Invited review

Recent progress in the chemistry of 1,3-diene complexes of niobium and tantalum

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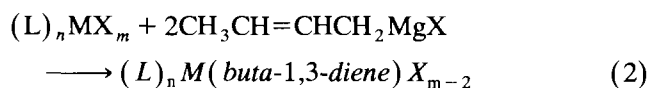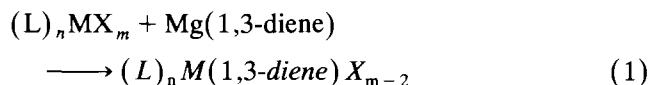
Abstract

This short review describes the preparation, structure and reactivity of 1,3-diene complexes of niobium and tantalum and presents a comparison with the similar diene complexes of metals of Group 2, 3 and 4.

Keywords: Niobium; Tantalum; Lanthanum; Lanthanides; Calcium; Strontium

1. Introduction

1,3-Dienes have been found to give a wide range of transition metal complexes with *s-cis* geometry [1,2]. In the early days of transition metal organometallic chemistry, these *s-cis*-diene complexes were prepared by simple thermal or photochemical reactions of zerovalent metal carbonyls with the diene. Relevant examples include CpCo(diene), Fe(CO)$_3$(diene), Cr(CO)$_4$(diene) and CpV(CO)$_2$(diene). However, these methods could not be extended to the synthesis of the diene complexes of early transition metals, especially the heavier ones such as the lanthanide metals, Zr, Hf, Nb and Ta.

Since the discovery of efficient methods of preparing 1,3-diene complexes of early transition metals utilizing enediylmagnesium reagents [3–13] or methyl-substituted allyl or homoallyl Grignard reagents [14–20], a remarkable array of new 1,3-diene complexes of Ti, Zr, Hf, Nb, Ta, Th and U has been prepared. Typical examples are shown in Eqs. (1) and (2).

$$(L)_n MX_m + Mg(1,3\text{-}diene)$$

$$\longrightarrow (L)_n M(1,3\text{-}diene) X_{m-2} \qquad (1)$$

$$(L)_n MX_m + 2CH_3CH=CHCH_2MgX$$

$$\longrightarrow (L)_n M(buta\text{-}1,3\text{-}diene) X_{m-2} \qquad (2)$$

Among such examples, *s-trans*-diene complexes of zirconium [21,22] present an interesting mode of coordination for a diene bound to mononuclear transition metals, although bridging *s-trans*-diene complexes of binuclear and trinuclear structures had been reported previously [23–25]. Early theoretical analysis of the bonding in these *s-cis*- and *s-trans*-diene complexes revealed a remarkable difference between the two modes of bonding [8,26–28]. Thus, the *s-cis* species is considered to be essentially a metallacyclopent-3-ene with intra-ring olefin coordination, whereas the *s-trans* form involves coordination of two monoenes. These modes are illustrated schematically in Fig. 1.

When the variation of the properties of transition metal across the Periodic Table is considered, the 1,3-diene complexes of Groups 5 and 6 seem to be intermediate in character between Group 4 and later transition metals. We therefore considered it of interest to prepare and characterize typical 1,3-diene complexes of niobium and tantalum. Apart from the theoretical aspects, the reactivity of some of these complexes has attracted
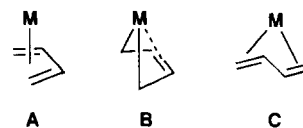
Fig. 1. Schematic drawings of three coordination modes of mononuclear diene complexes. **A** = η^4-diene; **B** = metallacyclopent-3-ene; **C** = *s-trans*-diene.

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much interest. In particular, catalysis such as that of olefin polymerization is characteristic of these early transition metal organometallics, and we have examined some such catalysed reactions involving assistance by organometallic activating agents. This short review summarizes the relevant aspects of the chemistry of niobium and tantalum.

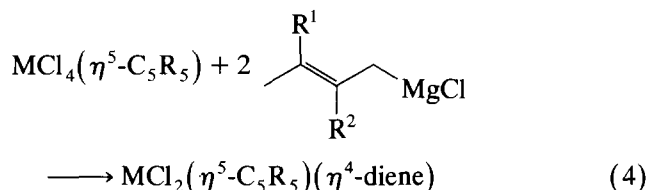## 2. Preparation of diene complexes of niobium and tantalum

Monodiene complexes of niobium and tantalum, $MCl_2(\eta^5\text{-}C_5R_5)(\eta^4\text{-diene})$ (M = Nb and Ta; R = H and Me; diene = buta-1,3-diene, isoprene, 2,3-dimethylbuta-1,3-diene), were prepared by two methods. First we used the reaction of $MCl_4(\eta^5\text{-}C_5R_5)$ with the corresponding 1,3-diene compounds of magnesium to afford monodiene complexes of niobium and tantalum (1-4) in modest yields (Eq. 3) [7,8].

$$MCl_4(\eta^5\text{-}C_5R_5) + 1/n[Mg(1,3\text{-diene})(THF)_2]_n$$

$$\longrightarrow MCl_2(\eta^5\text{-}C_5R_5)(\eta^4\text{-diene}) \qquad (3)$$
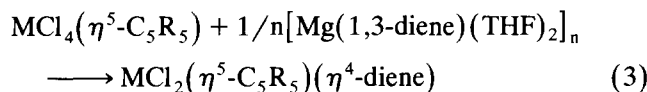
More recently, we have prepared the monodiene complexes by using methylated allyl Grignard reagents [14,29]. Treatment of $NbCl_4Cp^*$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) with 2 equiv. of 2-methylbut-
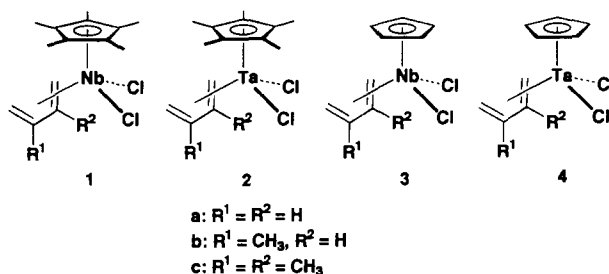
2-enyl Grignard reagent gave a deep green solution, from which $NbCl_2Cp^*(\eta^4\text{-isoprene})$ (1b) was obtained (Eq. 4). Analogous monodiene derivatives 1-4 of niobium and tantalum were prepared similarly. This second method has the advantage that it can be used to prepare a pentadiene complex, $TaCl_2Cp^*(\eta^4\text{-penta-1,3-diene})$ (5), whereas the first method using magnesium-diene adducts is available for 1,3-dienes such as butadiene, isoprene and 2,3-dimethyl-buta-1,3-diene [6,30,31].

$$MCl_4(\eta^5\text{-}C_5R_5) + 2 \quad \overset{R^1}{\underset{R^2}{\diagup}}\diagdown\diagup MgCl$$

$$\longrightarrow MCl_2(\eta^5\text{-}C_5R_5)(\eta^4\text{-diene}) \qquad (4)$$

In contrast, when we used 1-phenylallyl instead of methylated allyl, the reaction of $TaCl_4Cp^*$ with 4 equiv. of 1-phenylallyl Grignard reagent afforded a bis(1-phenylallyl)tantalum complex, $TaCp^*(1$-phenylallyl$)_2$ (6), together with the hexa-1,5-diene derivatives 7 (Eq. 5). The structure (Fig. 2) of 6 was characterized crystallographically to involve *supine-supine* geometry (for definition of terms, see below) [32,33].

$$TaCl_4Cp^* \quad + \quad 4 \quad Ph\diagdown\diagup\diagdown MgCl \quad \xrightarrow{THF}$$

$$\qquad (5)$$
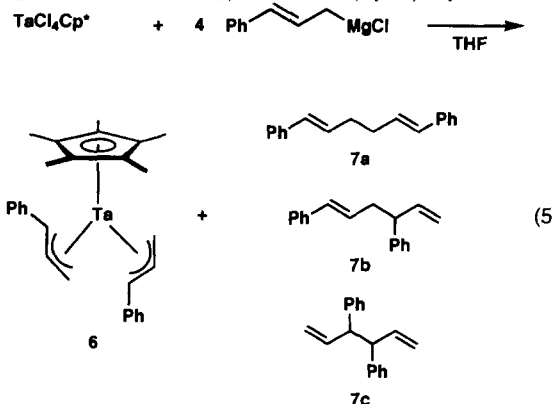
Bis(1,3-diene) complexes of niobium (8 and 9) and tantalum (10 and 11) were prepared by the reaction of

a: R¹ = R² = H
b: R¹ = CH₃, R² = H
c: R¹ = R² = CH₃
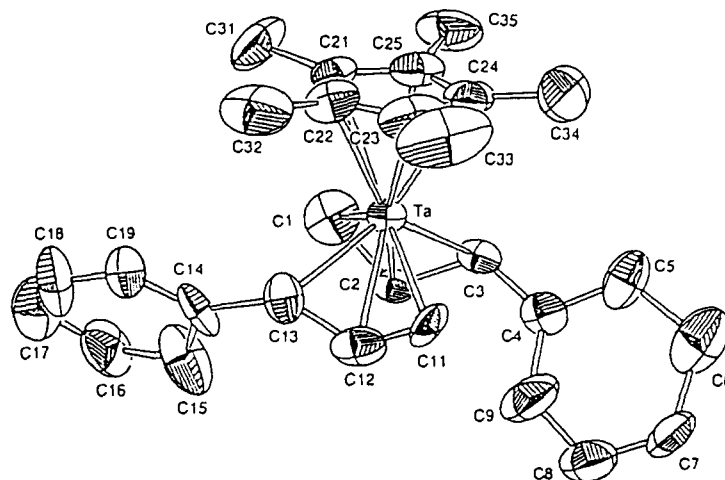

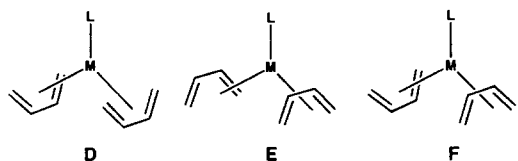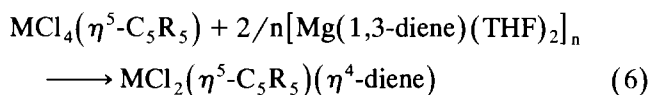Fig. 2. Drawing of complex 6 (from Ref. [32]).

Fig. 3. Schematic drawings of three different geometries in bisdiene complexes. **D** = *supine–supine* mode; **E** = *prone–prone* mode; **F** = *supine–prone* mode.

$MCl_4(\eta^5\text{-}C_5R_5)$ with 2 equiv. of Mg(1,3-diene) adduct (Eq. 6) [7,8,34].

$$MCl_4(\eta^5\text{-}C_5R_5) + 2/n[Mg(1,3\text{-diene})(THF)_2]_n$$

$$\longrightarrow MCl_2(\eta^5\text{-}C_5R_5)(\eta^4\text{-diene}) \qquad (6)$$

Dimethyl complexes of tantalum $Ta(CH_3)_2(\eta^5\text{-}C_5R_5)$(butadiene) (R = Me, **12**; R = H, **13**) were prepared in modest yield by treatment of **2** and **4** with 2 equiv. of MeMgI, while the reaction of **2a** with excess of PhMgI in THF afforded the monophenyl complex, $TaCl(C_6H_5)Cp^*$(butadiene) (**14**), and not the bis(phenyl) derivative. Methylation of **14** then gave a monomethylmonophenyl complex, $Ta(CH_3)(C_6H_5)$-Cp^*(butadiene) (**15**), thermolysis of which gave a new benzyne complex, $TaCp^*$(butadiene)(C_6H_4) (**16**), in which the benzyne moiety is coordinated to tantalum parallel to the Cp^* ligand [35]. This is in sharp contrast to the coordination of benzyne perpendicular to the Cp^* ligand in $TaMe_2Cp^*(C_6H_4)$ [36,37]. Reaction of **2a** with 2 equiv. of the benzyl Grignard reagent afforded a bis(benzyl) complex, $Ta(CH_2Ph)_2Cp^*$(butadiene) (**17**), thermolysis of which at 70°C in the presence of PMe_3 gave a benzylidene complex, $Ta(=CHPh)Cp^*$(butadiene)(PMe_3) (**18**) [35]. These reactions and the products resemble those found previously for metallocene complexes of Group 4 metals and the isoelectronic complexes bearing M(= NR)Cp (M = Group 5 metal) and $M(=NR)_2$ (M = Group 6 metal) fragments [38–43].

## 3. Structure and nature of the diene–metal bonding

The three structures (**D**, **E** and **F**) shown in Fig. 3 are considered for the bisdiene complexes. We have defined the terms *prone* and *supine*, which refer to the orientation of the coordinated dienes with respect to the Cp ligand (L in Fig. 3). So far all the known bisdiene complexes of Fe [44], Ru [45], Rh [46], Ir [47] and Mn [48,49] having idealized C_{2v} symmetry have *supine–supine* geometry (**D**), whereas the bisdiene complexes of niobium and tantalum involve non-equivalent diene coordination (*supine–prone* mode) and provide the first examples of such coordination. The conformation **F** is clearly favoured by the Extended Hückel level calculations since the nature of diene–metal bonding is different from that for late transition metals [8].

Comparison of the structural features and the nature of bonding for the bisdiene complexes of niobium and tantalum with those found for $Cp_2M(1,3\text{-diene})$ is of interest since the fragments MCp(1,3-diene) (M = Nb and Ta) are isoelectronic with the fragments MCp_2 (M = Zr and Hf). Determination of a series of X-ray structures of some of these bisdiene complexes revealed a marked change in the C–C bond lengths in the diene upon *s-cis* coordination. Thus, the originally short–long–short C–C distances in the 1,3-diene skeletons become long–short–long in these early transition metal complexes [6–8,34]. There is therefore a considerable amount of back bonding from the $d\pi$-orbital, and the extent of this is well correlated with the difference in the C–C lengths as shown in **B** in Fig. 1.

The ^1H NMR parameters assignable to the protons on the diene provide important information on the nature of bonding. The chemical shifts of the *anti*-protons are at very high fields, especially in the case of the Ta–diene complexes. The $^1J_{CH}$ values for these protons indicate a considerable weakening of the CH bonding, being lower by ca. 145 Hz than those (158–161 Hz) for conventional η^4-1,3-diene complexes. These values point to a considerable amount of σ-bonding for the terminal carbons of the diene ligand.

For the *s-trans*-diene coordination mode, the X-ray data and the NMR parameters both point to a marked difference in the coordination bonding; the C–C bonds are short–long–short, and there seems to be only weak back-donation to the diene. Therefore, the bonding should be weaker than the *s-cis*-diene bonding, and the *s-trans*-diene (i.e. *trans*-hexa-2,4-diene) in its zir-

8   **9**   **10**   **11**

a: R = H
b: R = CH₃
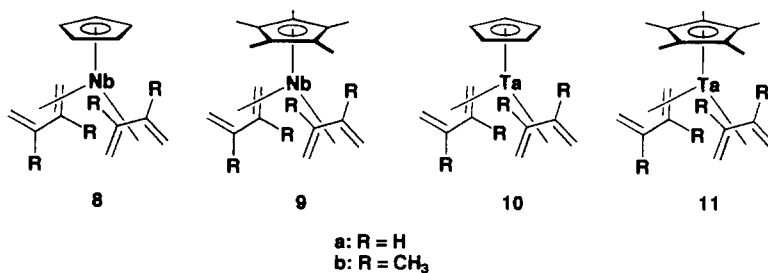
conocene complex is indeed found to be readily displaced on treatment with a monoene such as hex-1-ene [50].

The variation in the preference for s-cis- over s-trans-diene–metal bonding is intriguing. Comparison among metals of the same Group reveal clearly that for the heaviest metals the s-cis mode is favoured. For example, although zirconocene prefers the s-trans mode with 1,4-diphenylbuta-1,3-diene, hafnocene prefers the s-cis mode [6,11,22,51–53]. A similar trend was observed in the case of Nb and Ta, and the mononuclear s-trans-diene complexes have generally been reported for second-row transition elements such as molybdenum [54–58] and ruthenium [59,60]. Thus Nb prefers the s-trans mode for the second diene of the bis(butadiene) complex, CpM(butadiene)$_2$ [7,61,62], whereas the Ta analogue has two s-cis-butadiene ligands in supine–prone disposition [8,34]. Terminal substitution at the diene tends to give s-trans coordination, but internal substitution favours s-cis coordination, e.g. NbCp(s-cis-2,3-dimethylbutadiene)$_2$. These trends show up also in the EH–MO calculations [8].

The monodiene complexes have a considerable contribution from the metallacylopent-3-ene structure, as revealed by the fact that NMR data are similar to those for the bisdiene complexes. Two orientations are possible for the coordination in monodiene complexes, MCl$_2$Cp(diene) (M = Nb and Ta), as shown in G and H in Fig. 4. The crystal structures of several monodiene complexes of tantalum have all been shown to involve the supine mode G. Theoretical molecular orbital calculation on the diene complexes of Nb and Ta have been carried out at the Extended Hückel level [8]. The metallacyclopentene structure is definitely preferred for the s-cis-diene with the supine geometry, as in the case of the related metallocene diene complexes of Zr and Hf. Similar monodiene complexes of Group 4 metals, e.g. TiClCp*(diene) (diene = isoprene, 2,3-dimethylbutadiene) [63] and HfClCp*(2,3-dimethylbutadiene) [64], and also the formally Nb(IV) dimer [NbClCp*(butadiene)]$_2$ [7], exhibit the supine orientation G. In contrast, diene complexes such as TiClCp*(diene) (diene = butadiene, 1,4-diphenylbutadiene) [63,65], ZrCp(dmpe)(butadiene)H [66] and VCp(3,4-(E)-diphenylhexa-1,3-diene)(PMe$_3$) [67] exhibit the prone orientation H.
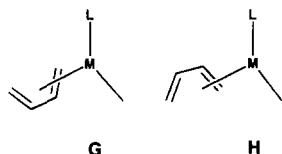
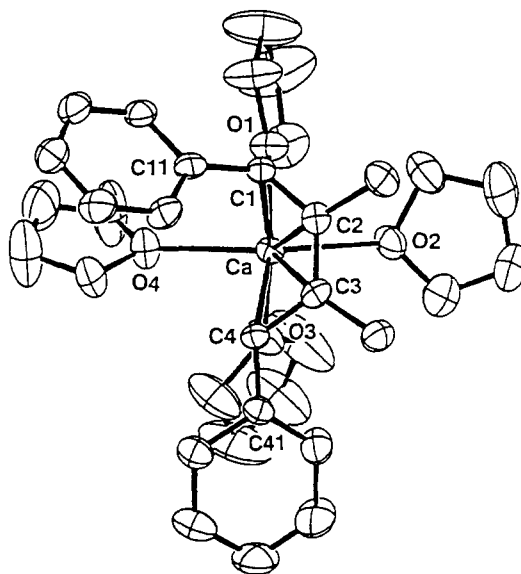Fig. 4. Schematic representation of the bonding modes for monodiene complexes: G = supine mode; H = prone mode.

Fig. 5. Drawing of complex 21 (from Ref. [70]).

We have studied the nature of the metal–diene bonding in the case of Main Group metals. In 1982 we reported the first X-ray structure of a complex involving such bonding, that of a complex with Mg as the metal [68]. In general, the diene–magnesium bonding was regarded as being of the dianion or σ^2-1,4-diyl (metallacyclic structure) type, and this was supported by the observation of long–short–long C–C bond lengths. The nature of the bonding of the diene ligand in Mg(1,4-diphenylbuta-1,3-diene)(thf)$_3$ (19) may be described as approaching the η^4-coordination mode, since the bond distances (2.52 and 2.56 Å) between magnesium and the central carbon atoms are not much longer than those (2.26 and 2.32 Å) to the outer carbon atoms of the diene unit [68]. This description is further supported by the chemical reactions. Thus, treatment of Mg(C$_4$H$_6$)(thf)$_2$ with 1,4-diphenylbuta-1,3-diene gives 19, with the release of free diene [69], and the reaction of Mg–butadiene with oxygen or iodine also releases the diene. The two methyl substituents at the 2- and 3-positions of 1,4-diphenylbutadiene stabilize the geometry by both steric and electronic effects. The diene moiety in Mg(1,4-diphenyl-2,3-dimethylbutadiene)(dme)$_2$ (20) has metallacyclic character since the $^1J_{CH}$ value is 127 Hz (corresponding to an sp$^{2.9}$ state) [70]. More recently we have succeeded in obtaining single crystals of the complexes of Ca (21) and Sr (22) with 1,4-diphenyl-2,3-dimethylbutadiene [70], the structures of which are presented in Figs. 5 and 6, respectively. In the case of Ca and Sr, the diene has s-cis geometry and the C–C bond lengths are long–short–long. The $^1J_{CH}$ values for the terminal diene carbons are 142 (sp$^{2.6}$) and 147 (sp$^{2.5}$) Hz, respectively, indicating that their structures lie between the η^4-diene and metallacyclopent-3-ene types. It is noteworthy that these values found for the calcium–
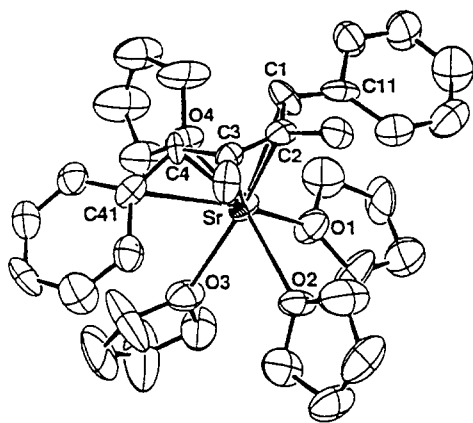
Fig. 6. Drawing of complex **22** (from Ref. [70]).

and strontium–diene complexes are comparable to those for the diene complexes of early transition metals, including niobium and tantalum. These results show that the diene–calcium (or strontium) bonding is more ionic and that there is efficient delocalization of the anionic charge into the two phenyl groups. In the case of strontium, the larger size of the metal allows more extended interaction with the diene, and so interaction of strontium atom with one of two phenyl groups at the diene terminals is observed.

Similar ionic bonding may be possible in the case of lanthanides. Our new preparative procedure starting from lanthanide metal and 1,3-diene in the presence of 2 equiv. of iodine gave an interesting binuclear complex, [LaI$_2$(thf)$_3$(μ-η^4:η^4-1,4-diphenylbutadiene)LaI$_2$(thf)$_3$] (**23**) [71], the structure of which is shown in Fig. 7. In complex **23**, the diene ligand is present in the bilateral coordination (μ-η^4:η^4) mode, just like that in dilithium–diene complexes such as [Li(tmeda)(μ-1,4-diphenylbuta-1,3-diene)Li(tmeda)] [72] and [Li(tmeda)-{ μ-1,4-bis(trimethylsilyl)buta-1,3-diene}Li(tmeda)] [73]. The presence of the terminal phenyl groups seems to be
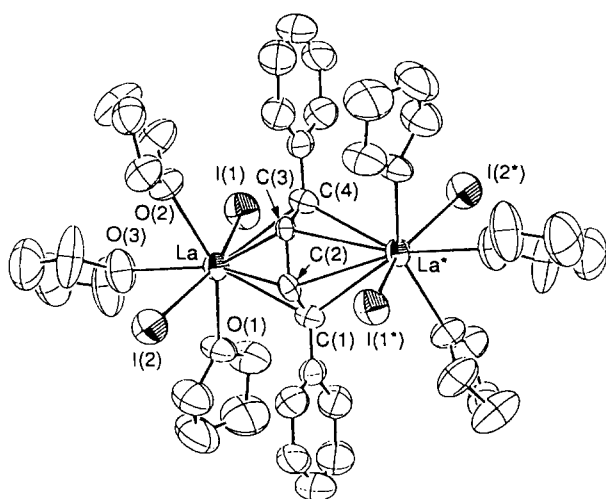
crucial for the successful isolation and characterization of the complexes. The diene C–C bond lengths are short–long–short (1.25, 1.49 and 1.25 Å). Such an inverse sandwich structure has been observed for [Sm{N(SiMe$_3$)$_2$}(μ-η^8:η^8-C$_8$H$_8$)Sm{N(SiMe$_3$)$_2$}$_2$] [74] and [(H$_4$B)$_3$U(μ-η^7:η^7-C$_6$H$_6$)U(BH$_4$)$_3$]$^-$ [75] and also for some early transition metal complexes such as [Hfl$_2$(PMe$_2$Ph)$_2$(μ-η^6:η^6-C$_6$H$_6$)Hfl$_2$(PMe$_2$Ph)$_2$] [76] and Hf$_3$Cl$_5$(C$_4$H$_4$)Cp$_3^*$ [77]. It is noteworthy that the corresponding monolithium–samarium complex [Li-(thf)$_2$(μ-η^2:η^8-C$_8$H$_8$)Sm{CH(SiMe$_3$)$_2$}$_2$] [78], the dipotassium compound [K(diglyme)(μ-η^8:η^8-C$_8$H$_4$-Me$_4$)K(diglyme)] [79] and the dilithium compound, [Li(tmeda){ μ-η^8:η^8-C$_8$H$_6$(SiMe$_3$)$_2$-1,4}Li(tmeda)] [80] have been prepared, indicating that the organosamarium(II) moiety shows analogy with the cations of alkali metals. Asymmetrically bridging s-cis-diene coordination (μ-η^1:η^3) has been found in [Cp$_2^*$ La(μ-η^1:η^3-butadiene)LaCp*(thf)] [81]. Such modes of diene coordination may be found in future for other metals with some degree of ionic metal–carbon bonding.

4. Catalytic properties of the diene complexes

As mentioned above, the fragments of MCp(1,3-diene) (M = Nb and Ta) are isoelectronic with those of MCp$_2$ (M = Zr and Hf). The 14-electron isoelectronic species for Group 3, 4 and 5 metals are shown schematically in Scheme 1. This analogy prompted us to investigate the ability of the diene complexes of niobium and tantalum to serve as catalyst precursors for olefin polymerization. We found that the system involving MX$_2$(η^5-C$_5$R$_5$)(η^4-diene) (M = Nb and Ta; R = H and CH$_3$; X = Cl and CH$_3$, X$_2$ = 1,3-diene) in the presence of an excess of MAO (methylaluminoxane) is a new catalyst precursor for the living polymerization of ethylene and gives rise to the narrowest polydispersity (M_w/M_n as low as 1.05) observed for polyethylene [29,82,83].

Dichloro and dimethyl complexes containing TaCp*-(η^4-1,3-diene) moieties, **2** and **12**, have almost identical catalytic properties, indicating that almost identical catalytically active species are formed. Methylaluminoxane acts as the methylation reagent and causes abstraction of the anionic ligand from tantalum, so giving cationic species.

Fig. 7. Drawing of complex **23** (from Ref. [71]).

group 3   group 4   group 5
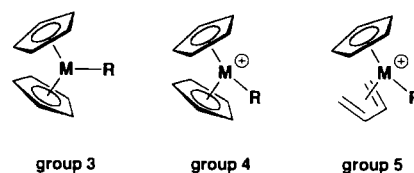
Scheme 1.

At $-20°C$, the polymerization of ethylene in toluene solution was found to be catalysed by the monodiene complexes of niobium or tantalum in the presence of an excess of MAO to give polyethylene with narrow polydispersity ($M_w/M_n = 1.05–1.51$), indicating that this polymerization is of the living type. In the conventional systems, consisting of MCl_2Cp_2 (M = Zr and Hf) and MAO, zirconocene is well known to have a higher activity than hafnocene. With our complexes, the niobium species are superior to the corresponding tantalum species as catalyst precursors. Moreover, the polyethylene obtained by use of catalysts **1a** and **1c** at $-20°C$ has the narrowest polydispersity ($M_n = 4 \times 10^4$, $M_w/M_n = 1.05$) observed to date.

The active species in this catalyst system are assumed to be cationic 14-electron entities similar to the cationic metallocene alkyls of Group 4 metals. Up to now the cationic complexes in our system have not been isolated pure, but the polymerization of ethylene was found to be catalysed by the catalyst system consisting of the dimethyl complex **12** and $B(C_6F_5)_3$ in the absence of MAO.

We found that bis(diene) complexes **9–11** were also active catalyst precursors for the polymerization of ethylene. One of the two diene centres underwent a ligand exchange reaction with methyl ligand on aluminum of MAO to generate the same active species as that formed from monodiene complexes and MAO, a result that might be attributable to the stability of the diene aluminium species generated by the selective ligand-exchange reaction [84]. Similar selective ligand-exchange reactions of one diene ligand in $Nb(\eta^5\text{-}C_5\text{-}Me_4Et)(butadiene)_2$ with cyclooctatetraene (cot) or with alkyne in the presence of PMe_3 have been reported to afford $Nb(\eta^5\text{-}C_5Me_4Et)(butadiene)(cot)$ and $Nb(\eta^5\text{-}C_5Me_4Et)(butadiene)(alkyne)(PMe_3)$, respectively, and the resulting complexes have the diene-*supine*-coordinated to tantalum [62,85], supporting the view that two diene ligands have different reactivities. Mixed bis(diene) complexes have been prepared from the monodiene complexes. In the case of tantalum, 2,3-dimethylbutadiene was found to prefer the *supine* position but butadiene was later found to take up the *prone* position, giving a complex that reacts faster with 2,4-dimethylpentan-3-one [34]. Since the diene in the *prone* position is replaced more easily in the presence of MAO, the bisdiene complexes have essentially the same activity as the monodiene complexes as catalyst precursors for ethylene polymerization.

Acknowledgements

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