Chapter 2

C-H Activation of Arenes by the Yttrium Hydride (Cp*₂YH)₂: Competition between Cp* Ligand Metallation, Arene Metallation and H/D Exchange

Introduction

The 14 electron group 3 and lanthanide compounds Cp*₂LnR (Cp* = η⁵-C₅Me₅, R = H, alkyl) are strong Lewis acids which, in the absence of Lewis bases, even may attack the electron density of C-H bonds, thus forming agostic interactions and activating these bonds. During our work on hydrocarbyl and hydride compounds Cp*₂LnR and (Cp*₂LnH)₂ with Ln = Y, La, Ce, we studied the activation of C-H bonds and observed that the crowded metal alkyls Cp*₂LnCH(SiMe₃)₂, though much less reactive, show a reactivity very related to that of the hydrides (Cp*₂LnH)₂. The yttrium compound (Cp*₂YH)₂ (1) appeared to be the most reactive of the series and therefore we focused on this compound. Its reactivity in solvents like alkanes, benzene and toluene and its reactions with halobenzenes were studied to determine the selectivity of C-H activation and possible competition between C-H and C-X activation with this type of compounds. The results are described below.

Results and Discussion

Competition between C-H Activation of a Cp* Ligand and C-H activation in Benzene and Toluene. Thermolysis of 1 in n-octane, cyclohexane or benzene leads to the internally metallated complex Cp*₂Y(μ-H)(μ-η⁵-C₅Me₅)₂YCp* (2) (eq 1). This reaction occurs in closed vessels but also when the hydrogen evolved is removed slowly. Binuclear complex 2 contains bridging hydride and tetramethylfulvene (Fv = CH₂C₅Me₅) ligands, the latter formed via hydrogen
abstraction from a Cp* ligand. A similar observation has been made for the analogous samarium hydride (Cp*$_2$SmH)$_2$, which emphasizes the strong resemblance of 1 and lanthanide hydrides. The formation of 2 is reversible and in closed systems a solution of 1, although it contains in part 2, reacts as if it were the intact dimeric hydride.

\[
(Cp^*YZH)_2 \rightleftharpoons Cp^*YZH(\mu-H)(\mu-\eta^1,\eta^5-CH_2C_6M\eta_4)YCp^* + H_2
\]  

(1)

In aromatic solvents a second C-H activation process is observed. When 1 is dissolved in deuterated benzene or toluene at room temperature, H/D scrambling between hydride ligands and solvent takes place at a rate too fast to follow experimentally, leading to formation of the deuteride (Cp*$_2$YD)$_2$ and it is impossible to observe hydride resonances in the $^1$H-NMR spectrum. The WD exchange with benzene and toluene was monitored by adding stoichiometric quantities of benzene-$d_6$ or toluene-$d_8$ to cyclohexane-$d_{12}$ solutions of 1. The loss of hydride intensity was attended by a matching increase in intensity of the benzene and toluene resonances respectively. Superimposed on this scrambling reaction is the thermolysis to 2. With toluene-$d_8$, after 26 h at room temperature, 20 % of the hydride ligands of 1 were still present and 30 % had been exchanged for deuteride ligands. The remaining 50 % of 1 had been converted to 2. The intensity ratio H(para) : H(meta) : H(ortho) : H(methyl) = 1.1 : 2.3 : 1.1 : 1.0 was observed, indicating a clear preference for H/D scrambling on the para and meta positions. These observations are in close agreement with the corresponding scandium system.

These results indicate that 1 is an efficient catalyst for the activation of C-D/C-H bonds in aromatic hydrocarbons. For non-deuterated aromatic hydrocarbons this is not a productive process however. In contrast to deuterated benzene and toluene, the sp$^3$ C-H bonds of cyclohexane-$d_{12}$ are not susceptible to H/D exchange and no significant H/D exchange was observed during the thermolysis of 1 in this solvent (several days at room temperature).

In addition to fast H/D exchange and the slow intramolecular C-H activation which gives 2, a third reaction was observed which, at an intermediate rate, leads to metallation of solvent molecules under formation of hydrogen (eq 2). This C-H activation competes with Cp*-metallation and compounds Cp*$_2$YR (R = Ph (3),
PhCH$_2$ (4) can be trapped as the kinetic products when the hydrogen is removed sufficiently rapidly.

\[
(Cp^*YH)_2 + 2 \text{RH} \rightarrow Cp^*YR + 2 \text{H}_2 \quad (2)
\]

\[
1 \quad 3, R = \text{Ph} \\
4, R = \text{CH}_2\text{Ph}
\]

The method is not clean, as small amounts of the bridged hydride fulvene 2 are obtained as well. For benzene this leads to a 6 : 1 mixture of 3 and 2. Toluene is metallated faster, resulting in a 11 : 1 ratio of 4 and 2. It is clear from competition experiments that 2 is the thermodynamic product, obtained when thermolysis of 1 is carried out slowly, i.e. when hydrogen is removed gradually during a couple of days at room temperature. Eq 2 is positioned strongly on the side of the starting material 1 and in closed NMR tubes less than 1 % of 1 is converted to metallation products.

In principle, H/D scrambling could take place via mettallation (Scheme I). After dissociation of 1,\textsuperscript{9} an arene molecule is metallated with formation of HD. The new Y-C bond can be hydrogenolyzed in the second step by HD to give Cp$^*$YD and protonated solvent. Another possibility is that after dissociation of 1, H/D scrambling involves the direct exchange of a proton for a deuteron between monomeric hydride and solvent. The fact that H/D scrambling between 1 and toluene-$d_8$ takes place dominantly at the aryl C-H positions while only the benzyl 4 can be obtained under dynamic vacuum, suggests that the pathway for H/D (H/H) exchange is different from that of metallation, because otherwise a mixture of yttrium tolyls \(\text{Cp}^*\text{YC}_6\text{H}_4\text{Me}\) and the benzyl 4 is expected.

Scheme I

\[
\text{Cp}^*\text{YH} + \text{RD} \rightarrow \text{Cp}^*\text{YR} + \text{HD} \\
\text{Cp}^*\text{YR} + \text{HD} \rightarrow \text{Cp}^*\text{YD} + \text{RH}
\]

The observation that H/D scrambling between H$_2$ (4 atm) and toluene-$d_8$ in the presence of 1 is slow, whereas in the same experiment scrambling between 1 and toluene-$d_8$ is fast, indicates that H$_2$, D$_2$ and HD are not intermediates in the latter
process. Ring metallation of toluene is therefore probably not on the reaction coordinate for H/D scrambling between 1 and solvent.

One way to account for the different observations within the framework of the well known σ-bond metathesis mechanism is that there are two possibilities for the incoming molecule RH to form a transition state. The most easily achieved considering steric interactions upon approach of molecule RH is situation A (Figure 1), with R symmetrically positioned between two hydrogen atoms, leading to non-productive metathesis when hydrogen atoms are involved and to catalytic H/D scrambling when deuterated substrates R-D are introduced. Situation B is the transition state normally anticipated and leads to a metallated species and H2 (or HD). So far, transition state A has hardly been mentioned as a possibility in early transition metal chemistry and theoretical analyses, but it has been proposed to explain H/D exchange between benzene-d6 and R3SiH by the d2 system C*p2NbH. Despite the fact that the transition state in the latter system is assumed to correspond to an oxidative addition of C-D respectively Si-H to a Nb(III) center, we believe that the steric aspects of the two systems are directly comparable.

The reactions with benzene and toluene show that 1 behaves very much like the Sc, Lu and other lanthanide analogues. Both (C*p2ScH)2 and (C*p2LuH)2 give facile H/D scrambling between the hydride ligands and deuterated benzene or toluene. They also form phenyl complexes when H2 is purged from the reaction mixture. Metallation of toluene to form the benzyl C*p2MCH(SiMe3)2 has also been observed for the cerium alkyl C*p2CeCH(SiMe3)2 and for the dimeric samarium hydride (C*p2SmH)2.

The formation of hydride fulvene complexes C*p2M(μ-H)(μ-η1,η5-CH2C5Me5)MCl has not been reported for M = Sc and Lu, although these systems have been studied under conditions comparable to those under which we

![Figure 1](image-url). Transition states in non-productive (A) and productive (B) σ-bond metathesis.
studied the thermolyses of 1 Bercaw et al.\textsuperscript{4} observed that, in aliphatic hydrocarbon solvents and under reduced hydrogen pressures, \((\text{Cp}^*\text{ScH})_2\) decomposes but the nature of the product(s) was not established. In the light of our results it seems likely that also for scandium the formation of a fulvene hydride \(\text{Cp}^*\text{Sc(\mu-H)(\mu-\eta^1,\eta^5-\text{CH}_2\text{C}_2\text{Me}_4})\text{ScCp}^*\) can take place when other possibilities are blocked. Evans et al.\textsuperscript{5} observed the formation of an analogous hydride fulvene complex from \((\text{Cp}^*\text{SmH})_2\) in alkanes and benzene i.e. under conditions close to those described by us for yttrium. These authors do not mention a transient side product \(\text{Cp}^*\text{SmPh}\), but in toluene they observe formation of a mixture of \(\text{Cp}^*\text{Sm(\mu-H)(\mu-\eta^1,\eta^5-\text{CH}_2\text{C}_2\text{Me}_4})\text{SmCp}^*\) and the benzyl \(\text{Cp}^*\text{SmCH}_2\text{Ph}\), which strongly suggests that the various C-H activation processes take place at samarium and therefore at other analogous lanthanide centers as well. The main difference will be the relative rates, which will determine the kinetic products, but also the thermodynamics may vary from metal to metal leading to variations in final product composition, although the differences probably will be marginal.

A prerequisite for high H/D scrambling and metallation activity seems to be the presence of a terminal hydride ligand.\textsuperscript{5,9-14} For \((\text{Cp}^*\text{LnH})_2\) complexes with small metal centers (\(\text{Ln} = \text{Sc}, \text{Lu}, \text{Y}\)) this is realized by dissociation of the dimeric hydride in solution. The similarities in behaviour of 1 and the scandium and lutetium analogues suggest that dissociation is at least kinetically within range. These considerations can also explain why the bridging hydride ligand in 2 does not undergo H/D exchange with benzene-\(d_6\) (18 h, room temperature) since breaking up of the hydride bridge is expected to be more difficult here.

The observations discussed above illustrate how subtle differences in experimental conditions can drastically influence the ultimate products from C-H activation reactions of 1. This is caused by the small differences in kinetics of the various C-H activation routes available. It is evident that 1 and the species derived from it through thermolysis and solvent metallation are very reactive. Their role should be taken into account when reactions of 1 with other substrates are studied.

**Metallation of Substituted Arenes PhX.** We were interested to see whether the presence of a substituent X in the substrate molecule would influence the selectivity of the C-H activation and especially whether activation of group X would compete. Therefore we studied the reaction of 1 with substituted aromatic compounds PhX (\(X = \text{F, Cl, Br}\)). From organolithium chemistry it is known that several substituents on
the aryl ring can function as an ortho-directing group, e. g. -OMe, -NMe₂, and -CH₂NMe₂.¹⁵

The reaction of 1 with PhX (X = F, Cl, Br) in cyclohexane-©₁₂ was instantaneous but a complicated mixture of yet unidentified compounds was formed. Formation of benzyne was indicated from GC/MS analysis after quenching the fluorobenzene reaction mixture with water. In addition to a significant amount of 2-fluorobiphenyl, three other major components were observed which, according to the molecular mass, were provisionally identified as resulting from attack of benzyne on Cp* ligands. Due to the complexity of the reaction and the resulting hydrolysis mixture, a detailed investigation of these systems was not pursued. However, in a preparative reaction of 1 with fluorobenzene, a biphenyl derivative Cp*₂Y(2-C₆H₄-C₆H₄F) (¹H-NMR) was isolated in low yield (6%). This indicates that C-X bonds are activated, possibly after initial ortho-metallation of fluorobenzene. C-C coupling can then take place either by attack of benzyne on a Cp* ligand, or by insertion into the Y-C bond of the initial metallation product Cp*₂Y(2-C₆H₄F). Since the ¹H-NMR spectra of the chloro- and bromobenzene reactions with 1 are very similar to that obtained with fluorobenzene, these benzene derivatives are assumed to react analogously.

**Concluding Remarks**

The yttrium hydride (Cp*₂YH)₂ (1) very easily enters various C-H activation processes and, in addition to non-productive H/H (H/D) exchange, competition between intramolecular activation of a pentamethylcyclopentadienyl ligand and intermolecular attack of aromatic solvents is observed. For most possibilities the activation barriers are comparable, thus leading to mixtures of kinetic products. Also the differences in free energies between the various products appear not to be very pronounced, so that frequently complicated equilibria result and separation of the various components is virtually impossible. In relatively inert solvents (alkanes) the dominant product is the fulvene hydride Cp*₂Y(μ-H)(μ-η¹;η⁵(CH₂C₅Me₄)YCp* (2), formed by extrusion of H₂ through activation of a methyl group on one of the pentamethylcyclopentadienyl ligands of the dimeric hydride.

In deuterated aromatic solvents fast H/D exchange between the hydride ligand and all solvent positions takes place indicating a low activation energy pathway for this, in general terms, non-productive σ-bond metathesis. This high H/D scrambling
activity seems to be related to the facile dissociation of 1 into reactive monomers. The metallation of benzene, toluene and PhX as well as the intramolecular sp³ C-H activation of the methyl group of a Cp* ligand to give the fulvene hydride 2 follows another pathway. With benzene and toluene the kinetic products are the phenyl complex Cp*-2YP (3) and the benzyl Cp*-2YCH2Ph (4), respectively. With PhX substrates with X = F, Cl, Br there were indications for activation of C-X bonds after initial metallation.

**Experimental Section**

**General Considerations.** All experiments were performed under nitrogen using standard Schlenk, glovebox (Braun MB200), and vacuum line techniques. Benzene, toluene, pentane, cyclohexane, benzene-d₆, toluene-d₈ and THF-d₈ were distilled from Na/K alloy and degassed prior to use. 1 was prepared according to a published procedure. Hydrogen (Hoek-Loos, 99.9995 %) was used without further purification. Other reagents, cyclohexane-d₁₂ and methylcyclohexane-d₁₄ were stored over mol sieves (4 Å) and degassed prior to use. NMR spectra were recorded on Gemini 200 (¹H: 200 MHz) and Varian VXR-300 (¹H: 300 Mhz, ¹³C: 75.4 MHz) spectrometers at ambient temperatures. GC/MS analyses (EI) were carried out on a Ribermag R 10-10 C instrument using a CP Sil 5 CB column.

**H/D Scrambling Reactions of (Cp*₂YH)₂ (1) with Benzene and Toluene.** 12 mg (0.017 mmol) of 1 was dissolved in 0.5 mL of benzene-d₆. Within 5 minutes volatiles were removed in vacuum and the residu was dissolved in 0.5 mL of cyclohexane-d₁₂. When the ¹H-NMR spectrum of this solution was compared to that of 1 in cyclohexane-d₁₂ the hydride resonances turned out to be absent. The C₅Me₅ resonance however was observed at the same chemical shift.

H/D scrambling reactions were followed by monitoring solutions of 0.037 mmol of benzene-d₆ or toluene-d₈ and 13.2 mg (0.018 mmol) of 1 in 0.6 mL of cyclohexane-d₁₂ with ¹H-NMR spectroscopy at room temperature. For toluene the volatiles were pumped off after 26 h and from the ¹H-NMR spectrum the ratio of proton incorporation into the different positions of toluene was established. To investigate the H/D scrambling between H₂ and toluene-d₈ by 1, an NMR tube containing 17 mg (0.024 mmol) of 1 in 0.61 mL (5.6 mmol) of toluene-d₈ was sealed under 4 atm (0.3 mmol) of H₂. The increase in the integration of the aryl
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resonances of the solvent was monitored by $^1$H-NMR spectroscopy at regular intervals during 5 d at room temperature. The methyl resonance of toluene was not observed due to overlap with the C$_5$Me$_5$ resonance of 1. Immediately after preparation of the NMR tube the intensity of the aryl-hydrogen signals of toluene corresponded to 0.05 mmol of hydrogen atoms and the hydride signal was absent. After 30 min the intensity of the aryl-hydrogen signals of toluene corresponded to 0.088 mmol hydrogen atoms. After 68 h at room temperature this value had increased to 0.17 mmol.

Metallation of Benzene by 1. 15 mg (0.021 mmol) of 1 was dissolved in 20 mL of benzene and stirred for 4 h under dynamic vacuum at room temperature. Volatiles were removed under vacuum and the $^1$H-NMR spectrum of the remaining oil in cyclohexane-$d_{12}$ indicated that a mixture of 68 % of 3, 11 % of 2 and some unidentified material had been formed. $^1$H-NMR of 3 (300 MHz, cyclohexane-$d_{12}$): δ 7.08 (t, $^3$J$_{HH}$ = 7 Hz, 2H, meta H's), 6.98 (t, $^3$J$_{HH}$ = 7 Hz, $^4$J$_{HH}$ = 1 Hz, 1H, para H), 6.72 (dd, $^3$J$_{HH}$ = 7 Hz, $^3$J$_{HH}$ = 1 Hz, 2H, ortho H's), 1.78 (s, 30 H, C$_5$Me$_5$).

Metallation of Toluene by 1. A stirred solution of 50 mg (0.069 mmol) of 1 in 2.5 mL of toluene was evaporated to dryness in 1/2 h at room temperature. The yellow oil which remained was dissolved in cyclohexane-$d_{12}$ and the $^1$H-NMR spectrum indicated that a mixture of 80 % of 4, 13 % of unreacted 1 and 7 % of 2 had been formed. $^1$H-NMR of 4 (200 MHz, cyclohexane-$d_{12}$): δ 6.92 (t, $^3$J$_{HH}$ = 7.3 Hz, 2H, meta H's), 6.63 ($^3$J$_{HH}$ = 6.8 Hz, 1H, para H), 6.53 (d, $^3$J$_{HH}$ = 7.3 Hz, 2H, ortho H's), 1.91 (d, $^3$J$_{HH}$ = 6.0 Hz, 2H, YCH$_3$), 1.83 (s, 30H, C$_5$Me$_5$).

NMR and GC/MS Analysis of the Reaction of 1 with Fluorobenzene. 8.8 µL (0.093 mmol) of fluorobenzene was added to a suspension of 34 mg (0.047 mmol) of 1 in 0.5 mL of cyclohexane-$d_{12}$. Immediately gas evolution was observed and 1 dissolved completely. $^1$H-NMR spectroscopy indicated that 1 had been converted to a complicated mixture of unidentified products. The NMR tube was opened and 1.5 mL of cyclohexane and 6 µL of water were added. After filtration over a column of MgSO$_4$ the mixture was analyzed by GC/MS. In addition to 2-fluorobiphenyl, three compounds with M$^+$ peaks at m/z = 212 were present.
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Preparative Scale Reaction of 1 with Fluorobenzene. A suspension of 1.09 g (1.51 mmol) of 1 in 40 mL of pentane was cooled to -70 °C and 284 μL (3.03 mmol) of fluorobenzene was added. The reaction mixture was allowed to warm to room temperature in 30 min during which gas evolution was observed and 1 dissolved completely. Volatiles were removed in vacuum and the remaining oil gave a cream-colored precipitate after washing with 2.5 mL of pentane. Crystallisation from 25 mL pentane at -80 °C gave 0.100 g of cream-colored crystals (0.19 mmol, 66%). 1H-NMR (200 MHz, benzene-d6): δ 7.77-7.66 (m, 2H, aryl H), 7.33-7.24 (m, 2H, aryl H), 6.94-6.57 (m, 3H, aryl H), 1.83 (s, 30H, C5Me3), an additional aryl signal overlapped with the solvent signal.

References and Notes

6 In contrast to what was published earlier by our group,7 the 1H-NMR data (300 MHz, methylcyclohexane-d14, 300 K) for 1 are as follows: δ 5.45 (broad s, 2H, Y-H-Y), 2.06 (s, 60 H, C5Me3). Heating the solution to 355 K did lead to a slightly sharpened hydride resonance, the high temperature limit could however not be reached due to severe thermal decomposition of the compound. On cooling, the broad singlet hydride resonance splits into a triplet (1JHY = 37.5 Hz) already at 288 K. Subsequent cooling to 195 K does not lead to further substantial changes of the NMR spectrum. This implicates that below room temperature 1 exists as a dimer with symmetrically bridging hydride ligands.
11 Curtis, M.D.; Bell, L.G.; Butler, W. Organometallics 1985, 4, 701.