Versatile Coordination Behaviour of Cyclopentadienyl-Arene Ligands on Early Transition Metals
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 1 Introduction

1.1. HOMOGENEOUS CATALYSIS

The manufacture of a vast majority of chemical products that we use in our everyday life, ranging from fuels to plastics and drugs, relies on catalytic conversions. The development of efficient catalytic processes has allowed many industrial processes to be operated with increased efficiency, giving improved yields of the desired products under milder conditions than was possible using traditional (stoichiometric) chemistry. For example, oil refineries make use of a range of heterogeneous catalytic processes to convert crude oil to useful products on a massive scale. These processes include catalytic reforming (to increase the octane number), catalytic cracking (to increase the amount of low molecular weight products required for gasoline), and hydrotreatment (to remove nitrogen- and sulfur-containing compounds that cause environmental concerns). Homogeneous catalytic processes, i.e. processes in which all reacting partners including the catalyst are in the same (liquid) phase, are usually associated with smaller-scale processes due to the higher operating costs and difficulties in catalyst recycling. Nevertheless, homogeneous catalysis is indispensable for the production of a wide range of fine chemicals both in industry and in the laboratory.

Homogeneous catalysis offers the possibility to study the structure of the catalyst precursor (typically an organometallic complex), and follow the intimate details of the reaction, for instance by NMR or IR spectroscopy. Organometallic complexes that are used as catalysts are in general discrete molecules that consist of a metal centre that is surrounded by a specific ligand environment. The ancillary ligands play a pivotal role in catalysis by modulating the steric and electronic environment around the metal centre. A detailed understanding of the mechanism of the catalysed reaction, combined with insight in how intermediates and/or transition states in the catalytic cycle are affected by the ligand environment allows homogeneous catalytic systems to be optimised in a rational manner.

As an example, phosphines form a class of ligands that have been studied extensively, and found widespread use as ligands in transition metal complexes and catalysts. Their electronic (σ-donating and π-accepting) properties have been evaluated by looking at the infrared CO stretching frequency in NiL(CO)₅, and this has been extended to other experimental and theoretical analyses. In addition to electronic effects, the steric properties of phosphines have a considerable influence on the structure and reactivity of their complexes. Generally, the rate and selectivity in reactions that are catalysed by transition metal complexes are profoundly influenced by the steric and electronic properties of the ligands, and development of new ligand systems with unusual properties has led to unprecedented catalysis.
Ligands with flexible coordination ability could potentially be useful in homogeneous catalysis. These offer the possibility to stabilise a variety of species along the reaction coordinate in a catalytic cycle, leading to improved selectivity or even new types of reactivity. Different types of flexibility may be envisaged, for instance the (reversible) accessibility of multiple binding modes or oxidation states of the ligand.

For mono(cyclopentadienyl-arene) complexes of titanium, the presence of a potentially coordinating arene moiety results in a drastic switch in catalytic behaviour: catalytic ethylene trimerisation instead of polymerisation takes place. This thesis deals with early transition metal compounds bearing an arene-substituted cyclopentadienyl ligand, and describes our efforts to obtain an understanding of how the flexible coordination behaviour of the cyclopentadienyl-arene ligand influences the structure and reactivity of its complexes.

1.2. OLEFIN OLIGO- AND POLYMERISATION USING EARLY TRANSITION METAL CATALYSTS

1.2.1. Catalytic olefin polymerisation and oligomerisation

The discovery by Ziegler in 1955 that ethylene could be converted to a high-molecular weight polymer under mild conditions using TiCl₄/Et₂AlCl as a catalyst was a breakthrough in polymer chemistry. Subsequently, Natta found that propylene was polymerised in a stereospecific manner using a related catalyst system. These findings have spurred academic and industrial researchers to gain insight in the mechanism of the polymerisation reaction. Soon after the first synthesis of group 4 metallocene complexes of general formula Cp₂MX₂ (Cp = cyclopentadienyl; M = Ti, Zr, Hf; X = halide, alkyl), several groups have investigated the catalytic olefin polymerisation characteristics of these homogeneous systems. Although the activity is relatively low and the polyethylenes obtained with the soluble Cp₂TiCl₂/alkylaluminun catalyst have somewhat different properties than those prepared with the Ziegler-Natta system, it was speculated that the polymerisation mechanism might be the same for the homogeneous and heterogeneous systems. In 1964, Cossee and Arlman proposed a mechanism for the Ziegler-Natta polymerisation that accounted for the experimental observations and, importantly, introduced a mechanistic link between the heterogeneous and homogeneous Ziegler-Natta systems. This now generally accepted mechanism involves chain growth by a linear mechanism in which ethylene coordinates to a vacant site at the transition metal centre, in a position that is cis to the metal-carbon bond. Migratory insertion can then take place to form a new C-C bond (Scheme 1.1).
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Scheme 1.1. Cossee-Arlman mechanism for olefin oligo- and polymerisation by Ziegler-Natta catalysts (linear mechanism).

Kaminsky and Sinn found in the 1980s that the polymerisation activity of metallocene/alkylaluminum catalysts was dramatically increased in the presence of trace amounts of water.20,21 This led to the development of methylaluminoxane (MAO, partially hydrolysed AlMe3) as an activator, which is still in use today. The active species in these mixtures has been a matter of considerable debate,22 but the characterisation of cationic species that are able to initiate ethylene polymerisation has led to a generally accepted view that 14-electron cations of the type \([\text{Cp}_2\text{MR}]^+\) are the catalytically active species.23,24 The development of new ligand systems has afforded a myriad of early transition metal catalysts that allow precise control over the microstructure of the polyolefins produced.25-27

An alternative to heterogeneous Ziegler-Natta catalysts based on group 4 metals was developed at Phillips Petroleum Co. in the 1950s.28 Currently, over one-third of the polyethylene that is produced world-wide is manufactured using this Phillips catalyst (silica-supported chromium; Cr/SiO2).29,30 The success of this system is due to its versatility and simple formulation: the catalyst is able to produce over 50 different types of polyethylenes (varying from high-density (HDPE) to linear low-density (LLDPE) polyethylenes) without the need for an activator. The nature of the active species in the Phillips catalyst is a long-standing matter of debate.30 Although it appears to involve Cr(II) surface species (generated by \textit{in situ} reduction with ethylene, or by pre-treatment with CO), the intimate details of the polymerisation reaction are still unclear. Several additives were found to modify the catalytic performance and lead to unique properties (e.g., single-site behaviour).31-33

The potential advantage of homogeneous systems in delineating certain mechanistic aspects has spurred interest in homogeneous models of the Phillips catalyst and related systems.34,35 This has afforded some very active polymerisation catalysts that appear to proceed by Ziegler-Natta type olefin insertion into the Cr-alkyl bond,36,37 but also here the nature of the active species and its relationship to the heterogeneous systems remains uncertain. Additionally, catalyst systems based on the group 5 metal vanadium have been investigated as olefin polymerisation catalysts.38,39 The activity of vanadium catalysts, however, is generally low due to competing deactivation reactions (reduction to inactive low-valent complexes). Nevertheless, because of the high \(\alpha\)-olefin incorporation in copolymerisation reactions with these catalyst, they provide access to unique elastomers,
such as EPDM rubbers. Also, high molecular weight polymers with narrow molecular weight distributions are accessible with vanadium catalysts.\textsuperscript{40,41}

A departure from conventional olefin conversion by Ziegler-Natta or Phillips type catalysts was found in the late 1970s, when workers at Union Carbide found that certain chromium(III) salts produced significant amounts of 1-hexene in addition to polyethylene.\textsuperscript{42} Briggs subsequently reported the first chromium-based systems that catalysed selective trimerisation of ethylene to 1-hexene.\textsuperscript{43} The involvement of metalacyclic intermediates in the ethylene trimerisation by chromium catalysts was proposed to account for the observed selectivity (Scheme 1.2).\textsuperscript{42,43} Chromium metalacycles were first prepared by Jolly and co-workers, who reported that decomposition of the metalacycloheptane indeed produces 1-hexene.\textsuperscript{44} The increasing demand for linear \(\alpha\)-olefins for the manufacture of copolymers, detergents, lubricants and plasticisers has drawn considerable attention to systems that (selectively) oligomerise ethylene. Since 2003, Chevron Phillips operates a 1-hexene production facility in Qatar that makes use of chromium-catalysed ethylene trimerisation.\textsuperscript{45} In the last couple of years, significant progress has been made in the field of chromium-catalysed selective oligomerisation.\textsuperscript{45,46} Several systems based on Cr(III) with PNP\textsuperscript{47-50} or SNS\textsuperscript{51-54} ligands have been shown to afford extremely active and selective ethylene trimerisation catalysts, and experimental evidence for a mechanism involving metalacyclic intermediates has been obtained.\textsuperscript{55,56} In addition, studies on chain growth in heterogeneous and homogeneous chromium ethylene polymerisation catalysts have revealed that this may also occur by a similar mechanism, affording large ring metalacycles.\textsuperscript{57,58} Recently, ethylene tetramerisation to 1-octene with up to 88\% selectivity has been achieved with related systems, a process that is also likely to be occurring through a cyclic mechanism (Scheme 1.2).\textsuperscript{56,59-62}

\begin{align*}
\text{Cr} \quad \text{Cr}^+ \quad \text{Cr}^{+2} \\
\text{insertion} \quad \text{metalacycle} \quad \text{decomposition} \\
\text{ethylene} \quad \text{1-hexene} \quad \text{higher oligomers or polymer} \\
\end{align*}

\textbf{Scheme 1.2.} Catalytic cycle for chromium-catalysed ethylene trimerisation, tetramerisation and polymerisation (cyclic mechanism).
1-Octene is in increasing demand as a co-monomer in the solution-phase synthesis of LLDPE, and alternative routes to the selective production of 1-octene have been sought. The Dow Chemical Company has recently started the on-purpose production of 1-octene starting from low cost 1,3-butadiene in a three step process. It involves initial telomerisation of 1,3-butadiene with methanol in the presence of a palladium catalyst to give 1-methoxy-2,7-octadiene, which is in a subsequent step hydrogenated to 1-methoxyoctane. Cracking of the 1-methoxyoctane then affords 1-octene and methanol (Scheme 1.3). Although the butadiene starting material is cheap and readily available, the multi-step nature of the process and the use of an expensive palladium catalyst compare unfavourably with the chromium catalysed tri- and tetramerisation discussed above.

\[
\begin{align*}
2 \text{C} &= \text{MeOH} \quad \text{[Pd]} \\
\text{H}_2 &\quad \text{catalytic hydrogenation}
\end{align*}
\]

Scheme 1.3. Production of 1-octene from 1,3-butadiene.

Despite the apparent similarities between the abovementioned group 4 Ziegler-Natta catalysts and group 6 (Cr) Phillips systems in terms of their reactivity towards olefins, until recently no group 4 metal catalysts were known to produce a specific \(\alpha\)-olefin other than 1-butene selectively. Oligomerisation of ethylene can be achieved by Ziegler-Natta catalysts by controlling the relative rates of olefin insertion and chain transfer reactions during linear chain growth. This is usually done by tuning the reaction conditions (temperature, ethylene pressure, metal/co-catalyst ratio, etc.), and affords a distribution (Flory-Schulz or Poisson) of higher olefins. A well-known example of this so-called ‘full range production’ of \(\alpha\)-olefins is the Shell Higher Olefin Process (SHOP) that makes use of a homogeneous nickel catalyst to produce a Flory-Schulz distribution of \(\alpha\)-olefins. Using homogeneous catalysts, modification of the ligand environment allows the rates of chain propagation and termination (and thus product distribution) to be controlled, but this still affords mixtures of higher oligomers from which the desired olefin has to be separated, e.g. by distillation. Cyclic processes related to those in the chromium systems described above are invoked for the selective dimerisation of olefins by tantalum complexes that were developed by Schrock and co-workers. However, insertion of ethylene into the 5-membered tantalacyclic intermediates to larger ring systems does not occur to an appreciable extent, since homologues higher than C4 are not observed.

As mentioned above, the notion that electron-deficient cationic metal-alkyl complexes are the active species in homogeneous Ziegler-Natta olefin polymerisation catalysts has stimulated the development of non-metallocene catalysts. Of special relevance to the work described in this thesis are monocyclopentadienyl (half-sandwich) complexes of the type
CpTiX₃ (X = halide, alkyl). Catalyst systems obtained from CpTiX₃/MAO were the first catalysts to polymerise styrene to the syndiotactic polymer (sPS). Baird and co-workers have studied the formation and polymerisation activity of cationic species derived from Cp*TiMe₃ (Cp* = η⁵-C₅Me₅) and showed that the highly electron-deficient cation [Cp*TiMe₂]⁺ may be stabilised by coordination of arenes. Ethylene polymerisation using Cp*TiMe₃/B(C₆F₅)₃ in several solvents has been reported to afford high molecular weight, linear polymers. Using slightly different polymerisation conditions, Pellecchia and co-workers found that Cp*TiMe₃/B(C₆F₅)₃ in toluene reacts with ethylene to give a polyethylene containing up to 5% butyl branches. The production of what appears to be an ethylene/1-hexene copolymer from ethylene alone suggests that ethylene is in situ trimerised to 1-hexene, which is subsequently incorporated into the polymer chain. Thus, a cyclic ethylene trimerisation mechanism could also be accessible for titanium catalysts.

1.2.2. Switching a titanium catalyst from ethylene polymerisation to trimerisation

Although the selectivity and activity for trimerisation/tetramerisation of ethylene with the chromium systems discussed in the previous section is unprecedented, they present some drawbacks. The toxicity of chromium salts requires special handling precautions, and therefore a selective ethylene oligomerisation system based on a non-toxic transition metal is desirable. In addition, the paramagnetic nature and the possibility of the involvement of multiple spin states for chromium catalysts complicates a detailed understanding of the reaction mechanism, and this has hampered rational improvements to the system. In 2001, Sen and co-workers reported an easy-to-prepare tantalum-based ethylene trimerisation catalyst (albeit with a low activity), that consists of TaCl₅ and an alkylating agent. The in situ reduction of R₂TaCl₃ to the tantalum(III) species “TaCl₃” is proposed to account for the metalacyclic Ta(III)/Ta(V) mechanism, which is similar in nature to that for the chromium systems described above.

The observation that the catalyst system Cp*TiMe₃/B(C₆F₅)₃ in toluene is partly transformed into an ethylene trimerisation catalyst (as discussed above), suggested that a related metalacyclic mechanism based on the Ti(II)/Ti(IV) redox couple may be operative. In 2001 our group reported that monocyclopentadienyl titanium catalysts can be switched from ethylene polymerisation to selective ethylene trimerisation by introduction of a pendant arene moiety on the cyclopentadienyl ring. It appeared that the coordination of the pendant arene to the metal centre (termed ansa-Cp-arene coordination, in analogy to ansa-metallocenes) diverts the catalyst to the Ti(II)/Ti(IV) redox cycle that is required for selective trimerisation. From subsequent experimental and computational studies, the mechanism as shown in Scheme 1.4 has emerged. The first steps to form the catalytically active species include (i) formation of a cationic species that is stabilised by intramolecular arene coordination (A), (ii) ethylene insertion to give a methyl n-alkyl species (B), and (iii) reduction of the metal centre by β-hydrogen transfer to give a titanium(II) species (C). This enters the catalytic cycle by capture of two ethylene
molecules (D), which subsequently are oxidatively coupled to give the metalacyclopentane species (E). The insertion of another molecule of ethylene affords a much more flexible 7-membered metalacycle (F), which allows rapid β-hydrogen transfer to give the titanium(II) 1-hexene adduct (G). Displacement of the coordinated 1-hexene by two molecules of ethylene closes the cycle. The selectivity for 1-hexene in this system arises from the fact that ethylene insertion into E is much faster than its decomposition (which would produce 1-butene). Once F is formed, β-hydrogen transfer to form 1-hexene is kinetically more facile than insertion of another molecule of ethylene (which would lead to formation of 1-octene, and eventually also higher olefins).

Scheme 1.4. Catalytic cycle for ethylene trimerisation by cationic ansa-Cp-arene complexes of titanium.

The decomposition of metalacyclic compounds can occur through various pathways, a review of which has recently appeared. Although a two-step mechanism (β- or γ-H elimination followed by reductive elimination) has usually been invoked to account for decomposition reactions of L₉MR₂ species (R = n-alkyl; R₂ = metalacycle), alternative pathways could be operative, including a concerted hydrogen-transfer. A concerted β-
hydrogen transfer pathway is indeed calculated to be favoured in the titanium complexes described here, and no discrete Ti-H species appear to be involved.\cite{89,91}

In the titanium-catalysed ethylene trimerisation cycle (Scheme 1.42), the role of the intramolecularly coordinated arene moiety is twofold: it is able to provide steric and electronic stabilisation when required, but can (partially) dissociate to allow insertion of ethylene into the metalacycle. Thus, it appears that coordination of the pendant arene moiety in these catalysts allows reversible switching between Ti(II) and Ti(IV) oxidation states. In combination with the hemilabile character of the ansa-Cp-arene coordination it enables this kind of catalysis, hitherto unknown for titanium.

1.3. HEMILABILE LIGANDS

Hemilabile ligands possess a combination of tightly bound and substitutionally labile groups, and are of interest as they can (transiently) stabilise intermediate reactive species, while still allowing subsequent reactivity.\cite{99,100} Pioneering work on such ligands was performed in 1974 by Knebel and Angelici, who developed phosphorus-nitrogen bidentate ligands. Kinetic and equilibrium studies showed that the reaction of $\text{M(CO)}_4(P\text{-N})$ ($\text{M} = \text{Cr, Mo, W}$; $P\text{-N} = \text{Ph}_2P(\text{CH}_2)_n\text{NR}_2$; $n = 2, 3$; $R = \text{H, Me, Et}$) with CO is dependent on the rate of N-donor dissociation (Scheme 1.5).\cite{101,102} Subsequently, Rauchfuss and co-workers reported metal complexes with chelating amine- and ether-substituted phosphines in which the more weakly coordinating O-donor is displaced by CO.\cite{103} It was, however, not until 1979 that the term hemilabile was coined by Jeffrey and Rauchfuss to describe the dynamic behaviour of o-(diphenylphosphino)anisole as a ligand on ruthenium(II).\cite{104}

\begin{center}
\textbf{Scheme 1.5.} Hemilabile coordination of a chelating phosphine-amine ligand.
\end{center}

Most hemilabile ligands are multidentates that feature one pendant Lewis base moiety that is less strongly binding than the others, and that can readily and reversibly dissociate. Phosphine ligands that contain additional labile donors, such as O- or N-based functionalities, have received most attention.\cite{105,106} Another prominent class of hemilabile ligands is formed by donor-functionalised cyclopentadienyl ligands, bearing pendant P, As, S\cite{111} or O groups\cite{112} that interact weakly with the metal centre; transition metal complexes of these are known across the periodic table. Ligands that combine an amido group with various neutral donor functions (e.g., amidoamine, amidopyridine or amidophosphine) have
been shown to support unique reactivity of their early transition metal complexes by virtue of the hemilabile character.\textsuperscript{113} Arene-substituted phosphine ligands, in which the pendant arene functions as weakly coordinating group are also known,\textsuperscript{114-116} and studies on arene exchange (hemilability) in such compounds have been reported.\textsuperscript{117-119} The combination of a monoanionic anchoring group with a pendant arene as labile moiety is less common,\textsuperscript{120} but aryloxide ligands that contain aromatic substituents on the 2,6-positions of the central phenoxide ring have been shown to coordinate to low-valent group 6 metals in a chelating (O,\ce{\eta^6}-arene) mode.\textsuperscript{121-124} A comprehensive review on the synthesis and properties of transition metal complexes of tethered arenes has recently appeared.\textsuperscript{125} However, virtually all such systems reported to date involve late transition metal centres that have d-electrons available for \(\pi\)-backdonation to the arene, and related early transition metal complexes (which favour high oxidation states) are scarce.\textsuperscript{126}

Although many complexes with potentially hemilabile ligands have been reported, studies that aim at a detailed understanding of how these ligands modulate the catalytic activity of their transition metal complexes remain scarce. The evaluation of kinetic effects that arise from hemilabile coordination has recently attracted some attention as a means to obtain a better understanding of hemilabile behaviour.\textsuperscript{127} Although the kinetic information gleaned from stoichiometric reactions provides useful information, it is less clear how this relates to multi-step catalytic processes. Indeed, the various intermediates and transition states in a catalytic cycle and their different affinities for the labile moiety of a hemilabile ligand are not easily studied experimentally.

As stated above, the ability of hemilabile ligands to stabilise reactive intermediates has the potential advantage of increased catalyst longevity by preventing decomposition reactions. For example, Buchwald and co-workers reported that palladium-catalysed amination of aryl chlorides, bromides and triflates works well when ligands of the type (\(\o\)-biphenyl)PR\(_2\) (R = 'Bu, Cy) are used, and speculated on the existence of a stabilising metal-arene interaction.\textsuperscript{128} Palladium complexes with similar ligands were shown to be very efficient catalysts for Suzuki cross-coupling reaction, and the occurrence of metal-arene interactions in these systems has been corroborated by crystallographic and computational studies.\textsuperscript{129-132} Related metal-arene interactions were also found in complexes with carbene ligands.\textsuperscript{133-135} In addition, similar catalytic reactions using palladium in combination with a hemilabile benzamide-derived P,O ligand proceed with remarkable productivity, presumably due to an increased catalyst lifetime.\textsuperscript{136,137} Weller and co-workers recently described a system that efficiently catalyses the intermolecular hydroacylation of alkenes using \(\beta\)-S substituted aldehydes.\textsuperscript{109} For unfunctionalised alkenes, decarbonylation of the intermediate metal-acyl species is a competitive decomposition pathway. By using a hemilabile P-O-P ligand, decarbonylation is sufficiently retarded so that productive catalysis occurs (Scheme 1.6).
Scheme 1.6. Rhodium-catalysed hydroacylation using a hemilabile P-O-P ligand that prevents decarbonylation.

1.4. REDOX-ACTIVE LIGANDS

The titanium catalysed ethylene trimerisation described above requires the operation of a redox mechanism that shuttles the catalyst between Ti(II) and Ti(IV) oxidation states. Reversible 2-electron redox processes, in particular reductive elimination reactions, are rare for the early transition metals (and certainly in catalytic processes) since the high-valent state is usually thermodynamically much more stable. Therefore, classical C-C bond forming processes mediated by group 4 metals (e.g., Ziegler-Natta type polymerisation) occur without changes of the oxidation state at the metal centre. In contrast, many bond forming reactions catalysed by late transition metals rely on a reductive elimination step to complete the catalytic cycle. 138-141 As an example, palladium-catalysed coupling reactions of organostannanes with organic electrophiles (the Stille reaction) form an important method for constructing C-C bonds. The three key steps in this transformation are (i) oxidative addition, (ii) transmetallation, and (iii) reductive elimination (Scheme 1.7). 139
Catalytic conversions by non-noble metals that rely on 2-electron redox processes remain scarce to date. The high cost of noble metals and the environmental concerns caused by many other late transition metals (e.g., cobalt, nickel, copper) has led to increased interest in alternative transition metals that are able to maintain 2-electron redox cycles. Particular emphasis has been placed on iron complexes as affordable and benign systems for performing a variety of catalytic conversions, including ones requiring oxidative addition / reductive elimination sequences. For example, ‘low-valent’ complexes are implicated in iron-catalysed cross-coupling, hydrogenation, cycloisomerisation of enynes, and cycloadditions.

For the [2+2] cycloaddition of $\alpha,\omega$-dienes mediated by bis(imino)pyridine iron complexes, the low-valent character of intermediates in the catalytic cycle is masked by the redox-active ligand, thereby preventing the formation of Fe(0) while still allowing oxidative cyclisation (Scheme 1.8). This example shows the potential for redox-active
(or non-innocent) ligands in catalysis. Although the main focus of research into non-innocent has mostly been on the (electronic) structure of their metal complexes, this type of ligands may also be useful in catalysis by stabilising metal centres in unusual (formal) oxidation states.

Some examples of reductive eliminations from early transition metal centres are known. For the group 4 metal zirconium, R-H elimination from alkyl hydrido and aryl hydrido zirconocenes occurs by ‘cyclometalation assisted’ and direct reductive elimination pathways, respectively. Recently, ligands that are able to function as an electron reservoir have received considerable attention as a means to support unusual redox chemistry for early transition metals. By using this strategy, Heyduk and co-workers were able to effect the direct reductive elimination of biphenyl from a group 4 metal complex bearing redox-active amidophenolate ligands (Scheme 1.9). A zirconium complex with a related ligand catalyses the disproportionation of 1,2-diphenylhydrazine to azobenzene and aniline. Also here, the required 2-electron redox changes at the catalytically active centre are facilitated by the ligand.

\[ \text{Scheme 1.9. Reductive elimination of biphenyl from a zirconium complex.} \]

1.5. OBJECTIVE

The apparent ability of the Cp-arene ligand to sustain the 2-electron redox switching necessary for titanium catalysed ethylene trimerisation has prompted us to investigate experimentally the coordination behaviour of the pendant arene moiety in systems that model the various intermediates in the catalytic cycle. We thus set out to prepare ansa-Cp-arene coordinated titanium cations with the metal centre both in the +4 and +2 oxidation state, and characterise the metal-arene interaction in these systems by crystallographic and spectroscopic means. Specifically, we were interested in the influence of ligand modifications on the ansa-Cp-arene coordination, and how this relates to ethylene trimerisation catalysis by these complexes.

The versatile coordination behaviour of Cp-arene ligands supports unique reactivity for cationic titanium complexes, and this could potentially be extended to other transition metals as well. In particular, the use of an intramolecularly coordinating arene group may present a strategy to add stability to low and intermediate valencies of early transition metals without the use of classic strong \( \pi \)-acceptor ligands. This possibility is evaluated for complexes of the group 5 metal tantalum.
1.6. OVERVIEW OF THE THESIS

The chemistry described in this thesis is focused on obtaining a better understanding of the versatile coordination behaviour of cyclopentadienyl-arene ligands and the way it allows stabilisation of (cationic) early transition metal complexes. In Chapter 2, the synthesis and characterisation of a series of titanium(IV) complexes with Cp-arene ligands will be presented. X-ray crystallographic studies on cationic derivatives thereof provide structural evidence that intramolecular coordination of the neutral arene moieties occurs (ansa-Cp-arene coordination) to alleviate steric and electronic unsaturation at the metal centre. This coordination mode is markedly affected by changes in the ligand structure, most prominently by the length of the bridge connecting the cyclopentadienyl and arene parts.

Chapter 3 aims to provide quantitative information on the strength of the interaction between the pendant arene moiety and the cationic metal centre in complexes of titanium(IV), and delineate how this interaction strength may be modulated by changes in the ligand architecture. These data are correlated to the activity of these complexes in ethylene trimerisation catalysis. It shows that stronger arene coordination results in diminished catalytic activity, but this may be offset by an increase in stability. The experimental results are substantiated by a computational study.

In Chapter 4, the synthesis of ansa-Cp-arene titanium(II) dicarbonyl cations is described. These serve as model systems for the low-valent intermediates in the ethylene trimerisation cycle. The X-ray crystal structure of such a titanium(II) cation shows that the pendant arene moiety stabilises this unusual species by virtue of its ability to function as an electron reservoir. The intramolecular arene coordination thus leads to considerable titanium(IV)/reduced arene character. The influence of ligand modifications is evaluated by infrared spectroscopy and DFT calculations.

In order to extend the concept of stabilising reactive species by intramolecular arene coordination with ansa-Cp-arene ligands to metals other than titanium, Chapter 5 deals with the preparation of tantalum(V) complexes bearing this ligand. Neutral or ionic complexes of tantalum(V) are reluctant to coordinate the Cp-arene ligand in a manner analogous to the titanium complexes described before, in part due to the increased coordination number for the group 5 metal tantalum. However, ortho-metalation of the pendant arene takes place by a series of β-hydrogen transfer reactions when n-alkyl ligands (ethyl, propyl) are attached to the metal centre. Significantly, the metalation of the arene ring is readily reversible.

In Chapter 6, we describe protonation reactions of neutral tantalum olefin adducts that have an ortho-metalated η^5-cyclopentadienyl-η^1-aryl ligand. This reaction results in the formation of cationic tantalum(III) complexes that are stabilised by ansa-η^5-cyclopentadienyl-η^6-arene coordination, similar to that observed for titanium. Also here, the low-valent character of these tantalum(III) species is moderated by (partial) reduction of the arene moiety.
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Chapter 7 addresses the reactivity of the *ansa*-Cp-arene tantalum(III) compounds. Conversion of the singly charged species to both neutral and dicationic complexes is described, both of which retain the *ansa*-coordination mode of the ligand. Although these compounds exhibit spectroscopic and structural characteristics that indicate considerable Ta(V) character due to π-backdonation into the arene, oxidative addition with liberation of the arene is possible, indicating that reactivity typical for Ta(III) takes place.
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