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Review

Properties of electron deficient 1,3-diene complexes of the group 4A metals

B. Hessen and J.H. Teuben *
Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

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Introduction

During the past decade the chemistry of early transition metal (groups 4A and 5A) complexes of conjugated dienes has seen important developments. Not only was the first mononuclear *s-trans* diene complex isolated and structurally characterized, namely Cp_2Zr(*s-trans*-1,3-butadiene) [1], but it was also shown that early transition metal *s-cis* diene complexes differed considerably in the bonding mode of the diene ligand (and concomitantly in reactivity) from their late transition metal congeners. In many early transition metal *s-cis* diene complexes the bonding of the diene ligand has pronounced σ^2,π-metallacyclopentene (**1**) character, in contrast to the η^4-diene structure (**2**) found for the late transition metals. **1** corresponds to a formal

(1)

(2)

oxidative addition of the diene to the metal center, which gives the diene terminal carbon atoms nucleophilic character. This makes these compounds very versatile as they can behave either as metallacyclopentene or diene complexes, depending on the nature of the substrate.

Extensive studies have been made of the structures and reactivities of the 18 electron complexes Cp_2M(diene) (M = Zr, Hf) by the groups headed by Erker and Nakamura [2], and have revealed many of the special features of the group 4A-diene complexes. Their reactions include for instance highly selective couplings between the diene ligand and various unsaturated organic substrates, e.g. ketones, aldehydes, esters, nitriles, and acetylenes. Although several electronically unsaturated early transition metal diene complexes are known, such as the 16 electron species $(diene)_2M(dmpe)$ (M = Ti, Zr, Hf) [3], $(C_8H_8)M(diene)$ (M = Ti, Zr, Hf) [4], $CpV(diene)(PR_3)$ [5] and $(C_5Me_5)Ta(diene)Cl_2$ [6], very little has been reported about their reactivity. Studies on the unsaturated 14 electron complexes $Cp^\star M$(diene)X (M = Ti [7], Zr, Hf [7,8]; X = Cl, alkyl, aryl; $Cp^\star = \eta^5\text{-}C_5Me_5$) indicate that electronic and steric unsaturation can cause significant changes in the reactivity and reaction selectivity of the diene ligand.

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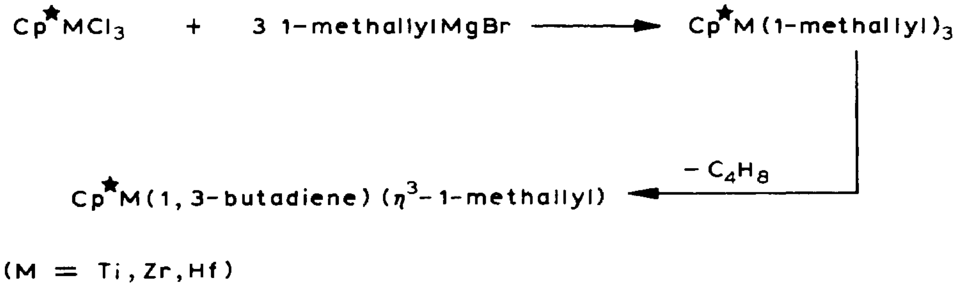
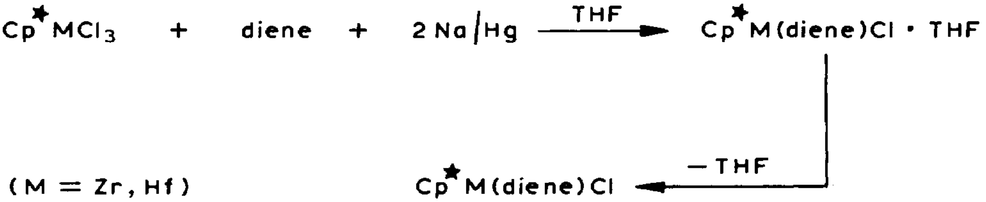
Synthesis and derivatization

The first observation of group 4A-diene complexes involved the discovery that reaction of $CpTiCl_3$ with 3 mol of 1-methallylMgBr gave the 16 electron complex CpTi(1,3-butadiene)(η^3-1-methallyl) by proton abstraction from one of the 1-methallyl ligands in the intermediate $CpTi(1\text{-methallyl})_3$ [9]. This procedure proved applicable to all the group 4A metals [10]:



A similar compound, CpZr(1,3-butadiene)(η^3-allyl), was prepared by reaction of $CpZr(allyl)Cl_2$ (formed in situ) with (butadiene)Mg · 2THF [11]. For the preparation of 14 electron complexes Cp*M(diene)Cl of Zr and Hf, Cp^*MCl_3 was reduced with Na/Hg in the presence of a substituted diene (e.g. isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene):



The reductive procedure is not successful for M = Ti, but Cp*Ti(diene)Cl can be prepared by reaction of Cp^*TiCl_3 with (diene)Mg · 2THF [7,12]. Additionally, the butadiene ligand present in Cp*M(1,3-butadiene)(1-methallyl) can be used to prepare Cp*M(1,3-butadiene)Cl (and the 14 electron complexes Cp*M(η^3-1-methallyl)-Cl_2) by comproportionation with Cp^*MCl_3 [7].

The compounds Cp*M(diene)Cl can readily be derivatized by substitution of the remaining chloride ligand to form Cp*M(diene)R with R = alkyl, aryl, η^3-allyl, η^2-BH_4 [7,8]. IR and NMR spectroscopic data indicate the presence of "agostic" [13] CH · · · M interactions in the 14 electron alkyl complexes, emphasizing the electron-deficient nature of these compounds [7]. Cp*M(diene)Cl can form 16 electron adducts Cp*M(diene)Cl · L with a variety of Lewis bases, such as trialkylphosphines, trialkylphosphites, pyridines, ketones, nitriles and THF [7]. For M = Ti, the adducts have so far only been observed for bases consisting of slender molecules, such as organic nitriles [14], owing to the fact that the coordination sphere of Ti is considerably smaller than that of Zr and Hf [15]. The formation of 16 electron adducts plays an important role in the reactions of the unsaturated diene complexes (vide infra).

Structure and bonding of the diene fragment

The bonding of the diene ligand in the electron deficient complexes Cp*M(diene)Cl and their Lewis base adducts has been studied by NMR spectroscopy and X-ray diffraction. The compounds Cp*M(diene)Cl (diene = 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene; M = Ti, Zr, Hf) contain *s-cis* diene ligands in "supine" conformation (i.e. with the diene methylene carbon atoms pointing towards the Cp* group). An indication of the amount of σ^2,π-metallacyclopentene character in the bonding of the diene fragment is given by the ^1J(CH) and ^2J(HH) NMR coupling constants of the diene methylene groups, since an increase in the metallacyclopentene contribution corresponds to a specific degree of rehybridization of these carbon atoms from sp^2 towards sp^3. In the electron deficient diene complexes ^1J(CH) varies from 138–142 Hz for the Zr and Hf complexes, to 147 Hz for Ti [7]. The values of ^2J(HH) for Cp*M(2,3-dimethyl-1,3-butadiene)Cl falls from 11.0 Hz for M = Hf to 8.7 Hz for M = Ti, indicating a decrease in the metallacyclopentene character of the complex in the sequence Hf > Zr > Ti [7]. This trend was also observed for the series (C_8H_8)M(1,3-butadiene) [16] and in comparative X-ray studies of analogous Cp_2Zr- and Cp_2Hf(diene) compounds [2b,17].

X-ray structural determinations of Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl (Fig. 1) and its pyridine adduct (Fig. 2) [7] show that both compounds contain an *s-cis* "supine" coordinated diene ligand. The terminal diene carbon atoms are bound considerably closer to the metal than the central diene carbon atoms, indicating σ^2,π-metallacyclopentene character. The distance difference $\Delta = (M{-}C_c) - (M{-}C_t)$

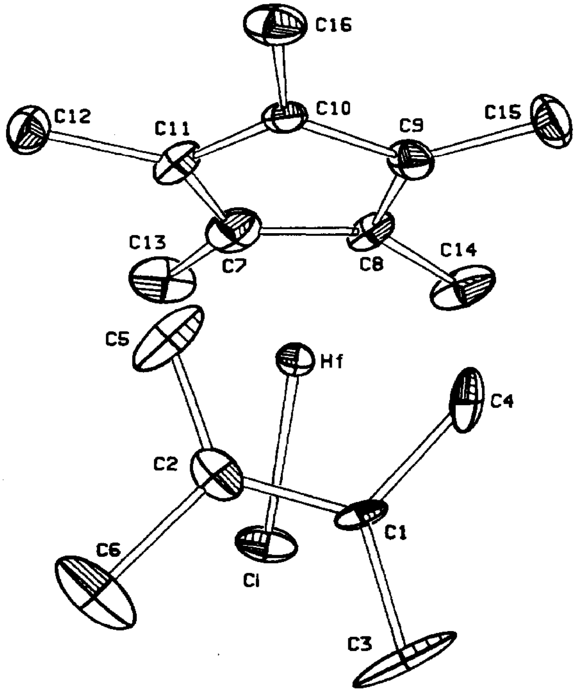


Fig. 1. Crystal structure of Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl [7].

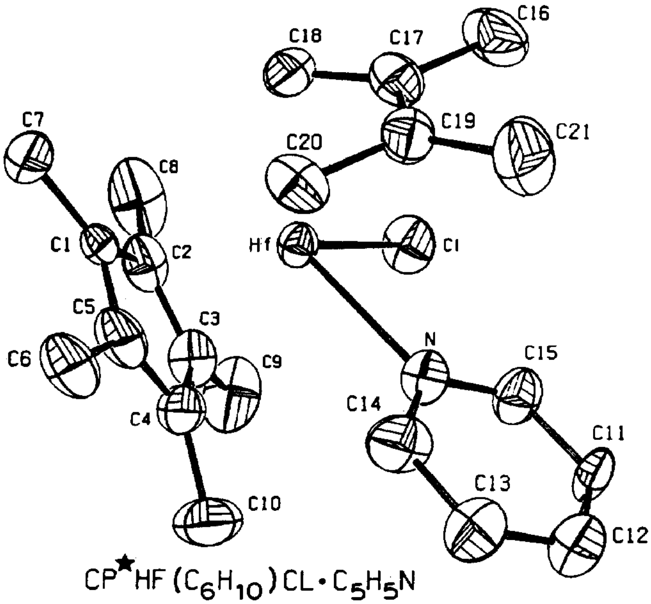


Fig. 2. Crystal structure of Cp* Hf(2,3-dimethyl-1,3-butadiene)Cl · pyridine [7].

is larger for the 14 electron complex (0.243 Å) than for the 16 electron complex (0.204 Å), indicating a decrease in metallacyclopentene character on complexation with the Lewis base. This is also reflected in the ^1H NMR data and in the results of EHMO calculations performed on the $CpZr(C_4H_6)Cl(\cdot L)$ model system [7]. Overall, the metallacyclopentene character is less pronounced than in the saturated Cp_2M(diene) ($M = Zr$, Hf) complexes, with values Δ of up to 0.465 Å for Cp_2Hf(1,2-dimethylenecyclohexane) [17]. It is noteworthy that the diene fragment in Cp* Ti(diene)Cl prefers a "prone" coordination geometry (i.e. with the diene methylene carbon atoms pointing towards the Cl ligand) when no substituents are present on the 2- and 3-positions of the diene. This was revealed by an X-ray structural study of Cp* Ti(1,3-butadiene)Cl [12], and suggests that there is only a small energy difference between the two coordination geometries.

Whereas the inversion of the double bond–single bond sequence within the diene ligand (compared to the free diene) observed in Cp* Hf(2,3-dimethyl-1,3-butadiene)Cl · py is normal for metallacyclopentene-like early transition metal diene complexes, the diene C–C distances in the 14 electron complex suggest that there is a significant participation of the asymmetric η^3,σ-resonance structure (3), and this

(3)

may be due to the electron deficiency of the metal center. So far we have no evidence that this asymmetry plays any significant role in the reactivity of the compound. In all the compounds studied the diene fragments did not show any fluxional behaviour, such as *cis–trans* interconversion, in keeping with the rigidity observed for the diene fragment in $Cp^*Ta(diene)Cl_2$ [6].

Reactivity towards ketones and nitriles

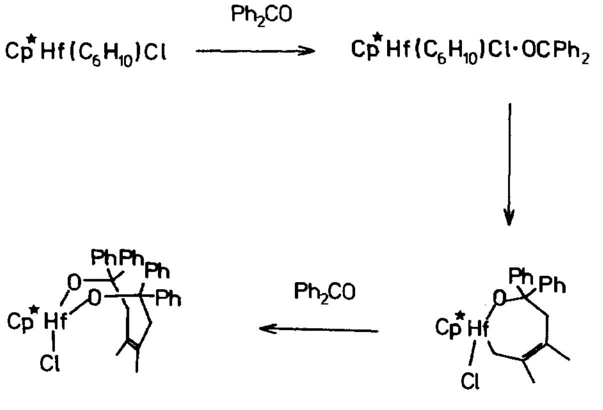
Cp*M(2,3-dimethyl-1,3-butadiene)Cl (M = Ti, Hf) readily react with benzophenone to form CC-coupled products through sequential insertion of ketone molecules into the M–C bonds (Scheme 1) [18]. The possibility of forming doubly inserted products despite the 2,3-disubstitution of the diene, and the retention of the *cis*-configuration of the diene ligand in the final product, represent differences in behaviour with respect to that of the Cp$_2$Zr(diene) system. The steric saturation in these complexes allows the second coupling step to take place only after an intramolecular rearrangement (which is unfavourable for substituted dienes) that involves inversion of the configuration around the double bond [19]. At the same time the unsaturation in Cp*M(diene)Cl reduces to zero the high regioselectivity observed in the first ketone insertion for Cp$_2$Zr(2-methyl-1,3-butadiene) [20]; Cp*Hf(2-methyl-1,3-butadiene)Cl reacts with one mole of benzophenone to form nearly equimolar amounts of the two regioisomers, the electronic preference for the substituted-side [20c] and the steric preference for the unsubstituted-side of the diene effectively cancelling each other [14].

Organic nitriles also form coupling products with Cp*M(diene)Cl through intermediate adduct formation, but whereas for M = Ti the single insertion product is formed, Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl · RCN undergoes disproportionation into Cp*Hf(diene)Cl and the doubly inserted product Cp*Hf(Cl)N=C(R)CH$_2$C(Me)=C(Me)CH$_2$C(R)=N [14].

The ambivalent nature of the diene ligand in early transition metal *s-cis* diene complexes is demonstrated in the reaction of Cp*Hf(diene)Cl with 1,2-diketones: in this case no insertion into the M–diene bond is observed, but free diene is eliminated to form enediolate complexes Cp*Hf(OC(R)=C(R)O)Cl (R = Ph, *p*-C$_6$H$_4$Me) [14]. Diene elimination is also observed in reactions of Cp*M(diene)Cl with other "hard" reagents such as O$_2$ [7], dibenzoylperoxide [14], and azobenzene [21], yielding $\{$Cp*Hf(O)Cl$\}_x$, Cp*Hf(O$_2$CPh)$_2$Cl, and the dimeric imido complex [Cp*Hf(μ-NPh)Cl]$_2$, respectively, as products.

Reactions with acetylenes and olefins

Cp*M(2,3-dimethyl-1,3-butadiene)Cl (M = Ti, Hf) reacts with disubstituted acetylenes RC≡CR (R = Ph, Me) by release of the coordinated diene and oxidative



Scheme 1

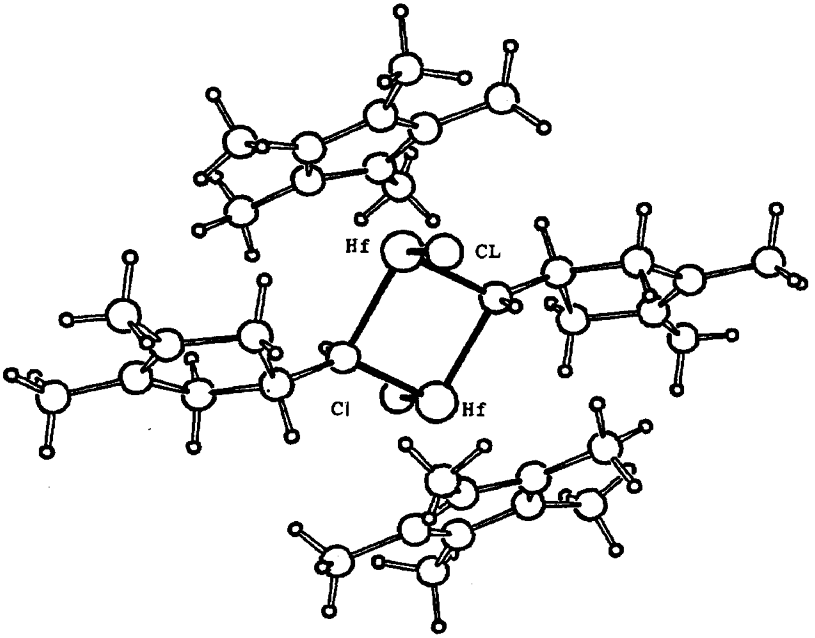
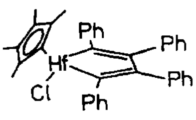


Fig. 3. Crystal structure of $\{Cp^{\star}HfCl[\mu\text{-}CH\overline{CHCH_2C(Me){=}C(Me)C}H_2]\}_2$ [24].

coupling of two acetylene molecules to form metallacyclopentadiene complexes. Both monomeric ($Cp^{\star}Hf(\sigma^2\text{-}C_4Ph_4)Cl$ (4)) and dimeric ($Cp^{\star}Ti(Cl)(\sigma^2,\eta^4\text{-}C_4Me_4)\text{-}Ti(Cl)Cp^{\star}$ (5)) compounds of this type have been isolated [22]. Release of



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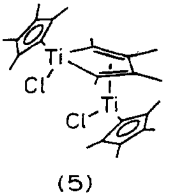
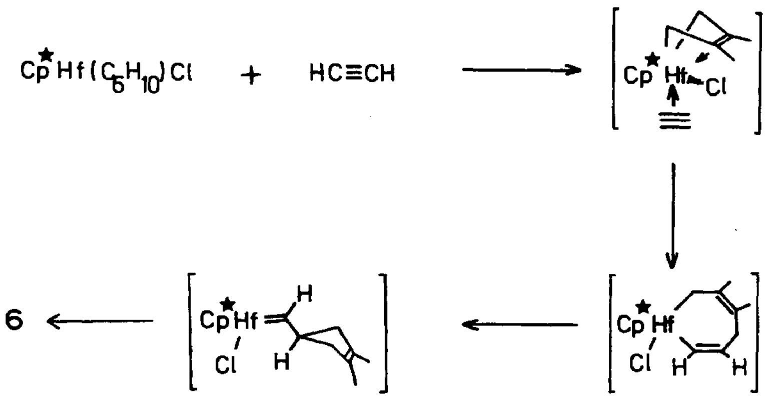


(5)

the diene and oxidative coupling of acetylenes is also seen for Cp_2Zr(diene) when diarylacetylenes and weakly bound dienes (such as 2,4-hexadiene) are used [1a,19]. No coupling reactions between the diene ligand and substituted acetylenes (such as in the reaction of Cp_2Zr(2-methyl-1,3-butadiene) with 2-butyne [23]) have been observed.

With unsubstituted acetylene, $Cp^{\star}Hf$(2,3-dimethyl-1,3-butadiene)Cl reacts to form an unusual asymmetric 1,3-dihafnacyclobutane complex (6, Fig. 3) with one carbon atom of the acetylene bound to two Hf atoms and the other to the two methylene carbon atoms of the original diene ligand [24]. The most likely reaction sequence (Scheme 2) involves linear insertion of the acetylene into the Hf–diene bond, followed by a ring contraction to yield a carbene intermediate. In contrast, the analogous Ti-diene complex reacts with acetylene by quantitative elimination of the diene. Apparently the metallacyclopentene character in the Ti compound is sufficiently lower than that in the Hf compound to lead to a different reaction path.

Erker et al. showed that Cp_2M(butadiene) ($M = Zr$, Hf) can react with ethylene only via the *s-trans* conformation [25]. Thus it is not surprising that $Cp^{\star}M$(diene)Cl, with exclusively *s-cis* diene ligands, does not react with ethylene (up to 40 atm).



Scheme 2

However, the methyl derivative Cp*Hf(2,3-dimethyl-1,3-butadiene)Me polymerizes ethylene (25 atm, 0 °C) without a cocatalyst [26]. Cp*Hf(diene)R is formally isoelectronic with the 14 electron compounds $\mathrm{Cp}_2^{\star}$ScR [27] and $[\mathrm{Cp_2MR}]^+$ (M = Ti, Zr) [28], currently of interest because of their potential as polymerization catalysts. Cp*Hf(diene)Me is not active towards propylene or styrene, but does promote the polymerization of 2-vinylpyridine (2VP) to highly isotactic ($\geq$ 98% it) high molecular weight poly-2VP [29]. Coordination of the pyridine to Hf probably plays an important role in determining the tacticity of the polymer. A labile adduct, Cp*Hf(2,3-dimethyl-1,3-butadiene)Me · 2VP, has been isolated [30]. With 2-methylpyridine, α-metallation takes place to give the stable Cp*Hf(2,3-dimethyl-1,3-butadiene)(η^2-NC$_5$H$_3$Me) [30], and this represents a possible deactivation mechanism for the catalytic process. Cp*Hf(diene)Cl is a olefin hydrogenation catalyst precursor, reacting with hydrogen to form a tetrameric hydride, $[\mathrm{Cp^{\star}Hf(H)_2Cl}]_4$

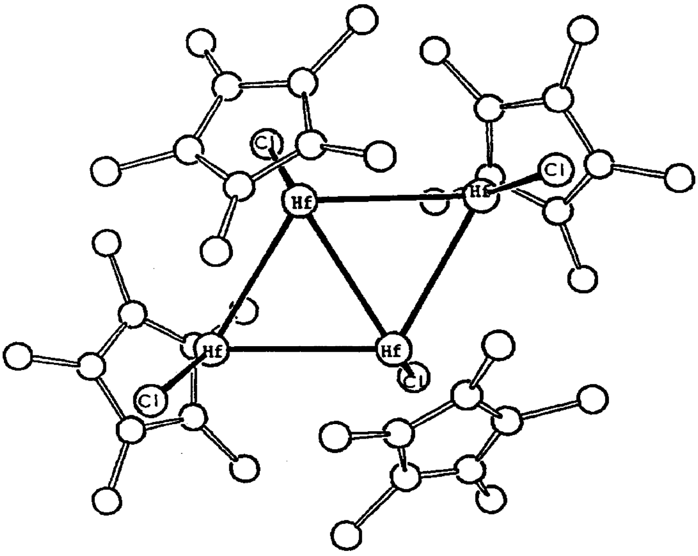
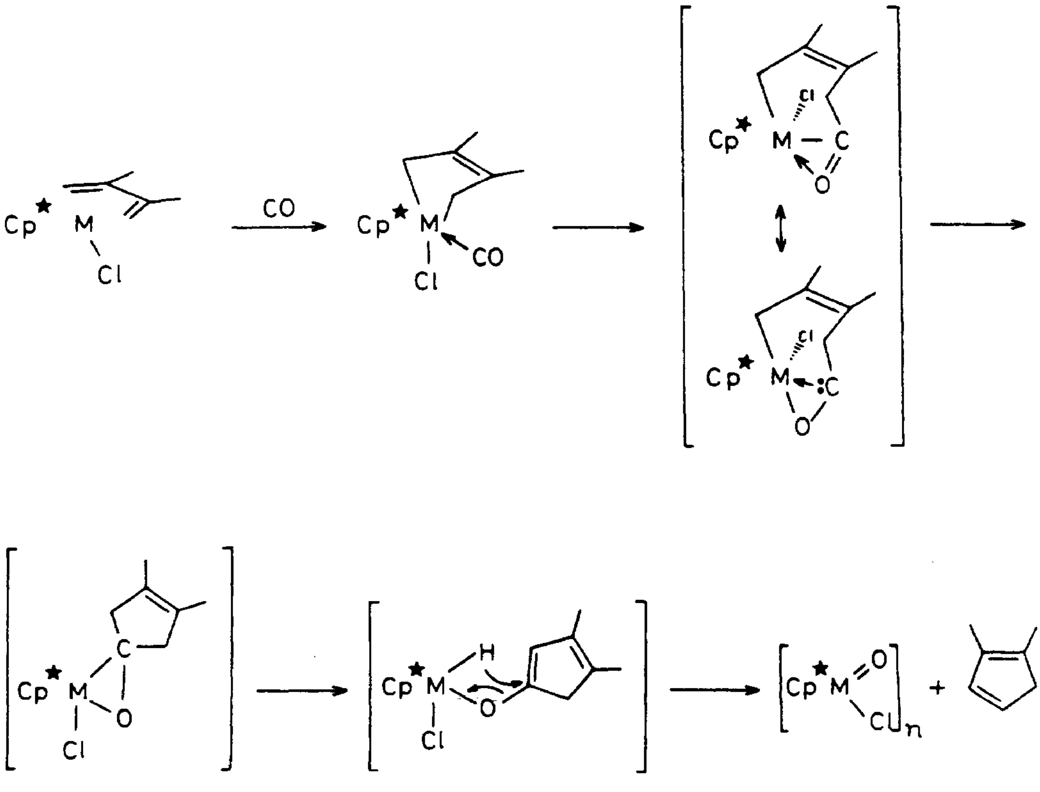


Fig. 4. Crystal structure of $[\mathrm{Cp^{\star}Hf(H)_2Cl}]_4$·benzene [31].

(Fig. 4) [31], which catalyses the hydrogenation of both terminal and internal olefins [32].

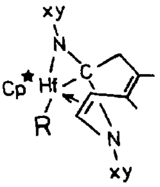
Reactions with CO and isonitrile

Metallacyclic compounds of the group 4A metals are known to react with carbon monoxide by insertion of CO into the M–C bonds, the final product depending on the oxophilic nature of the metal: 1,4-tetramethylenebis(cyclopentadienyl)Ti forms $Cp_2Ti(CO)_2$ by release of cyclopentanone [33], while with 1,4-tetramethylenebis(pentamethylcyclopentadienyl)Zr a Zr–O bond persists in the final enolate hydride product [34]. Cp_2Zr(*s-cis*-diene) complexes react similarly with CO, and after acidolysis cyclopentenones can be isolated in 10–70% yield, depending on the nature of the diene [35]. The electron-deficient nature of the 14 electron complexes $Cp^{\star}M(diene)Cl$ (M = Zr, Hf) causes the CO reaction to proceed beyond this stage, effecting complete fission of the carbon monoxide CO bond: after initial adduct formation, substituted cyclopentadienes are formed, together with oligomeric $[Cp^{\star}M(O)Cl]_x$ [8] (Scheme 3). The location of the CO carbon atom was confirmed by ^{13}C-labelling experiments. The less electropositive Ti cannot perform this CO bond cleavage. Instead the reaction of CO with $Cp^{\star}Ti$(2,3-dimethyl-1,3-butadiene)Cl stops after formation of the η^2-cyclopentenone product, which dimerizes to the titanaoxirane $[Cp^{\star}Ti(\mu\text{-}O\overline{CCH_2C(Me)=C(Me)C}H_2)Cl]_2$ [36].



Scheme 3

Reaction of the alkyl derivative Cp*Hf(2,3-dimethyl-1,3-butadiene)Me with CO yields, after acidolysis, a mixture of organic products with CH_2=C(Me)C(Me)CH_2-C(Me)H as main product [32]. This compound probably arises by initial insertion of CO into the Hf–Me bond followed by the reaction of the formed acyl/oxycarbene with one of the diene M–C bonds. Since organic isonitriles are isoelectronic with CO, and are frequently used as models for CO reactions, we also examined the reactions of 2,6-xylylisonitrile with the unsaturated diene complexes. Cp*Hf(2,3-dimethyl-1,3-butadiene)Me reacts with 2,6-xylylisonitrile by selective insertion into the Hf–Me bond to give the iminoacyl Cp*Hf(2,3-dimethyl-1,3-butadiene)(η^2-N(xy)=CMe) [32,37], but no further reaction of the iminoacyl ligand with the diene could be induced. Increase in the steric bulk of the metal-bound alkyl group can change the insertion preference of the incoming isonitrile: in Cp*Hf(2,3-dimethyl-1,3-butadiene)R (R = Np, Ph, Cl) the isonitrile attacks specifically the Hf-diene M–C bonds to form the unusual hetero-spiro compounds Cp*Hf(R)N(xy)CCH_2C-(Me)=C(Me)CH_2N(xy) (7) [32,37]. The formation of these compounds involves a



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1,2-hydrogen shift after initial insertion of isonitrile into the Hf–diene bond, followed by a second isonitrile insertion and a ring closure. In this case the occurrence of the 1,2-H shift causes the deviation from the reaction path followed in the CO reaction.

In the reaction of Cp*Ti(2,3-dimethyl-1,3-butadiene)Cl with 2,6-xylylisonitrile

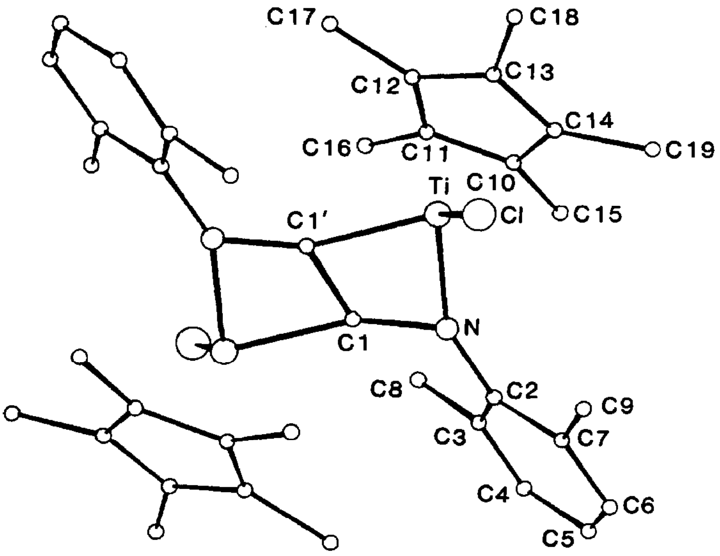
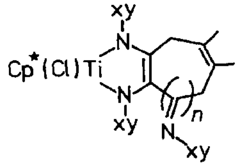


Fig. 5. Crystal structure of $(Cp^*TiCl)_2[\mu-N_2C_2(C_6Me_2H_3)_2]$ [37].

the relative weakness of the Ti–diene bond is again reflected: the main product is $(Cp^{\star}TiCl)_2(\mu\text{-}N_2C_2xy_2)$ (Fig. 5), formed by diene elimination and CC-coupling of two isonitrile molecules between two electron deficient Ti-centers [37]. Minor products are enediamide complexes (**8**), formed through insertion of two or three isonitriles into the Ti–diene bonds, followed by CC-coupling of two iminoacyl carbon atoms. This behaviour is similar to that of the electron deficient dibenzyl compounds $(ArO)_2Ti(CH_2Ph)_2$ [38] and $(ArO)_3Ta(CH_2Ph)_2$ [39] in their reactions with isonitriles.



$n = 0,1$

(8)

Concluding remarks

The complexes $Cp^{\star}M(s\text{-}cis\text{-diene})X$ (M = Ti, Zr, Hf; X = Cl, hydrocarbyl) form a class of electronically and sterically unsaturated complexes with interesting properties. The reactions of the diene fragment can be roughly divided into two types, involving: (a) insertion of substrate into the M–diene bonds, and (b) elimination of free diene. Reactions of the first type tend to have a selectivity different from that in analogous reactions in the Cp_2M(diene) (M = Zr, Hf) system owing to the unsaturation of the mono(pentamethylcyclopentadienyl) complexes (ketones, nitriles). Furthermore, a number of reactions initiated by insertion into the M–diene bond proceed beyond the product formation stage observed in the metallocene diene system (CO, acetylene). In reactions of the second type the very unsaturated $Cp^{\star}MX$ (10 electron) fragments are generated, leading to "classical" (acetylenes) and "nonclassical" (isonitrile) oxidative coupling reactions of the substrates. Another interesting aspect is the availability of these complexes for all the group 4A metals, which allows comparison between them. The Ti compounds display a reactivity compatible with the presence of less σ^2,π-metallacyclopentene character in the Ti–diene bond than in Zr– or Hf–diene bonds.

Acknowledgement

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