 18), 187 (1), 181 (100), 169 (27), 161 (21), 158 (24). GC-MS, m/z (calc., found): 211 (0.4, 0.3), 210 (9.6, 8.7), 209 (100, 100).

2,4-Bis(1-pentafluorophenyl)-3-methylhexa-2,4-diene-d3: 1H NMR (C6D6, 25 °C, 400 MHz): δ 5.45 (m, CH2, 1 H), 1.57 (m, CH3, 3 H), 1.48 (d, JCH = 6.8 Hz, CH2, 3 H). GC-MS, m/z (relative intensity): 417 (1), 416 (10), 415 (M' - 50, 50), 401 (18), 400 (M' - CH2, 100), 385 (M' - 2 CH2, 11), 350 (17), 205 (17), 188 (16), 187 (23), 182 (32), 181 (59). GC-MS, m/z (calc., found): 417 (2.2, 1.8), 416 (19.0, 19.6), 415 (100, 100).

**Thermolysis of Cp*2LaCH2CCPh.** NMR Scale. 
Cp*2LaCH2CCPh (15.0 mg, 28.6 µmol) was dissolved in toluene-d5 and heated in a sealed NMR tube for 12 days at 100 °C and then for 27 days at 120 °C. The progress of the reaction was monitored with 1H NMR spectroscopy. The mixture was quenched with methanol-d5. GC/GC-MS analysis indicated the presence of Cp*H-d5, Cp*H-d6, and two compounds of m/z 233-235 and 232-234, respectively. The latter two have been identified as oligodeuterated isomers of C15H15, based upon the identical retention times with nondeuterated C15H15 isomers found in other reactions. The mixture of deuterated isomers rendered the quantitative evaluation of the fragmentation pattern for each compound unreliable.

**Thermolysis of Cp*2-YCH2CCPh.** NMR Scale. 
Cp*2-YCH2CCPh (15.0 mg, 31.6 µmol) was dissolved in benzene-d6 and heated in a sealed NMR tube for 30 days at 120 °C. The progress of the reaction was monitored with 1H NMR spectroscopy. After completion the mixture was quenched with methanol and GC/GC-MS analysis indicated the presence of Cp*H-d6 (n = 4-5) and three deuterated isomers of C10H12.

C10H12: GC-MS, m/z (relative intensity): 235 (7), 234 (M' - 36), 220 (19), 219 (100), 205 (17), 204 (53), 157 (14), 141 (23), 128 (22), 115 (47). GC-MS, m/z (calc., found): 235 (0.1, 0.0), 234 (1.8, 2.3), 233 (19.6, 22.3), 232 (100, 100).

C10H12: GC-MS, m/z (relative intensity): 236 (1, 23), 235 (21), 232 (M', 99), 217 (M' - CH2, 24), 216 (23), 215 (37), 202 (M' - 2CH2, 22), 153 (27), 141 (74), 128 (45), 115 (100, 91), 97 (76). GC-MS, m/z (calc., found): 235 (0.1, 0.1), 234 (1.8, 2.3), 233 (19.6, 21.6), 232 (100, 100).

**Thermolysis of Cp*2-LahCH2CCPh.** NMR Scale. 
Cp*2-LahCH2CCPh (15.0 mg, 29.6 µmol) was dissolved in benzene-d6 in the glove box. 1H NMR spectroscopy indicated the clean formation of Cp*2-Lah(1-CH2CCPh)(THF). The reaction mixture was monitored with 1H NMR for 2 days at room temperature, before heating to 50 °C. After 1 day at 50 °C, the mixture was...
quenched with methanol-d₆ and GC/GC-MS analysis indicated only the presence of an unidentified C₆H₅H₂. Besides the expected quenching products Cp*D and THF.

Cp*₂La(η⁵-C₅H₅)CH₂CCPh(THF): ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.37 (m, CH₂, β-CH₃, 4 H), 1.97 (s, Cp*, 30 H), 2.95 (s, CH₃, 2 H), 3.55 (m, OCH₃, α-CH₃, 4 H), 6.95 (d, δJ = 7.4 Hz, 3H, 2-H), 7.11 (dd, δJ = 7.4 Hz, 7.6 Hz, 2-H). ¹C NMR (75 MHz, C₆D₆, 25 °C): δ 11.02 (C₃(H)), 52.63(CH₂CC₆H₅), 25.68 (β-CH₃), 68.35 (α-CH₃), 118.86 (CMe), 124.91 (p-CH), 128.84 (p-CH), 128.55 (m-CH), 129.05 (o-CH). Signals corresponding to CH₂CC and CH₂CC not observed.

C₆H₅H₂ - GC/MS, m/z (relative intensity): 234 (2), 233 (17), 232 (M⁺, 84), 218 (21), 217 (M⁺ - CH₃, 100), 216 (43), 215 (67), 203 (17, 2) (M⁺ - 2CH₃, 60), 189 (23), 115 (55). GC/MS, m/z (calc., found): 235 (0.1, 2.2), 234 (1.8, 1.9), 233 (19.6, 18.6), 232 (100, 100).

Cp*₂La(η⁵-C₅H₅)CH₂CCPh(pyr) (7apy). Pyridine (8.0 µL, 98 µmol) was added with a microsyringe to a solution of Cp*₂LaCH₂CCPh (50 mg, 95 mmol) in hexanes (2 mL) in the glove box. Stirring for 2 h at room temperature produced a clear light-yellow solution. Cooling and concentrating the solution in vacuo afforded yellow crystals suitable for X-ray analysis. Isolated yield: 52 mg (80%).

¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.94 (s, Cp*, 30H), 3.16 (s, CH₂, 2H), 6.51 (dd, δJ = 7.7 Hz, 3J = 4.5 Hz, δJ = 1.5 Hz, β-H, 2 H), 6.81 (tt, δJ = 7.6 Hz, 1J = 1.9 Hz, γ-H, 1 H), 6.96 (tt, δJ = 7.4 Hz, 6J = 1.2 Hz, p-H, 1 H), 7.13 (d, J = 7.4 Hz, m-H, 2 H), 7.24 (d, δJ = 7.9 Hz, o-H, 2 H), 8.40 (dd, δJ = 4.5 Hz, J = 1.9 Hz, α-H, 2 H). ¹C NMR (125.7 MHz, C₆D₆, 25 °C): δ 11.55 (q, δJ = 125.1 Hz, C₆(CH₃)), 51.07 (t, δJ = 159.5 Hz, CH₂CC), 117.96 (m, CMe), 123.72 (dd, 1J = 153.6 Hz, p-CH, 127.39 (ddd, 1J = 165.6 Hz, β-CH), 128.58 (m- and o-CH), 136.43 (m, i-C), 137.04 (d, J = 163.3 Hz, α-CH), 152.16 (s, CH₂CC). The signal corresponding to CH₂CC was not observed. IR (nujol, [cm⁻¹]): 2923 (s), 2853 (s), 2713 (m), 1793 (m), 1743 (w), 1594 (m), 1459 (s), 1377 (m), 1215 (m), 1150 (m), 1067 (m), 1021 (m), 898 (m), 838 (m), 748 (m), 684 (m), 477 (s). Anal. Calcld. for C₆H₅La(N): 603.62 C, 67.65% H, 7.01%. Found: C, 67.51%, H, 6.90%.

Cp*₂La(η⁵-C₅H₅)CH₂CCPh(ppy) (7bpy). Pyridine (20.5 µL, 253 µmol) was added with a microsyringe to a stirred solution of Cp*₂LaCH₂CCPh (120 mg, 253 µmol) in hexanes (2 mL) in the glove box. Immediately the orange solution turned pale yellow. Upon standing at room temperature, the orange solution gradually turned red and a dark red suspension formed after 1 day. NMR and GC/GC-MS analysis suggested decomposition of the initially formed base adduct into several unidentified compounds. Cooling a freshly prepared solution afforded off-white crystals. Isolated yield: 88.3 mg (63%). After isolation the crystals turned red within several hours at room temperature.

Cp*₂Y(CH₂CC₆H₅)CH₂CCPh(ppy): ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 1.93 (s, Cp*, 30H), 2.71 (s, CH₂, 2H), 6.65 (dd, δJ = 5.4 Hz, 3J = 5.4 Hz, β-CH, 2 H), 6.94 (m, γ-CH, 1 H), 6.97 (dd, δJ = 7.6 Hz, 1J = 7.6 Hz, p-CH, 1 H), 7.09 (dd, δJ = 7.7 Hz, 3J = 7.7 Hz, m-CH, 2 H), 7.22 (dd, δJ = 7.8 Hz, 1J = 7.8 Hz, o-CH, 2 H), 8.53 (m, α-CH, 2 H). ¹C NMR (125.7 MHz, C₆D₆, 25 °C): δ 11.21 (q, δJ = 125.8 Hz, C₆(CH₃)), 47.22 (dt, δJ = 157.2 Hz, δJ = 7.7 Hz, CH₂CC), 104.88 (d, δJ = 9.7 Hz, CH₂CC), 117.65 (m, CMe), 123.46 (d, δJ = 163.0 Hz, β-CH), 126.39 (d, J = 160.9 Hz, C₆(CH₃)), 128.57 (dd, δJ = 168.4 Hz, 1J = 7.6 Hz, m-CH), 132.06 (ddd, δJ = 159.3 Hz, 1J = 6.3 Hz, 3J = 1.9 Hz, o-CH), 132.68 (m, i-C), 135.49 (d, δJ = 160.8 Hz, γ-CH), 150.27 (d, δJ = 179.4 Hz, α-CH), 151.58 (s, CH₂CC). IR (nujol, [cm⁻¹]): 2925 (s), 2854 (m), 2727 (w), 2148 (m), 1920 (w), 1588 (w), 1462 (m), 1377 (m), 1238 (m), 1021 (m), 855 (w), 800 (w), 759 (w), 705 (m), 520 (s).

Reaction of Cp*₂LaCH₂CCPh with 1-phenyl-1-propyne. NMR Scale. Cp*₂La(η⁵-C₅H₅)CH₂CCPh (10.0 mg, 19.7 µmol) was dissolved in 0.50 mL of a benzene-d₆ solution of hexafluorobenzene (1.4 mM). After addition of 1-phenyl-1-propyne (47.5 µL, 381 µmol) in benzene-d₆ (0.50 mL). ¹H NMR spectroscopy indicated the formation of Cp*₂La(η⁵-C₅H₅)CH₂CCPh(ppy). The reaction mixture was quenched with methanol-d₆. GC/GC-MS analysis indicated the presence of 1-phenyl-1-propene-d₁, 1-phenyl-1-propyne-d₂, and α-15 isomers of C₆H₅H₂. The three major C₆H₅H₂ isomers were assigned to the three major products which were characterized by 1D and 2D NMR spectroscopy (Chapter 3).

Reaction of Cp*₂LaCH₂CCPh with 1-pentafluorophenyl-1-propyne. NMR Scale. Cp*₂LaCH₂CCPh (10.0 mg, 19.7 µmol) was added to a solution 1-pentafluorophenyl-1-propene (78.6 mg, 381 µmol) in benzene-d₆ (0.50 mL). ¹H NMR spectroscopy indicated the formation of Cp*₂La(η⁵-C₅H₅)CH₂CCPh(ppy). The reaction mixture was quenched with ¹H and ¹³C NMR for 20 days at 80 °C, quenching with methanol-d₆. GC/MS analysis indicated the presence of 1-pentafluorophenyl-1-propene-d₁, pentafluorophenylpropadiene-d₁, Cp*₂D, 1-phenyl-1-propyne and several organic compounds of which the major products were identified as C₆H₅DF₆ (m/z 413) and four isomers of C₅H₇DF₁₀ (m/z 529) on the basis of their fragmentation pattern.
Rare-earth metallocene propargyl/allenyls

C_{18}H_{5}DF_{10}: GC-MS, \( m/z \) (relative intensity): 413 (M +, 49), 412 (100), 398 (21), 397 (M + - CH_{3}, 47), 378 (87), 328 (21), 245 (25), 232 (10), 231 (37), 205 (82), 193 (41), 181 (96), 161 (26).

\[ \text{GC-MS, } m/z (\text{calc.}, \text{found}): 416 (0.1, -), 415 (1.8, 1.5), 414 (19.5, 17.6), 413 (100.0, 100.0). \]

C_{27}H_{13}DF_{10}: GC-MS, \( m/z \) (relative intensity): 531 (1), 530 (11), 529 (M +, 38), 514 (M + - CH_{3}, 17), 407 (12), 379 (12), 347 (28), 181 (39), 123 (84), 122 (100), 121 (38), 108 (37), 107 (27), 106 (39), 92 (26), 91 (24).

\[ \text{GC-MS, } m/z (\text{calc.}, \text{found}): 532 (0.4, -), 531 (4.0, 4.6), 530 (29.3, 27.7), 519 (100.0, 100.0). \]

Reaction of Cp^{*}2LaCH_{2}CCPh with an excess of 1-hexene. NMR Scale.

A solution of Cp^{*}2LaCH_{2}CCPh (5.0 mg, 9.5 µmol) in 0.50 mL of benzene-d_{6} containing hexamethyldisiloxane (4.5 mM) was prepared and transferred into a NMR tube. After addition of 1-hexene (173 µL, 1.38 mmol, 145 equiv.) the tube was sealed off and heated to 100 °C. The progress of the reaction was monitored with 1H NMR spectroscopy.

After 3.59 days at 100 °C no changes were observed and the reaction mixture was heated to 120 °C for 74 days. The reaction mixture was quenched with methanol-d_{4}. GC and GC-MS analysis indicated the presence of 1-hexene, hexane, \( \text{cis} \)- and \( \text{trans} \)-2-hexene, \( \text{cis} \)- and \( \text{trans} \)-7-methyl-4-undecene and 3-dodecene. The unidentified organic compounds with \( m/z \) 170 (C_{12}H_{26}), 166 (two isomers of C_{12}H_{22}), 154 (M + - CH_{3}, 17), 407 (12), 379 (17), 347 (28), 181 (39), 123 (84), 122 (100), 121 (38), 108 (37), 107 (27), 106 (39), 92 (26), 91 (24).

\[ \text{GC-MS, } m/z (\text{calc.}, \text{found}): 168 (0.8, 1.0), 167 (13.3, 14.3), 166 (100.0, 100.0). \]

Table 2-9: Summary of crystallographic data of the Cp^{*}_{2}La(η^{3}-CH_{2}CCPh) (7a), Cp^{*}_{2}Y(η^{3}-CH_{2}CCPh) (7b) and [Cp^{*}_{2}La(η^{3}-CH_{2}CCPh)(NC_{5}H_{5})] (7a·py) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>7a</th>
<th>7b</th>
<th>7a·C_{5}H_{5}N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>$C_{29}H_{37}La$</td>
<td>$C_{29}H_{37}Y$</td>
<td>$C_{34}H_{42}LaN$</td>
</tr>
<tr>
<td>FW</td>
<td>524.52</td>
<td>474.52</td>
<td>603.62</td>
</tr>
<tr>
<td>T, K</td>
<td>100(1)</td>
<td>100(1)</td>
<td>100(1)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pna2_{1}</td>
<td>Pca2_{1}</td>
<td>P1,2</td>
</tr>
<tr>
<td>a, Å</td>
<td>20.064(1)</td>
<td>16.464(9)</td>
<td>8.7176(4)</td>
</tr>
<tr>
<td>b, Å</td>
<td>10.051(2)</td>
<td>10.5009(6)</td>
<td>9.6510(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>12.233(3)</td>
<td>14.7315(8)</td>
<td>18.4630(9)</td>
</tr>
<tr>
<td>$a^{\circ}$</td>
<td>-</td>
<td>-</td>
<td>78.405(1)</td>
</tr>
<tr>
<td>$\beta^{\circ}$</td>
<td>-</td>
<td>-</td>
<td>87.337(1)</td>
</tr>
<tr>
<td>$\gamma^{\circ}$</td>
<td>-</td>
<td>-</td>
<td>72.103(1)</td>
</tr>
<tr>
<td>$V$, Å$^{3}$</td>
<td>2466.9(8)</td>
<td>2547.0(2)</td>
<td>1447.86(11)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$\rho_{calc}$, g cm$^{-3}$</td>
<td>1.412</td>
<td>1.277</td>
<td>1.385</td>
</tr>
<tr>
<td>F(000)</td>
<td>1072</td>
<td>1000</td>
<td>620</td>
</tr>
<tr>
<td>$\mu$(Mo K$\alpha$), cm$^{-1}$</td>
<td>17.44</td>
<td>23.02</td>
<td>14.97</td>
</tr>
<tr>
<td>$\theta$ range (°)</td>
<td>2.27, 27.48</td>
<td>2.30, 28.28</td>
<td>2.26, 28.28</td>
</tr>
<tr>
<td>$w$(R(F$^{2}$))</td>
<td>0.0990</td>
<td>0.0858</td>
<td>0.0666</td>
</tr>
<tr>
<td>Refined reflections</td>
<td>5124</td>
<td>4224</td>
<td>6966</td>
</tr>
<tr>
<td>Refined parameters</td>
<td>276</td>
<td>419</td>
<td>493</td>
</tr>
<tr>
<td>R(F) for Fo &gt; 4.0</td>
<td>0.0463</td>
<td>0.0297</td>
<td>0.0307</td>
</tr>
<tr>
<td>$\sigma$(Fo)</td>
<td>$\text{Goof}^{2}$</td>
<td>1.025</td>
<td>1.030</td>
</tr>
<tr>
<td>Weighting (a, b)</td>
<td>0.0, 0.0</td>
<td>0.0393, 0.0</td>
<td>0.0316, 0.0</td>
</tr>
</tbody>
</table>

C_{12}H_{26}: GC-MS, \( m/z \) (relative intensity): 168 (0.8, 1.0), 167 (1.8, 1.5), 141 (19.5, 17.6), 413 (100.0, 100.0).

Two isomers of C_{12}H_{22}: GC-MS, \( m/z \) (calc., found): 168 (0.8, 1.0), 167 (13.3, 14.3), 166 (100.0, 100.0).

C_{15}H_{20}: GC-MS, \( m/z \) (calc., found): 202 (0.8, 1.0), 201 (16.5, 19.9), 200 (100.0, 100.0).

C_{15}H_{17}: GC-MS, \( m/z \) (calc., found): 199 (1.1, 2.1), 198 (16.5, 23.0), 197 (100.0, 100.0).

C_{15}H_{15}: GC-MS, \( m/z \) (calc., found): 197 (1.1, 2.3), 196 (13.3, 14.7), 195 (100.0, 100.0).
Two isomers of C\textsubscript{18}H\textsubscript{28}: GC-MS, \textit{m/z} (calc., found): 253 (0.1, 0.0), 252 (1.8, 2.8), 251 (20.0, 24.5), 250 (100.0, 100.0); \textit{m/z} (calc., found): 253 (0.1, 1.4), 252 (1.8, 8.1), 251 (20.0, 20.5), 250 (100.0, 100.0).

Three isomers of C\textsubscript{18}H\textsubscript{28}: GC-MS, \textit{m/z} (calc., found): 284 (0.2, 0.0), 283 (2.6, 5.9), 282 (23.1, 36.1), 281 (100.0, 100.0); \textit{m/z} (calc., found): 285 (0.1, 1.4), 252 (1.8, 8.1), 251 (20.0, 20.5), 250 (100.0, 100.0).

**X-ray crystallography.** In the glovebox, the crystals were transferred from the reaction vessels to a Petri dish filled with a small amount of light mineral oil. A suitable crystal was chosen by examination under a microscope. This crystal was attached to glass fiber which was mounted in a cold nitrogen stream on a Bruker SMART APEX CCD diffractometer for data collection. Data collection and structure solution were conducted at the University of Groningen. The structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF. Relevant crystal and data collection parameters are given in Table 2-9.

### 2.8. References and notes


In contrast to bromo- and chlorodediazotization reactions, the use of copper is generally assumed not to be required in iododediazotization reactions. The replacement of the diazonium group by bromide or chloride in the presence of the appropriate copper(I) salts represents the most widely used method to prepare arylbromides and -chlorides (the Sandmeyer reaction). The Sandmeyer reaction is believed to occur via the reduction of diazonium salts by copper(I) species to give aryl radicals that subsequently abstract halogen from copper(II) halides. The use of finely divided (i.e. freshly precipitated) copper or copper bronze is known to act catalytically in the decomposition of diazonium salts, but the yields in the preparation of arylhalides (Gatterman reaction) are usually not as high as those obtained by the Sandmeyer reaction. For a review on palladium-catalyzed alkynylation, see: (b) Negishi, E.; Kotora, M.; Xu, Caiding, Organometallics 1990, 9, 1508. (b) Heeres, H. J. Ph. D. Thesis, University of Groningen, 1990; Chapter 5.


22 Lithiation or stannylation of 2,6-diisopropylbromobenzene followed by iodinolysis was not explored in this study as a synthetic route towards the desired iodo compound. For examples of this approach in the preparation of 2,6-dimethylidodo-benzene, see: (a) Sasaki, Y.; Hirabuki, M.; Ambo, A.; Ouchi, H.; Yamamoto, Y. Bioorg. Med. Chem. Lett. 2001, 11, 327. For a review on the synthesis of iodoarenes, see: (b) Merkushev, E. B. Synthesis 1988, 923.


24 Performing cross-coupling reactions with sterically hindered substrates represents, in fact, one of the major challenges in this area of research and efforts aimed at developing catalyst systems that are able to bring about this type of reactions are ongoing. Some progress has recently been achieved, but most examples involve either catalysts that are not readily available or the cross-coupling of two sp² carbons in the synthesis of hindered biaryl compounds. Only recently, efficient catalysts for the Sonogashira coupling of sterically hindered aryl halides with 1-alkynes have been described. For examples, see: (a) Hundermark, T.; Littke, A. F.; Buchwald, S. L.; Wy, G. C. Org. Lett. 2000, 2, 1729. (b) Köllhofer, A.; Pullmann, T.; Plenio, H. Angew. Chem. Int. Ed. 2003, 42, 1056. (c) Feuerstein, M.; Berthiol, F.; Doucet, H.; Santanelli, M. Synthesis 2004, 1281 and references therein.

25 For example, reactions of 2,6-diisopropylamine with n-butyl nitrite and several iodinating agents (i.e. iodine, potassium and copper iodide, freshly precipitated copper(I) iodide and methyl iodide), under a nitrogen atmosphere and in air, in the presence and absence of a crown ether, in a variety of solvents (i.e. chloroform, dichloromethane, tetrachloromethane, benzene and THF mixtures of the aforementioned solvents) and at different reaction temperatures yielded mixtures containing the desired iodo compound only in low crude yields (2-20%, GC/GC-MS).


27 It has been reported that the Negishi reaction tolerates sterically congested substrates better than the Sonogashira reaction and other palladium-catalyzed cross-coupling protocols based on organomagnesium and -tin reagents (the Stille reaction).

28 Performing cross-coupling reactions with sterically hindered substrates represents, in fact, one of the major challenges in this area of research and efforts aimed at developing catalyst systems that are able to bring about this type of reactions are ongoing. Some progress has recently been achieved, but most examples involve either catalysts that are not readily available or the cross-coupling of two sp² carbons in the synthesis of hindered biaryl compounds. Only recently, efficient catalysts for the Sonogashira coupling of sterically hindered aryl halides with 1-alkynes have been described. For examples, see: (a) Hundermark, T.; Littke, A. F.; Buchwald, S. L.; Wy, G. C. Org. Lett. 2000, 2, 1729. (b) Köllhofer, A.; Pullmann, T.; Plenio, H. Angew. Chem. Int. Ed. 2003, 42, 1056. (c) Feuerstein, M.; Berthiol, F.; Doucet, H.; Santanelli, M. Synthesis 2004, 1281 and references therein.


Copper(I) acetylides are dangerous, because they undergo hazardous explosions, when shocked or exposed to heat. Because of their high sensitivity to shock, friction and heat, copper acetylides must be handled with extreme care. They must be kept cool and, if they are to be stored, should be kept wet. See: (a) Bretherick, L. Dangerous Properties of Industrial Materials, 5th edition, Reinhold: New York, 1979. (b) Sax, N. I. Dangerous Properties of Industrial Materials, 5th edition, Reinhold: New York, 1979. (c) Brameld, V. F.; Clark, M. T.; Seyfang, A. P. Handb. Chem. Ind. 1947, 66, 346.

According to a general procedure in which copper(I) acetylides are prepared from organolithium or -magnesium reagents in ether or THF, propynylmagnesium bromide was added to a suspension containing copper(I) iodide in ether at 0 °C. However, replacing ether in vacuo by solvents with higher boiling points such as THF, di-n-butyl ether (bp 141 °C), dimethylformamide (bp 153 °C), and pyridine (bp 115 °C) and the subsequent addition of the iodoarene did not result in the formation of the desired substitution product after prolonged reaction times and at refluxing temperatures. Also the use of THF and freshly precipitated copper(I) iodide in the preparation of the copper(I) acetylide did not change this outcome. Analogous reactions using propynylmagnesium as a starting material (formed in situ from propyne gas and n-butyl lithium in THF according to reported procedures\(^{127}\)) failed also to give the desired propynylarene. For general synthetic procedures towards starting material (formed in situ from reaction of Cp*₂YCl with 2-methyl-2-propenylmagnesium chloride led instead to the formation of Cp*₂Y(CH₂CMe=CH₂)·[MgCl₂·2THF], see: den Haan, K. H.; Wielstra, Y.; Eshuis, J. J. W.; Teuben, J. H. Chim. Pays-Bas 1987, 106, 709. (c) Brandsma, L.; Verkuijse, H. D. Preparative Polar Organometallic Chemistry, Springer: Berlin, Vol. 1., p. 42. (d) Taylor, R. J. K. In Organocopper Reagents: A Practical Approach, Taylor, R. J. K. (ed.); Chapters 1 and 2. For the preparation of propynylmagnesium, see: (e) Midland, M. J. J. Org. Chem. 1975, 40, 2250. (f) Taschner, M. J.; Rosen, T.; Heathcock, C. H. Org. Synth. Coll. Vol. 7, 226. (g) Stang, P. J.; Boeshar, M.; Wingert, H.; Kitamura, T. J. J. Am. Chem. Soc. 1988, 110, 3272. (h) Marshall, J. A.; Wang, X. J. J. Org. Chem. 1991, 56, 960.


Remarkably, further additions of freshly prepared propynyl copper did not result in the complete consumption of the iodoarene.


Only recently, allyl derivatives, Cp³⁺Ln(η⁵-C₅H₅(CH²CMe=CH₂)), have been recognized as a convenient starting material in organo rare-earth metal chemistry, as they exhibit greater stability in terms of storage and handling than alkyls or hydrides, see: Evans, W. J.; Kozimor, S. A.; Brady, J. C.; Davis, B. L.; Nyce, G. W.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. Organometallics 2005, 24, 2269 and references therein.


No acidity constants were found in literature for propynylbenzenes. If the transmission of electronic effects via a carbon-carbon triple bond is similar to that of a carboxylic group, a large effect can be anticipated upon substituting the phenyl group with the pentafluorophenyl group. For example, substitution of the phenyl group of benzenecarboxylic acid C₆H₅CO₂H (pKₐ = 4.20 \(^{42}\)) by the


In an attempt to determine the relative (kinetic) acidity of 1-phenyl-1-propyne (1) and 1-pentafluorophenyl-1-propyne (5), n-butyllithium was added to a stirred solution of 1 (1.0 equiv.) and 5 (1.0 equiv.) in THF at -80 °C. Instead of the expected formation of allenylic and acetylenic quenchings products after addition of trimethylsilylchloride (TMSCl), a complicated mixture containing a multitude of unidentified compounds was obtained.

For example, the reaction of [Cp*₂Sm(µ-H)]₂ with propene, 1-butene and allylbenzene forms the corresponding n'-allyl complex in hexane, but gives Cp*₂SmCH₂Ph, exclusively, in toluene.⁵⁴

Dissociation of the dimer [Cp*₂Y(µ-H)]₂ to the monomer Cp*₂YH in reactions of [Cp*₂Y(µ-H)]₂ with alkenes has been studied in detail. See: Casey, C. P.; Tunge, J. A.; Lee, T.-Y.; Carpenter III, D. W. Organometallics 2002, 21, 389.

The reaction of [Cp*₂La(µ-H)]₂ with pyridine (2 equiv.) in benzene-d₅ produces a 1:1 mixture of Cp*₂La(η²-2-C₅H₄N) and Cp*₂La(NC₅H₅) instantaneously. The formed products were rationalized by ortho-metalation of pyridine resulting in the formation of Cp*₂La(η²-2-C₅H₄N) and H₂. This reaction is followed by the rapid capture of the formed H₂ by Cp*₂La(η²-2-C₅H₄N) to afford Cp*₂La(NC₅H₅). In marked contrast to this efficient hydrogen trapping is the independent reaction of Cp*₂La(η²-2-C₅H₄N) with excess H₂ (4 atm.). In this case, the hydrogenation product Cp*₂La(NC₅H₅)(CH₅H) is formed quantitatively after 1 day at 20 °C. See: (a) Ringelberg, S. N. Ph. D. Thesis, University of Groningen, 2001; Chapter 5. For another example of efficient hydrogen trapping, see: (b) Hao, L.; Harrod, J. F.; Lebuis, A.-M.; Mu, Y.; Shu, R.; Samuel, E.; Woo, H.-E. Angew. Chem. Int. Ed. 1998, 37, 3126.

Sung et al. proposed the steric substituent constant Sₐ based on isodesmic reactions and ab initio calculations of substituted adamantine systems. According to the Sₐ scale, the phenyl (Sₐ = -5.10) is larger than the methyl group (Sₐ = -2.02), see: (a) Sung, K.; Chen, F.-L. Org. Lett. 2003, 5, 889. For reviews on steric effects, see: (b) Gallo, R. Prog. Phys. Org. Chem. 1983, 14, 115. (c) Förster, H.; Vögtle, F. Angew. Chem. Int. Ed. Engl. 1977, 16, 429.


Reversible insertion of the carbon-carbon triple bond of diphenylacetylene into the metal-hydrides of Cp*₂LaH should yield Cp*₂La(Ph)₃=CH(Ph) upon standing in benzene-d₆, due to the well-known tendency of Cp*₂LaH to undergo H/D exchange with benzene-d₆.¹² However, the intensity of the vinyl proton in Cp*₂La(Ph)=CH(Ph) relative to that of the Cp* groups did not change after
standing for 14 days at room temperature, thereby providing evidence against the formation of 
\[ \text{Cp}^*\text{La(Ph)\ldots} \text{C(Ph)D} \text{ via reversible insertion of diphenylacetelyne into } \text{Cp}^*\text{LaH.} \]

Catalytic hydrogenation of alkynes and alkenes, via alkylidene and alkyl intermediates, is well-
established for rare-earth metallocene hydrides.57-64

For examples, see: (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.;
Mauermann, H.; Schumann, H.; Marks, T. J. J. Am. Chem. Soc. 1985, 107, 8111. (c) den Haan, K. H.;
Wielstra, Y.; Teuben, J. H. Organometallics 1987, 6, 2053. (d) Jeske, G.; Lauke, H.; Mauermann, H.;
Sweptson, P. N.; Schumann, H.; Marks, T. J. J. Am. Chem. Soc. 1985, 107, 8091. (e) Jeske, G.;
Schock, L. E.; Sweptson, P. N.; Schumann, H.; Marks, T. J. J. Am. Chem. Soc. 1985, 107, 8103. (f)
Watson, P. L.; Parshall, G. W. Acc. Chem. Res. 1985, 18, 51. (g) Evans, W. J.; Ulibarri, T. A.; Ziller,
1986, 682. (j) Booij, M.; Deelman, B. J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H.
Organometallics 1993, 12, 3531.

Interestingly, the samarium allyl complexes \[ \text{Cp}^*\text{Sm(\eta^3-CH}_2\text{CHCHR)} \text{ (R = H, Me, Ph) are also} \]
reported to be extremely soluble in alkane solvents and an increasing tendency to crystallize was
found for the methyl and phenyl derivatives. \[ \text{Cp}^*\text{Sm(\eta^3-CH}_2\text{CHCHPh)} \text{ could, in fact, only be} \]
obtained as a tractable solid after recrystallization in the presence of a coordinating solvent forming
the corresponding adduct. See: Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. J. Am. Chem. Soc. 1990,
112, 2314.

Heeres \textit{et al.} also commented on the extreme solubility of \[ \text{Cp}^*\text{CeCH}_2\text{CCMe} \text{ and attempts to obtain} \]
single crystals for \[ \text{Cp}^*\text{LnCH}_2\text{CCR (Ln = Ce, Y; R = Me, Ph)} \text{ reported to be unsuccessful}.46-48

Kretschmer, W. P., personal communication

(a) Kalinowski, H.-O.; Berger, S.; Braun, S. Carbon-13 NMR Spectroscopy; Wiley: Chichester, 1991,
Chapter 4. (b) Friebolin, H. Basic One- and Two-Dimensional NMR Spectroscopy; Wiley-VCH:
Weinheim, 1998; Chapter 3.3; p. 97.

Reich, H. J.; Thompson, J. L. Org. Lett. 2000, 2, 785. (c) Reich, H. J.; Holladay, J. E.; Walker, T. G.;
1993, 58, 6377.

Infrared absorptions at 1850-1900 cm\(^{-1}\) are assigned to allenyl structures and those >2000 cm\(^{-1}\) to
propargyl structures in organolithium chemistry, see: (a) Jaffe, F. J. Organomet. Chem. 1970, 23, 53-
62. (b) Priester, W.; West, R.; Chwang, T. L. J. Am. Chem. Soc. 1976, 98, 8413. (c) West, R.; Jones,
1973, 576. For examples of organozinc and -magnesium compounds, see: (e) Ref. 2b. For examples
of organotitanium compounds, see: (f) Ishiguro, M.; Ikeda, N.; Yamamoto, H. J. Org. Chem. 1982,
1984, 57, 2768.


The paramagnetic \[ \text{Cp}^*\text{Ti(\eta^3-CH}_2\text{CCPh)} \text{ was furthermore characterized by elemental analysis, see:} \]

Carfagna, C.; Deeth, R. J.; Green, M.; Mahon, M. F.; McHnes, J. M.; Pellegrini, S.; Woolhouse, C. B.
Organometallics 1999, 18, 837.

(a) den Haan, K. H. Ph. D. Thesis, University of Groningen, 1986; Chapter 6. (b) den Haan, K. H.;
Wielstra, Y.; Teuben, J. H. Organometallics 1987, 6, 2053.


(a) Ringelberg, S. N. Ph. D. Thesis, University of Groningen, 2001; Chapter 2. (b) Ringelberg, S. N.;
No inductive/field parameters were found in literature for these metals, but the higher inductive/field
techniques are not well-established. The twist angle is defined as the average of the five smallest dihedral angles formed between the ten
planes which consist of a ring carbon and the two centroids. The corresponding protons of pentafluorophenyl-1-propyne and 1-pentafluorophenylpropa-1,2-diene resonate at 6.1.47 and 4.72 ppm, respectively, see Experimental Section. Ionic radii for eight-coordinate complexes: La$^{3+}$ (1.160 Å) and Y$^{3+}$ (1.019 Å), see: Shannon, R. D. and Mason, S. A. Acta Crystallogr., Sect. A 1976, 32, 751.

No inductive/field parameters were found in literature for these metals, but the higher inductive/field
effect of Y$^{3+}$ versus La$^{3+}$ is apparent from the carbon chemical shift of the metal-bound methine carbon in Cp$_2$LaCH(SiMe$_3$)$_2$ (δ 44.69 ppm) versus Cp$_2$YCH(SiMe$_3$)$_2$ (δ 25.19 ppm) in benzene-d$_6$ solution. In support, the electronegativity of Y$^{3+}$ (X = 1.22) is higher than that of La$^{3+}$ (X = 1.10), according to the Pauling scale, see: CRC Handbook of Chemistry and Physics, Lide, D. R. (Ed.); CRC Press: Boca Raton; 1999.

The average Ln-(C$_5$Me$_5$)$_2$ (C$_5$H$_5$) and Ln-(C$_5$Me$_5$)$_2$ (C$_5$H$_5$) versus Ln-(C$_5$H$_5$)$_2$ (C$_5$H$_5$) is more acidic than phenylacetylene (362.6). For reviews on carbon acids, see: (a) Cram, D. J. Ionisation of Carbon Acids, Academic Press: New York, 1965. (b) Jones, J. R. Fundamentals of Carbanion Chemistry, Academic Press: New York, 1965. (c) Gerald, J.; Schock, L. E.; Siewert, P. N.; Schumann, H.; Marks, T. J. J. Am. Chem. Soc. 1985, 107, 8103. (d) Ref. 40. (e) Ref. 54.


The twist angle is defined as the average of the five smallest dihedral angles formed between the ten
planes which consist of a ring carbon and the two centroids.


The reactions of CpxLaMe3 and CpxSiEt3 with allene are reported to proceed via C-H activation, forming the allenyl CpxLn(C≡CCH=CH2) and allyl CpxSc(μ-CH=CH=CH2), respectively. The lanthanide alkenyl derivatives CpxLn(C≡C(CH₂)=CH₂) are believed to be reactive intermediates in numerous catalytic reactions, such as 1-alkyne oligomerization, alkyne hydroamination and alkyne hydrosilylation, and are presumed to undergo insertion reactions with unsaturated substrates and C-H activation reactions with Bronsted acids. However, -to best of our knowledge- no (systematic) reactivity studies of well-defined lanthane oligoalkenyl derivatives are reported in literature.

The observation of acetylenic and allenylic phenylacetylene trimers C₂₅H₂₀ (for details, see Chapter 4) with GC-MS provides circumstantial evidence that organic compounds C₂₅H₂₀ are stable under the present experimental conditions.

The Lewis-base-free complex CpxZrMe[B(4-C₆H₄F)₄] undergoes selective insertion of 1,2-propadiene at -30 °C, but a complicated mixture is formed upon warming with the excess amount of 1,2-propadiene present. The reaction with 3-methyl-1,2-butadiene is reported to afford a complex mixture of unidentified products. See: Horton, A. D. *Organometallics* 1992, 11, 3271.


Thermolysis of CpxCeCH(SiMe₃)₂ indicated a similar compound.


Regionrandom insertion of phenyllallene into the La-CH₂ of CpxLa(q-CH₂CCPh) affords, in principle, four different products after protonolysis, whereas 1-phenyl-1-propyne yields only two. Because insertion is believed to proceed regionrandomly at 120 °C, internal metalation producing 1-phenyl-1-propyne is presently favored.

No NMR spectral data were found in literature for (monomeric) CpxLaCH₃ complexes, but analogous CpxYCH₃ derivatives have α-CH proton resonances in the range from δ 0.66 to -0.08 ppm, see: Casey, C. P.; Tunge, J. A.; Lee, T.-Y.; Fagan, M. A. *J. Am. Chem. Soc.* 2003, 125, 2641.


Following the previous line of reasoning², insertion of 1-phenyl-1-propyne into the La-CH₂ bond of CpxLa(q-CH₂CCPh) is likely to occur regioselectively at 50 °C, affording only one dimer after protonolysis.


Chapter 2


Hazar, P. N.; Bruno, J. W.; Schulte, G. K. Organometallics 1990, 9, 416.


Although the fluorine atom is larger than the hydrogen atom, both the pentafluorophenyl group and the phenyl group are planar structures.

It can be anticipated that the decrease of electron density at the triple bond will weaken the interaction with the electrophilic lanthanide metal. On the other hand, polarization of the triple bond, as to induce a partial positive charge at the \( \beta \)-position and a partial negative charge at the \( \alpha \)-position of the four-centered insertion transition state is well-known to facilitate insertion into electrophilic metal-carbon bonds. For examples, see: (a) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. J. Am. Chem. Soc. 1988, 110, 3134. (b) Doherty, N.; Bercaw, J. E. J. Am. Chem. Soc. 1985, 107, 2670. (c) Halpern, J.; Okamoto, T.; Zakhariev, A. J. Mol. Catal. 1976, 2, 65-68. (d). Lisi, Z.; Marks, T. J. J. Am. Chem. Soc. 1990, 112, 5515. (e) Ref. 102a.


To the best of our knowledge, only one example of CO insertion into a Ln-C(alkenyl) bond has been reported in literature, see: Evans, W. J.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. J. Am. Chem. Soc. 1986, 108, 1722.


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