

Alkyl- η^2 -alkene niobocene and tantalocene complexes with the allyldimethylsilyl- η^5 -cyclopentadienyl ligand: synthesis, NMR studies and DFT calculations†

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Group 5 metal complexes $[M(\eta^5-C_5H_5)\{\eta^5-C_5H_4SiMe_2(CH_2-\eta^2-CH=CH_2)\}X]$ ($M = Nb$, $X = Me, CH_2Ph, CH_2SiMe_3$; $M = Ta$, $X = Me, CH_2Ph$) and $[Ta(\eta^5-C_5Me_5)\{\eta^5-C_5H_4SiMe_2(CH_2-\eta^2-CH=CH_2)\}X]$ ($X = Cl, Me, CH_2Ph, CH_2SiMe_3$) containing a chelating alkene ligand tethered to a cyclopentadienyl ring have been synthesized in high yields by reduction with Na/Hg ($X = Cl$) and alkylation with reductive elimination ($X = alkyl$) of the corresponding metal(IV) dichlorides $[M(\eta^5-Cp)\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}Cl_2]$ ($Cp = C_5H_5$, $M = Nb, Ta$, $Cp = C_5Me_5$, $M = Ta$). These chloro- and alkyl-alkene coordinated complexes react with CO and isocyanides $[CNtBu, CN(2,6-Me_2C_6H_3)]$ to give the ligand-substituted metal(III) compounds $[M(\eta^5-Cp)\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}XL]$ ($X = Cl, Me, CH_2Ph, CH_2SiMe_3$). Reaction of the chloro-alkene tantalum complex with LiNHtBu results in formation of the imido hydride derivative $[Ta(\eta^5-C_5Me_5)\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}H(NtBu)]$. NMR studies for all of the new compounds and DFT calculations for the alkene-coordinated metal complexes are compared with those known for related group 4 metal cations.

Introduction

Alkene coordination to a group 4 d^0 transition metal alkyl cation has been proposed¹ to precede the migratory insertion for a Ziegler-Natta polymerization process.² The resulting $16e^-$ alkyl-alkene species has a very low thermal stability, because the metal-alkene interaction is usually only due to the poor σ -donor capacity of the alkene. More stable alkyl-alkene chelates have still to be studied at temperatures lower than $-40^\circ C$ to prevent their decomposition or reactions with the solvent.

We reported^{3,4} previously the synthesis of group 4 metal dialkyls containing an allyldimethylsilyl-cyclopentadienyl ligand, which after treatment with a Lewis acid $B(C_6F_5)_3$, coordinate the olefinic system of the allyl moiety to give alkyl cations with a chelated η^5 -Cp- η^2 -alkene ligand. Exchange between two enantiomeric structures was observed and studied by DNMR spectroscopy³ between 193 and 253 K.

The corresponding neutral d^2 group 5 metal(III) $18e^-$ compounds are structurally similar, but it was expected that they would be more stable, because the metal-alkene bond is now composed of σ -donor and π -acceptor interactions. These compounds may therefore be easily accessible models to compare some aspects of their structural behaviour with those found for d^0 metal complexes.

Many hydrido-alkene group 5 metallocenes have been isolated⁵ by reaction of the alkene with the metal trihydrides $[MCp_2H_3]$. Similar compounds were also isolated by alkylation of the metallocene dichlorides $[MCp_2Cl_2]$ with β -hydrogen containing alkyl groups and simultaneous reduction to give $[MCp_2R]$, which are transformed into the corresponding hydrido-alkene derivatives by β -hydrogen elimination.^{5b,d,6} It has been observed that all these hydrido-alkene complexes show easy hydrogen exchange processes, which are due to alkene insertion into the metal-hydride

bond followed by β -hydrogen elimination. This leads to a dynamic behaviour, which can be studied by variable-temperature NMR spectroscopy. The structure of various hydrido-alkene niobocene and tantalocene complexes and the kinetics of their insertion reactions have been extensively studied⁵⁻⁷ and the behaviour of *ansa*-metallocenes in comparison with their non-bridged systems has been reported recently.⁸

Related chloro-alkene group 5 metal(III) compounds have occasionally been singularly isolated by reduction of dichloro-metallocenes in the presence of olefin,⁹ but relatively few alkyl-alkene compounds have been reported. Ligand promoted olefin insertion into the niobium-hydrido bond of permethylniobocene $[NbCp^*(olefin)H]$ complexes to give the ligand-trapped alkyl compounds has been reported only for small ligands (CO, CNMe),^{6d} whereas the related niobocene complexes have been shown to afford either ligand-trapped alkyl compounds,^{5a,6b} or the olefin substitution hydrido products.^{5d} Severe restrictions were also found for the permethyltantalocene complex^{5c} whereas the related tantalocene $[TaCp_2(C_2H_4)H]$ compound reacted with excess ethylene to give the trapped ethyl-ethylene complex at elevated temperatures^{5d} and similar CO and CNR promoted insertions have been shown to afford a group of ligand-trapped tantalocene alkyl $[TaCp_2RL]$ complexes.¹⁰ Attempts to induce similar olefin insertion and to trap the resulting alkyl compounds failed when *ansa*-metallocene olefin hydrides were used.^{6e}

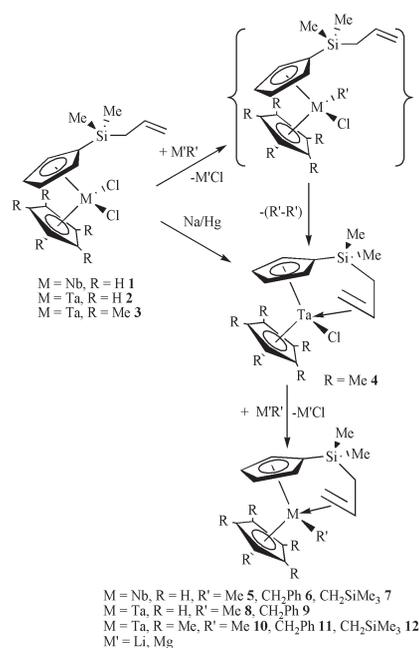
In this study we report the synthesis of the chloro- $[Ta(\eta^5-C_5Me_5)\{\eta^5-C_5H_4SiMe_2(CH_2-\eta^2-CH=CH_2)\}Cl]$ and alkyl-alkene coordinated niobium and tantalum derivatives $[M(\eta^5-C_5R_5)\{\eta^5-C_5H_4SiMe_2(CH_2-\eta^2-CH=CH_2)\}R']$ ($M = Nb, Ta$; $R = H, Me$; $R' = Me, CH_2Ph, CH_2SiMe_3$) obtained from the dichloro metal(IV) compounds $[M(\eta^5-C_5R_5)\{\eta^5-C_5H_4SiMe_2(CH_2CH=CH_2)\}Cl_2]$ ($M = Nb, Ta$; $R = H, Me$) prepared previously.¹¹ The NMR behaviour of these compounds is compared to that known for related group 4 metal cations. DFT calculations were carried out on model complexes to support the structures of these complexes and the mechanisms for their dynamic behavior.

† Electronic supplementary information (ESI) available: Full synthetic and structural data for compounds **13a-d** and **14a-g**. ¹H NMR data of the dimethylsilylallyl moiety for complexes **4-12** in C_6D_6 at $20^\circ C$. DFT Calculations. See <http://www.rsc.org/suppdata/dt/b4/b406747a/>

Results and discussion

Synthesis of chloro- and alkyl-alkene complexes

The dichloro metal(IV) complexes $[M(\eta^5\text{-Cp})\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\text{Cl}_2]$ (Cp = C₅H₅, M = Nb **1**, Ta **2**, Cp = C₅Me₅, M = Ta **3**) were prepared previously by the reaction of the monocyclopentadienyl compounds with the corresponding lithium cyclopentadienides and simultaneous reduction with Na/Hg.¹¹ Related reduction of toluene solutions of **1** and **2** with Na/Hg gave brown solids, presumably chlorine bridged¹² species, which did not contain the coordinated olefin and were not further studied. However, in an analogous reaction, reduction of the chloro tantalum complex **3** bearing the bulkier and more donating permethylated cyclopentadienyl ligand takes place with coordination of the alkene system to give $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\text{Cl}]$ **4** isolated in 65% yield as a yellow-green solid characterized by elemental analysis and NMR spectroscopy (see Scheme 1). Complex **4** is soluble in pentane and reacts with chlorinated solvents, being stable at room temperature for months under inert atmosphere.



Scheme 1

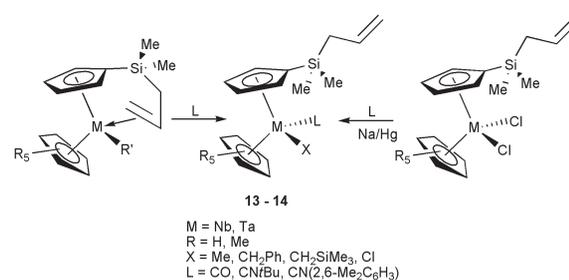
A more convenient method to prepare this type of alkyl-alkene metal compounds was based on the alkylation of the dichloro complexes **1–3**, which, in the presence of excess alkylating agent induced simultaneous reductive elimination of alkane and immediate coordination of the alkene tethered to the cyclopentadienyl ring. As shown in Scheme 1, addition of 1 equiv. of MgRCl (R = Me, CH₂Ph) or LiCH₂SiMe₃ to toluene solutions of complexes **1–3** apparently did not allow isolation of the monoalkyl species with the free non-coordinated allyl group, nor could these species be observed spectroscopically. This reaction always resulted in formation of inseparable mixtures of products. This behaviour could indicate that coordination of the tethered alkene moiety has a significantly higher thermodynamic stability. When the same reaction was carried out using 2 equiv. of the alkylating agents, pure alkyl-alkene metal complexes $[M(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\text{R}]$ (M = Nb, R = Me **5**, CH₂Ph **6**, CH₂SiMe₃ **7**; M = Ta, R = Me **8**, CH₂Ph **9**) and $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\text{Me}]$ **10** could be obtained. Compounds **5–10** were isolated as brown (**5–9**) and green (**10**) solids in 65–75% yields after purification. All of them were characterized by NMR spectroscopy and elemental analyses. However, reactions of **3** with 2 equiv. of Mg(CH₂Ph)Cl and LiCH₂SiMe₃ led to the formation of mixtures containing variable proportions of the chloro-alkene **4** and the corresponding alkyl-alkene complexes $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\text{R}]$ (R = CH₂Ph **11**, CH₂SiMe₃ **12**), indicating that these reactions occur through the

reduction of the chloro-alkyl compounds and lead to the chloro-alkene complex **4**, which is then further alkylated. Consequently, these mixtures were transformed into the pure alkyl compounds **11** and **12** by addition of excess alkylating agent, or even better, by direct alkylation of **3** with 3 equiv. of MgRCl. The tantalum complexes **10–12** may also be prepared treating the isolated chloro complex **4** with 1 equiv. of the corresponding alkylating agent. Compound **11** was isolated as a green solid in 75% yield whereas **12** resulted as a brown solid in 65% yield after purification and both were characterized by elemental analysis and NMR spectroscopy. All compounds **4–12** were very soluble in alkanes and stable under inert atmosphere into a dry-box.

All these features observed in the synthesis may be explained assuming that formation of the final alkyl-alkene metal compounds may take place through the initial formation of the chloro-alkyl derivative, which may then be followed by its reduction to the chloro metal(III) compound. These chloro metal(III) complexes allow facile coordination of the tethered alkene, particularly when bulkier alkyl (CH₂Ph and CH₂SiMe₃) and ring (C₅Me₅) substituents are present, and finally the chloro-alkene derivatives are easily alkylated. However formation of intermediate dialkyl complexes cannot be excluded.¹³

Reactivity

All of the chloro- η^2 -alkene **4** and alkyl- η^2 -alkene complexes **5–12** described above react with CO and isocyanides CNtBu and CN(2,6-Me₂C₆H₃) to give the olefin substitution products as a new group of the very well known¹⁴ alkyl metal(III) complexes $[M(\eta^5\text{-C}_5\text{R}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-CH}=\text{CH}_2)\text{XL}]$ (M = Nb, R = H, X = CH₂Ph, L = CO **13a**, CNtBu **13b**; M = Ta, R = Me, X = Cl, L = CO **14a**, CNtBu **14b**, CN(2,6-Me₂C₆H₃) **14c**; X = Me, L = CO **14d**; X = CH₂Ph, L = CO **14e**, CN(2,6-Me₂C₆H₃) **14f**; X = CH₂SiMe₃, L = CN(2,6-Me₂C₆H₃) **14g**) as illustrated in Scheme 2. Reactions of complexes **10–11** with the bulkier permethylated ring required heating at 90 °C for 24 h whereas complexes **5–9** with the unsubstituted ring took place in 16 h at room temperature. The same tantalum complexes **14a–14c** and related chloro niobium(III) derivatives (M = Nb, L = CO **13c**, CNtBu **13d**) can also be obtained by reduction of the corresponding metal(IV) dichloro compounds with Na/Hg in the presence of the ligand. These compounds were characterized by elemental analysis and IR and ¹H, ¹³C NMR spectroscopies. Full synthetic and structural data for compounds **13a–d** and **14a–g** are given in the ESI.†

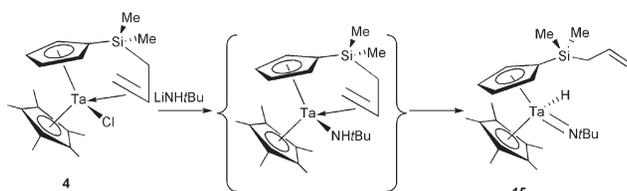


Scheme 2

Ligand promoted migration of the alkyl group to the alkene moiety was not observed for any of these reactions, probably due to the kinetic stability of the low-valent 18e⁻ metal alkyl-alkene compounds. As expected, neither insertion of CO nor of CNR into the metal-alkyl bond was observed.

An interesting behaviour was observed when the reaction of the chloro tantalum complex **4** with 1 equiv. of LiNHtBu was monitored by ¹H NMR spectroscopy in a Teflon valved NMR tube. As shown in Scheme 3, formation of the intermediate amido-alkene derivative was not observed, because rapid transfer of a hydrogen atom to the metal with simultaneous dissociation of the alkene moiety took place to give the imido hydride complex $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\text{H}(\text{NtBu})]$ **15**. The ¹H and ¹³C NMR spectra of complex **15** are consistent with those expected

for an asymmetric molecule, showing typical resonances for the non-coordinated allyl moiety, two singlets (^1H and $^{13}\text{C}\{^1\text{H}\}$) for Me-Si groups and four (^1H) and five (^{13}C) signals for the silylated cyclopentadienyl ring. The hydride ligand is significantly shifted low field being observed as a singlet at δ 5.95 (see Experimental section). Although this is the region where the bridging $\text{Ta}(\mu\text{-H})$ hydride signals are observed for monocyclopentadienyl complexes containing bulky imido ligands,¹⁵ it was reported that this is also the region where the hydride signal of terminal Nb-H^{16} and Ta-H^{17} bonds are observed for this type of dicyclopentadienyl imido complexes. The difference between the ^{13}C quaternary and methyl carbon resonances of the *tert*butylimido group is 30.8 ppm suggesting a linear disposition of the $\text{Nb-N-}t\text{Bu}$ ligand in complex **15**.



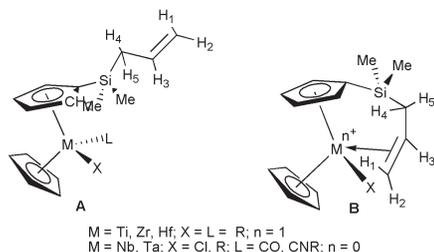
Scheme 3

NMR spectroscopic studies

Despite the fact that crystals of good quality suitable for X-ray diffraction studies could not be obtained of any of these compounds, all of the chloro-alkene (**4**), alkyl-alkene (**5–12**) and chloro- and alkyl-ligand (**13**, **14**) niobocene and tantalocene complexes were fully characterized by NMR spectroscopy in solution. All of them are asymmetric molecules with a chiral metal center and their NMR spectra show the following common features. All of the NMR spectra exhibit two singlets for the Me_2Si group and four multiplets (^1H) and five signals (^{13}C) for the ring system of the ($\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{allyl})$) ligand. They also show one signal (^1H , ^{13}C) for the ($\eta^5\text{-C}_5\text{H}_5$) (**5–9**, **13**) and one singlet (^1H) and two signals (^{13}C) for the ($\eta^5\text{-C}_5\text{Me}_5$) ligands (**4**, **10–12**, **14**). In addition the expected singlets are observed for the Me-M (**5**, **8**, **10**, **14a**), Me_3Si (**7**, **12**, **14d**), *t*Bu (**13b** and **13d**) and 2,6- $\text{Me}_2\text{-C}_6\text{H}_3$ (**14c**, **14d**, **14g**) groups. The typical C_{2v} local symmetry multiplets for C_6H_5 and 2,6- $\text{Me}_2\text{-C}_6\text{H}_3$ and the AB spin systems for the diastereotopic methylene protons of CH_2Ph and CH_2SiMe_3 substituents were also observed in the ^1H NMR spectra.

NMR studies related to the allylic $\text{Si-CH}_2\text{-CH=CH}_2$ fragment. The most significant structural data are associated to the NMR behaviour observed for the $\text{Si-CH}_2\text{-CH=CH}_2$ system. The ^1H NMR spectra in C_6D_6 for all complexes containing the free non-coordinated allylic moiety (Scheme 4, A) exhibit one multiplet at δ ~5.6–5.9 (internal = CH^3), two multiplets at δ ~4.9 ($J_{\text{cis}} \approx 10$ Hz, $J_{\text{trans}} \approx 16$ Hz, $J_{\text{gem}} \approx 4$ Hz) (terminal = CH^1H^2) and one doublet at δ ~1.5–1.8 ($J \approx 8$ Hz) (SiCH^3H^5). This is consistent with the three ^{13}C signals observed at δ ~134–136 (internal = CH), δ ~113–114 (terminal = CH_2) and δ ~25–26 (SiCH_2). The chemical shifts and coupling constants of these signals are only very slightly affected by the remaining substituents being almost the same for group 4 metal(IV)^{3,4} and for group 5 metal(III) complexes **13** and **14**.

Coordination of the terminal vinyl moiety to the metal center in the chloro- and alkyl-alkene metal compounds **4–12** (Scheme 4, B) is clearly demonstrated by the high-field shift of the typical vinyl

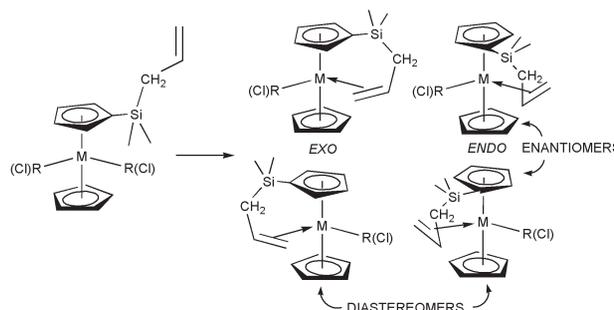


Scheme 4

-CH=CH_2 and Si-CH_2 multiplets which appear at $\delta < 2.5$ and δ 1–4 respectively of a ABCDE spin system. The very large shielding of the vinyl resonances is consistent with the change of carbon atoms hybridization from sp^2 in **13**, **14** to sp^3 in **4–12** metal complexes. Similar changes of chemical shifts ($\Delta\delta < 55$ ppm) were observed in the ^{13}C NMR spectra (see Experimental section). This behaviour is consistent with the metallacyclopropane character reported^{5d,6e,18} for this type of compounds. Moreover, the direct $\text{C}_1\text{-H}_2$ and $\text{C}_2\text{-H}_3$ ($^1J \approx 143\text{--}150$ Hz) spin coupling constants found for the ^{13}C signals of the terminal and internal carbon atoms are also consistent with their sp^3 hybridization, being smaller than the value reported¹⁹ for cyclopropane (161 Hz) due to the influence of the metal, assuming the positive sign of these spin–spin coupling constants.²⁰

In contrast, coordination of the vinyl moiety to the cationic group 4 metal complexes^{3,4} produce similar high-field shifts of the terminal = CH^1H^2 olefinic protons whereas the internal = CH^3 proton is remarkably shifted low-field to $\delta \sim 7.30$ ppm, demonstrating the high polarization of the olefinic system when it is coordinated to a d^0 metal center.

The dichloro niobium(IV) and tantalum(IV) **1–3** and the dialkyl group 4 metal complexes $[\text{M}(\eta^5\text{-C}_5\text{R}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-CH=CH}_2)\text{R}'_2]$ used as precursors for the preparation of the olefin coordinated compounds are symmetric molecules for which both right and left equatorial positions are equivalent. Therefore, treatment with either, a reducing agent (Na/Hg for **4**), an alkylating agent (**5–12**) or $\text{B}(\text{C}_6\text{F}_5)_3$ (cationic group 4 metal compounds) may eliminate any of the two symmetric chloro or alkyl ligands. After coordination of the terminal alkene moiety all the resulting compounds are characterized by two chiral principles, namely the enantioface of the coordinated vinyl moiety and the metal atom. They should therefore lead to the formation of any of the *endo* or *exo* diastereomers with their pairs of enantiomers represented in Scheme 5.



Scheme 5

A new remarkable difference between the group 4 (d^0) and group 5 (d^2) metal complexes was observed when their NMR spectroscopic behaviour was studied at variable temperature. A common feature to all of the benzyl cationic group 4 metal derivatives is that one single set of resonances is observed at 193 K. Taking into account that values of kinetic barriers for alkene dissociation should be similar to those found for other related zirconium d^0 species^{1c,e,3} this set of resonances has to be assigned to the averaged spectrum in the fast exchange regime occurring between the two *exo/endo* diastereomers represented in Scheme 5. An additional reversible exchange can be detected in the NMR spectra. In fact, formation of related methyl cationic species at 193 K always led to spectra with mixtures of *exo/endo* diastereomers, for which, however, the complexity of the NMR spectra observed between 193 and 253 K prevented detailed studies of their dynamic behaviour.⁴

In contrast, the ^1H NMR spectra of most of the d^2 niobium(III) and tantalum(III) **4–12** complexes show the presence of two sets of signals corresponding to the *endo/exo* diastereoisomers which are not temperature dependent and do not show spin exchange between 193 and 343 K. This behaviour demonstrates that both *endo/exo* isomers are simultaneously formed and their interconversion by alkene dissociation/association processes require higher activation energies. This feature is also significantly different from that found for related hydrido-alkene complexes reported previously, which

show isomerism due to the restricted rotation of the alkene, which is not only hindered by their high metallacyclopropane character^{5b,d} but also prevented by formation of a rigid cyclic system with the cyclopentadienyl-pendant alkene. In addition a high barrier of activation²¹ prevents the insertion of the alkene into the metal–alkyl bond.

Two sets of signals of the same ABCDE spin system were clearly observed in the ¹H and ¹³C NMR spectra of the tantalum chloro–alkene **4** and methyl–alkene **10** complexes (3:2 and 3:1 molar ratio, respectively), for which we propose the *exo* and *endo* structural conformations represented in Fig. 1, as metallacyclopropane compounds.

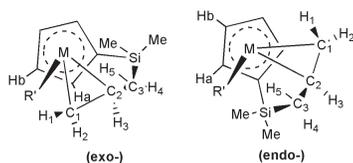


Fig. 1 Labelling of the *exo*- and *endo*-isomers.

Assignments of the signals observed in the ¹H spectrum of complex **10** to the *exo* and *endo* stereoisomers was accomplished by NOE spectroscopy. Selective excitation (PFG WFG NOESY1D pulse sequence) of the *Me*–Ta resonance at δ 0.14 for the major stereoisomer (see Experimental section) afforded an enhancement in the two ring proton resonances at δ 4.48 and 5.11 of the (η^5 -C₅H₄SiMe₂CH₂CHCH₂) ligand and in one of the two terminal =CH₂ protons at δ 1.25. Similar excitation of the *Me*–Ta resonance at δ 0.33 for the minor component produced the enhancement in the resonances at δ 5.48 for only one of the ring protons, at δ 2.58 for one of the CH₂–Si protons and an almost insignificant enhancement in the resonance at δ 1.04 for one of the terminal =CH₂ protons.

In agreement with these results we suggest that the *endo* isomer represented in Fig. 1 corresponds to the minor species whereas the major component is the *exo* isomer. Following this assignment all the remaining signals observed in the ¹H NMR spectra of **10** can be unequivocally assigned (see Experimental section).

The metallacyclopropane system is characterized by the same values of the vicinal proton–proton coupling constant (³*J*_{H1–H3} and ³*J*_{H2–H3}), which mainly depend on the dihedral angles between the corresponding planes, whereas the negative values of the geminal ²*J*_{H1–H2} coupling constants and their chemical shifts are controlled by the electron-donor character of the (η^5 -C₅R₅) and R' ligands. The short distances between the *Me*–Ta group and only one proton of the terminal CH₂ group observed for **10-exo** in the NOESY spectra suggest that the C₁, C₂, Me and Ta atoms are not exactly coplanar.

Taking into account the large (more than two times) difference between the vicinal ³*J*_{H3–H4} coupling constants observed for *exo* and *endo* isomers of **10**, we suggest to assign the *exo* diastereomer to the minor component of solutions of complex **4** (³*J*_{H3–H4} = 6.5 Hz) whereas the *endo* diastereomer would correspond to the major component (³*J*_{H3–H4} = 3.0 Hz). The methyl complexes **5** and **8** containing the unsubstituted cyclopentadienyl ligand, which are more closely related to complex **10** were however found as almost just one single component with a very small amount of a minor one which could only be detected by their η^5 -C₅H₅ singlets, whereas signals due to their vinyl moiety could not be identified. Even smaller, almost undetectable amounts of the minor component were observed for complexes **6**, **7**, **9**, **11** and **12**. It has been reported⁵ previously that the geminal ²*J*_{H1–H2} coupling constants are larger for *exo*- than for *endo*-isomers of related hydrido-alkene complexes. The analysis of the spectral data observed for complexes **5–9** and **11**, **12** allowed us to make only tentative assignments of the *exo/endo* configurations for these compounds. However, strong general support is given by the following theoretical analysis.

Theoretical calculations. In order to obtain further informations about the energetic preferences for the *endo/exo* conformations we carried out density functional calculations (DFT) on different conformations of the d⁰ and d² silyl-bridged alkyl–alkene coordinated

Table 1 Relative energies (kcal mol⁻¹) for different conformations of complexes [M(η^5 -C₅H₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}CH₂Ph] with M = Sc, Zr⁺, Hf⁺, Nb and Ta

Conformation	M = Sc	Zr ⁺	Hf ⁺	Nb (6)	Ta (9)
I(Bn)-exo	0.0	0.0	0.0	0.0	0.0
II(Bn)-endo	-0.1	5.4	5.8	1.2	1.0
III(Bn)-open-exo					
η^1 -CH ₂ Ph	— ^a	20.1	14.9	22.1	21.8
η^3 -CH ₂ Ph	0.7	4.9	6.6	15.2	18.6
IV(Bn)-open-endo					
η^3 -CH ₂ Ph	-1.1	3.6	5.5	14.9	18.5

^aNo local minimum could be found.

transition metal derivatives [M(η^5 -C₅H₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}R] for M = Sc, Zr⁺, Hf⁺, Nb and Ta, and R = Me and CH₂Ph. The calculations presented here utilize fairly large basis sets, but do not include solvation effects, as well as influences of counterions. Before we discuss some of the structural data in more detail, we will briefly comment on the bonding interactions between a C=C double bond and a transition metal center. The classical Dewar–Chatt–Duncanson^{22,23} model of the L_nM–olefin interaction involves σ -donation from the π HOMO of the olefin to an empty metal orbital, as well as back donation of electrons from filled d-orbitals, usually the HOMO, into the olefin's empty π^* LUMO. For d⁰ systems σ -donation is the only possible orbital interaction, whereas for d²-systems backdonation may additionally exist. Besides orbital interaction, there are also electrostatic forces present, which become of major importance when charged species are involved. The experimentally studied alkyl–alkene niobocene and tantalocene d² complexes with coordination of the terminal olefin to the metal center showed NMR spectra containing two diastereomers with *endo* and *exo* coordination of the olefinic moiety in variable proportions. In all these compounds we have two chiral principles: the metal center and the enantiotopic face of the olefin and therefore two enantiomeric pairs of diastereomers could be involved (*endo* and *exo*). We first studied both *exo* and *endo* conformations for the five selected group 3, 4 and 5 transition metal complexes [M(η^5 -C₅H₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}CH₂Ph].

The calculated conformations **I(Sc,Bn)-exo** and **II(Sc,Bn)-endo** of the scandium complex (Fig. 2) are very close in energy with an energy difference ΔE of about 0.1 kcal mol⁻¹ (Table 1). In both cases, the olefinic unit is relatively far away from the metal center. The pendant olefin group in **I(Sc,Bn)-exo** is coordinated to the Sc in an unsymmetrical fashion, primarily through the terminal carbon atom C1 (Sc–C1 2.856 Å, Sc–C2 3.252 Å). In **II(Sc,Bn)-endo**, the Sc–C separations are still larger and the main part of the coordination consists of the interaction with the terminal carbon atom C1 (Sc–C1 2.903 Å, Sc–C2 3.327 Å). The chelating alkene is tipped significantly from the equatorial plane containing the metal center and perpendicular to that defined by the metal center and the centroids of the two Cp rings, in such a way that the dihedral angle C3(Me)–Sc–C1–C2 is 56.8°.

Turning to the coordination geometries of the other d⁰ complexes with group 4 cationic Zr and Hf centers, we observe that the olefinic unit is now bound closer to the metal center, indicating a stronger bonding interaction (Fig. 3). Also, the metal bound C=C bond is now slightly more elongated. This is a first indication of the enhanced

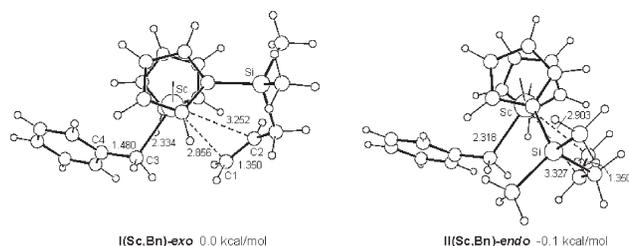


Fig. 2 Optimized geometries **I(Sc,Bn)-exo** and **II(Sc,Bn)-endo** of the scandium complex [Sc(η^5 -C₅H₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}-CH₂Ph].

stabilizing influence of electrostatic effects on this particular bonding interaction. Nevertheless, the almost symmetrical coordination of the olefin observed for the zirconium compound **II(Zr,Bn)-endo** (Zr–C1 2.796 Å, Zr–C2 2.865 Å) is disfavored by 5.4 kcal mol⁻¹ over the **I(Zr,Bn)-exo** conformation and its unsymmetrical bonding mode (Zr–C1 2.608 Å, Zr–C2 3.125 Å). This suggests that the electronic stabilization between the olefin and the zirconium center is less important than the overall steric influences.

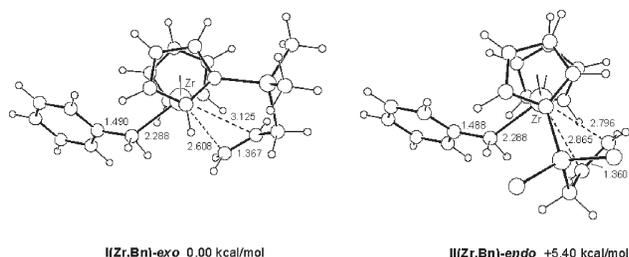


Fig. 3 Optimized geometries **I(Zr,Bn)-exo** and **II(Zr,Bn)-endo** of the zirconium complex $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{-CH}_2\text{Ph}]^+$.

For Nb and Ta, where backbonding is possible, we find in both conformations C1 and C2 very close to the metal center with M–C bond distances in the range of 2.297–2.431 Å and a substantially elongated C=C bond between 1.425 Å and 1.444 Å to form a sort of metallacyclopropane system (Fig. 4). Compared to the relative high energy differences between the *exo* and *endo* geometries of 5–6 kcal mol⁻¹ calculated for the group 4 transition metal complexes, the *exo* conformations of the Nb and Ta complexes are only slightly favored over the *endo* ones by only 1.2 and 1.0 kcal mol⁻¹.

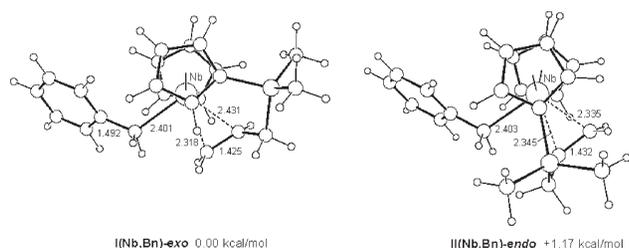


Fig. 4 Optimized geometries **I(Nb,Bn)-exo** and **II(Nb,Bn)-endo** of the niobium complex $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{-CH}_2\text{Ph}]$.

Fig. 5 shows the energy levels of the frontier molecular orbitals for the three complexes **I(Sc,Bn)-**, **I(Zr,Bn)-**, and **I(Nb,Bn)-exo**. The three well known frontier metal orbitals 1a₁, 1b₂ and 2a₁ of C_{2v} MCP₂ complexes are hybrid metal orbitals interacting with high p atomic orbital character of the benzyl group to form a σ bond (HOMO for **I(Sc,Zr)**), and with the π orbital of the olefin as the dative bond (LUMO for **I(Sc,Zr)** and HOMO for **I(Nb)**). The back-bonding from the d² niobium center is established by the HOMO of **I(Nb)** with the π* orbital of the olefin.

The mechanism for the interconversion of the *exo* and *endo* diastereomers was expected to involve (i) dissociation of the olefin,

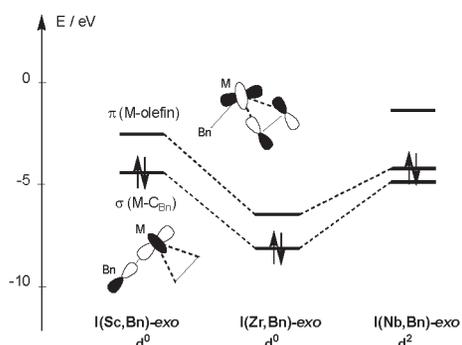
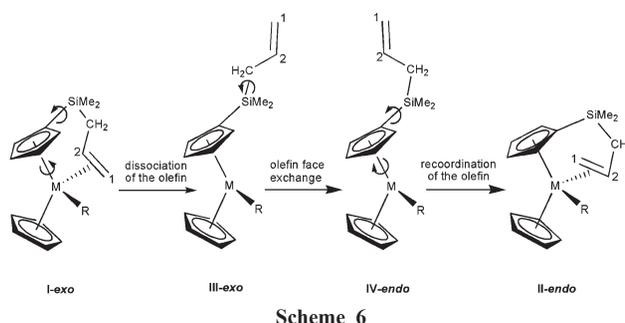


Fig. 5 Energy levels of frontier molecular orbitals for the *exo* conformations of the three complexes **I(Sc-Bn)**, **I(Zr,Bn)** and **I(Nb,Bn)**.

(ii) rotation of the cyclopentadienyl ring, (iii) rotation of the pendant group around the Si–C and C–C bonds, (iv) recoordination of the alkene through the opposite enantioface. Thus further calculations were carried out on different conformations of the pendant olefin. To obtain reference energies for the olefin face exchange, we optimized two different conformations **III** and **IV** for each complex with the olefin not bound to the metal center. The fully optimized geometries **III** and **IV** are interconverted by simple rotation of the pendant group around the C(Cp)–Si bond starting from the previous stable conformations **I** and **II**. Then, we assumed that the olefin enantioface seen by the metal center is unchanged during the processes **I-exo** → **III-exo** and **II-endo** → **IV-endo**, and that the olefin face exchange occurs during **III-exo** → **IV-endo** by rotation of the CH₂–CH=CH₂ fragment around the Si–C bond (Scheme 6).



The coordination geometry for the open complexes **III(Bn)-exo** suggests that the benzyl ligand is bound to the metal center *via* three carbon atoms (Figs. 6–8). The separations lie in the ranges 2.338–2.863, 2.358–2.636, 2.337–2.617, 2.330–2.601 and 2.324–2.594 Å for the Sc, Zr⁺, Hf⁺, Nb, and Ta complexes, respectively. Similar separations are also found for **IV(Bn)-endo** complexes in the ranges 2.341–2.800 (Sc), 2.352–2.633 (Zr⁺), 2.332–2.616 (Hf⁺), 2.322–2.585 (Nb), and 2.309–2.574 (Ta).

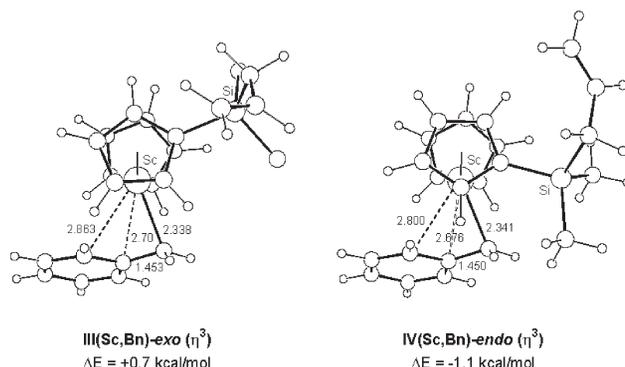


Fig. 6 Optimized geometries **III(Sc,Bn)-exo** (η^3) and **IV(Sc,Bn)-endo** (η^3) of the scandium complex $[\text{Sc}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{-CH}_2\text{Ph}]$.

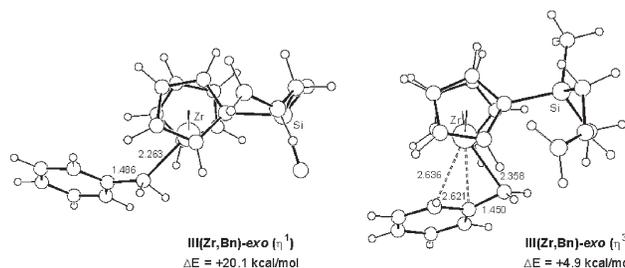


Fig. 7 Optimized geometries **III(Zr,Bn)-exo** (η^1) and **III(Zr,Bn)-exo** (η^3) of the zirconium complex $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{-CH}_2\text{Ph}]^+$.

The second highest filled molecular orbital of the niobium complex **III(Nb,Bn)-exo** depicted in Fig. 9 clearly shows the η^3 -coordination mode of the benzyl unit. Analyzing the reaction energies **I** → **III**, we obtain values of 0.7, 4.9, 6.6, 15.2 and

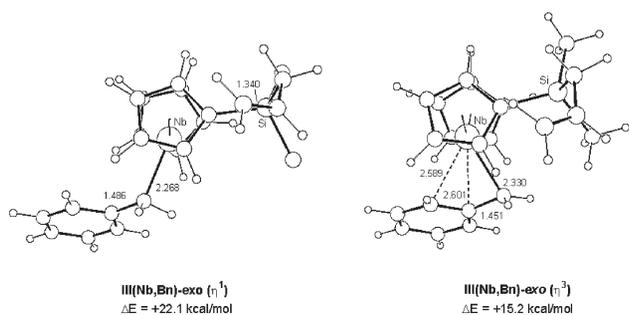


Fig. 8 Optimized geometries **III(Nb,Bn)-exo** (η^1) and **III(Nb,Bn)-exo** (η^3) of the niobium complex $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{CH}_2\text{Ph}]^+$.

18.6 kcal mol⁻¹ for Sc, Zr⁺, Hf⁺, Nb and Ta, respectively (Fig. 10). Comparing the values for the d⁰ complexes, we see that the coordination of the olefin in **I(Sc,Bn)-exo** is really weak and not really preferred over the η^3 -coordination of the benzyl, and that the electrostatic contribution, which stabilizes the Zr⁺-complex is estimated to about 5 kcal mol⁻¹. For the neutral group 5 metal complexes, where electrostatic interactions are of minor importance, we have a larger stabilization of 15.2 and 18.6 kcal mol⁻¹, mainly due to backbonding into the π^* orbital.

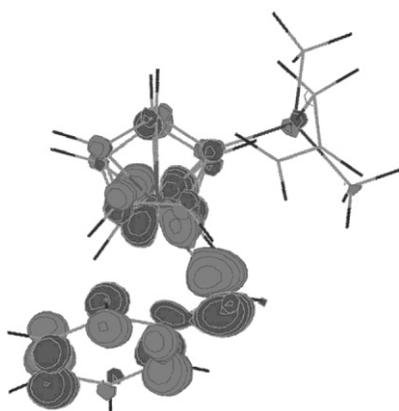


Fig. 9 MOLDEN plot of the second highest occupied molecular orbital of the optimized geometry **III(Nb,Bn)-exo** (η^3) of the niobium complex $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{CH}_2\text{Ph}]$.

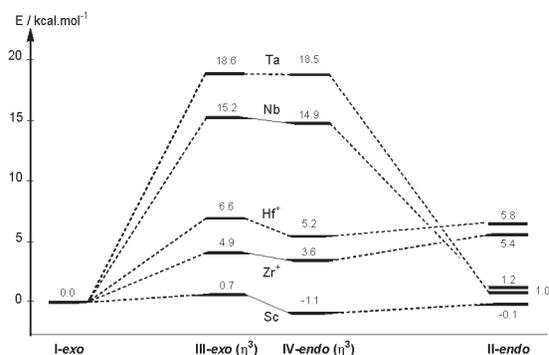


Fig. 10 Relative energies (kcal mol⁻¹) calculated for different conformations of complexes $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{CH}_2\text{Ph}]$ with M = Sc, Zr⁺, Hf⁺, Nb and Ta.

We calculated also a different conformation of the non-olefin coordinated complex having additionally an η^1 -coordinated benzyl ligand. The optimized geometries led to relatively high energetic barriers, depending on whether we take into account this conformation (about 15 to 20 kcal mol⁻¹ for Hf and Zr) or the η^3 -benzallylic intermediates (about 5 to 7 kcal mol⁻¹). From our point of view the η^1 conformations are too “artificial”, because in solution such molecules would be stabilized by interactions with surrounding solvent molecules. In the gas phase optimized η^1 -benzallylic geometries, the transition metals try to compensate the vacancy left by the olefin by agostic interactions with hydrogens from the H_2CSiMe_3

Table 2 Relative energies (kcal mol⁻¹) for different conformations of complexes $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{CH}_3]$ with M = Sc, Zr⁺, Hf⁺, Nb and Ta

Conformation	M=Sc	Zr ⁺	Hf ⁺	Nb (5)	Ta (8)
I(Me)-exo	0.0	0.0	0.0	0.0	0.0
II(Me)-endo	0.5	0.2	-0.1	-0.4	-0.6
III(Me)-open exo	4.6	16.7	17.6	22.7	22.6
IV(Me)-open endo	4.1	15.6	16.7	21.6	22.1

or H_2CPh groups. Consequently, η^3 binding seems to be more appropriate for the estimation of the energetic barriers.

When single sets of resonances were observed at 193 K for the cationic group 4 metal derivatives low *exo/endo* interconversion energies are expected and the calculated low energetic barriers of 4.9 and 6.6 kcal mol⁻¹ for $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{CH}_2\text{Ph}]$ with M = Zr⁺ and Hf⁺, respectively, support this picture. The *exo-endo* interconversions are thus expected to be fast on the NMR time scale, even at very low temperatures, and should therefore show averaged signals in a wide temperature range. Concerning the group 5 metal complexes a decoordination of the olefin would involve breakage of the metallacyclopropane with strong backbonding interactions. Furthermore the vacancy of the olefin cannot fully be compensated with a η^3 -benzallylic rearrangement. Consequently, higher energetic barriers are observed for the Nb and Ta complexes (15–19 kcal mol⁻¹) despite relatively small thermodynamic differences between the *exo* and *endo* diastereomers. In addition the calculated differences in energy between *exo* and *endo* are actually too small (less than 1.2 kcal mol⁻¹ for Bz compounds) to predict a preference for any conformer.

The influence of the η^3 -coordination mode of the benzyl ligand has been studied comparing the previous results with DFT calculations for the methyl complexes $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{CH}_3]$ (M = Sc, Zr⁺, Hf⁺, Nb and Ta) (Table 2). Except for the scandium complex, for which the energetic barrier between *exo* and *endo* remains relatively low (4.6 kcal mol⁻¹), we observe higher relative energies between the coordinated and noncoordinated olefin states. In fact, a stabilizing influence of the η^3 -coordinated benzyl group can not be found in comparison with the methyl substituted system. Rather we find a preference for the already seen agostic interactions between the metal centers and hydrogens from H_2CSiMe_3 or H_2CPh . Based on the very small thermodynamic energy differences between the *exo* and *endo* conformers (less than 0.6 kcal mol⁻¹) together with the relatively high kinetic barriers (16–23 kcal mol⁻¹), we therefore expect for all group 4 and 5 metal complexes the presence of two sets of signals in the ¹H NMR spectra corresponding to the *endo/exo* diastereomers, irrespective of the averaged resonances for the benzallylic group 4 (d⁰) metal complexes. The ¹H NMR spectra of the related methyl substituted cationic species showed at 193 K the expected mixtures of *exo-endo* diastereomers, but unfortunately the complexity of the spectra observed between 193 and 253 K prevented an assignment to the respective structures.

Conclusions

The work presented herein outlines the synthesis of a new type of chloro- and alkyl-dicyclopentadienyl niobium and tantalum d² complexes $[\text{M}(\eta^5\text{-Cp})\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH=CH}_2)\}\text{X}]$ (M = Nb, Ta; Cp = C₅H₅, X = Me, CH₂Ph, CH₂SiMe₃ and M = Ta, Cp = C₅Me₅, X = Cl, Me, CH₂Ph, CH₂SiMe₃) containing the alkene moiety of an allyldimethylsilyl group tethered to one of the cyclopentadienyl rings. The success of the synthesis of all of these alkyl compounds is based on the facile reduction of the starting dichloro metal(IV) complexes $[\text{M}(\eta^5\text{-Cp})\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH=CH}_2)\}\text{Cl}_2]$ (Cp = C₅H₅, M = Nb **1**, Ta **2**, Cp = C₅Me₅, M = Ta **3**) when they were treated with different alkylating agents. Reduction with Na/Hg was required to isolate the chloro tantalum derivative.

¹H NMR studies demonstrate that two *endo/exo* diastereoisomers are simultaneously formed for all of these compounds and their inter-

conversion by alkene dissociation/association processes does not take place, as their ^1H NMR spectra are temperature independent and do not show spin exchange between 193 and 343 K. This behaviour is in agreement with the high energetic barriers required for breaking the metallacyclopropane system with strong back-bonding interactions through a η^3 -benzallylic rearrangement, as evaluated by DFT theoretical calculations for Nb and Ta benzyl complexes (15–19 kcal mol $^{-1}$), in spite of the relatively small thermodynamic differences (less than 1.2 kcal mol $^{-1}$) between the *exo* and *endo* diastereomers. These barriers are much higher than those found for related Zr^+ and Hf^+ cationic derivatives (4.9 and 6.6 kcal mol $^{-1}$) for which rapid spin exchange between *exo/endo* diastereomers was observed at 193 K.

Neither ligand promoted migration of the alkyl group to the alkene moiety nor insertion of CO and CNR into the metal–alkyl bond was observed. Addition of these ligands always results in displacement of the coordinated alkene with formation of neutral $[\text{M}(\eta^5\text{-Cp})\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-CH}=\text{CH}_2)\}\text{XL}]$ niobium(III) and tantalum(III) compounds. However formation of the imido hydride complex $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{H}(\text{NtBu})]$ was observed when the corresponding chloro derivative was treated with LiNHtBu .

Experimental

General remarks

All experiments were carried out under argon using a Vacuum Atmospheres glove box or standard Schlenk techniques. Hydrocarbon solvents and THF were distilled from Na/benzophenone and stored under argon prior to use. Complexes $[\text{M}(\eta^5\text{-Cp})\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_2]$ (Cp = C_5H_5 , M = Nb **1**, Ta **2**, Cp = C_5Me_5 , M = Ta **3**) were prepared by methods reported 11 previously. NMR spectra were recorded at 20 °C on Unity-300 and Unity Plus 500 instruments in Teflon-valved tubes. ^1H and ^{13}C NMR chemical shifts were measured relative to the resonances of C_6D_6 used as solvent. Coupling constants are reported in Hz. C, H, and N analyses were carried out with a Perkin-Elmer 240 C analyzer.

$[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\}\text{Cl}]$ (**4**). A solution of $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_2]$ (**3**) (1.005 g, 1.82 mmol) in toluene (75 cm 3) was added to 10% Na/Hg (0.042 g, 1.82 mmol) and the mixture was stirred for 60 h at room temperature. NaCl was separated by filtration and the solvent was removed under vacuum from the resulting green solution. The residue was extracted into hexane (50 cm 3) and the solution was concentrated to 10 cm 3 and cooled at -40 °C to give a mixture of (**4-*exo*** + **4-*endo***) (0.610 g, 1.18 mmol, 65%) as a yellow green solid (Found: C, 46.30; H, 5.96%. $\text{C}_{20}\text{H}_{30}\text{ClSiTa}$ requires C, 46.65; H, 5.87%); (**4-*endo***): δ_{H} (C_6D_6) 0.25, 0.27 (2s, $2 \times 3\text{H}$, SiMe_2), 1.00 (dd, $^2J = 6.5$ Hz, $^3J = 11.0$ Hz, 1H, =CH $_2$), 1.39 (m, 1H, =CH), 1.49 (s, 15H, C_5Me_5), 1.59 (dd, $^2J = 6.5$ Hz, $^3J = 11.5$ Hz, 1H, =CH $_2$), 3.12 (dd, $^2J = 14.5$ Hz, $^3J = 4.5$ Hz, 1H, SiCH_2), 3.86 (dd, $^2J = 14.5$ Hz, $^3J = 3.0$ Hz, 1H, SiCH_2) and 4.02, 4.65, 6.15, 6.35 (4m, $4 \times 1\text{H}$, C_5H_4); δ_{C} (C_6D_6) 0.3, 0.5 (SiMe_2), 11.6 (C_5Me_5), 32.2 (SiCH_2), 38.3 (=CH $_2$), 49.4 (=CH), 93.6, 97.1, 109.9, 135.6 (C_5H_4), 105.8 (C_5H_4 *ipso*) and 108.1 (C_5Me_5). (**4-*exo***): δ_{H} (C_6D_6) 0.04, 0.13 (2s, $2 \times 3\text{H}$, SiMe_2), 0.90 (dd, $^2J = 7.0$ Hz, $^3J = 10.5$ Hz, 1H, =CH $_2$), 1.53 (s, 15H, C_5Me_5), 1.81 (m, 1H, =CH), 1.91 (dd, $^2J = 7.0$ Hz, $^3J = 12.0$ Hz, 1H, =CH $_2$), 2.13 (dd, $^2J = 15.0$ Hz, $^3J = 6.5$ Hz, 1H, SiCH_2), 2.49 (dd, $^2J = 15.0$ Hz, $^3J = 5.0$ Hz, 1H, SiCH_2) and 4.14, 5.03, 5.50, 5.82 (4m, $4 \times 1\text{H}$, C_5H_4); δ_{C} (C_6D_6) -1.9 , 0.1 (SiMe_2), 11.9 (C_5Me_5), 30.1 (SiCH_2), 47.3 (=CH $_2$), 55.0 (=CH), 95.4, 108.6, 118.4, 120.4 (C_5H_4), 104.9 (C_5H_4 *ipso*) and 107.8 (C_5Me_5).

$[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\}\text{R}]$ (R = Me **5**, CH_2Ph **6**). A solution of MgCl_2 (R = Me 1.7 cm 3 , 5.1 mmol; R = CH_2Ph 2.55 cm 3 , 5.1 mmol) in THF was added at -78 °C to a solution of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_2]$ (**1**) (1.00 g, 2.55 mmol) in toluene (50 cm 3) The mixture was stirred for 16 h at room temperature. MgCl_2 was separated by filtration,

the solvent was removed under vacuum from the resulting brown solution and the residue was extracted into hexane (30 cm 3). The solution was concentrated to 10 cm 3 and cooled at -40 °C to give **5** (0.60 g, 1.80 mmol, 70%) and **6** (0.61 g, 1.45 mmol, 60%) as brown solids which were dried under vacuum.

(**5**): (Found: C, 56.93; H 6.73%. $\text{C}_{16}\text{H}_{23}\text{NbSi}$ requires C, 57.14; H 6.89%); δ_{H} (C_6D_6) 0.10, 0.18 (2s, $2 \times 3\text{H}$, SiMe_2), 0.27 (s, 3H, NbMe), 1.14 (dd, $^2J = 14.6$ Hz, $^3J = 8.2$ Hz, 1H, SiCH_2), 1.34 (dd, $^2J = 5.4$ Hz, $^3J = 11.8$ Hz, 1H, =CH $_2$), 1.50 (dd, $^2J = 5.4$ Hz, $^3J = 9.9$ Hz, 1H, =CH $_2$), 2.15 (dd, $^2J = 14.6$ Hz, $^3J = 7.5$ Hz, 1H, SiCH_2), 2.33 (m, 1H, =CH), 4.44 (s, 5H, C_5H_5) and 3.81, 4.61, 4.77, 5.21 (4m, $4 \times 1\text{H}$, C_5H_4); δ_{C} (C_6D_6) -3.5 , 1.6 (SiMe_2), 1.3 (NbMe), 28.2 (SiCH_2), 41.5 (=CH $_2$), 48.0 (=CH), 91.7, 98.2, 100.9, 119.6 (C_5H_4), 98.6 (C_5H_5) and 106.0 (C_5H_4 *ipso*).

(**6**): (Found: C, 64.38; H, 6.81%. $\text{C}_{22}\text{H}_{27}\text{NbSi}$ requires C, 64.07; H 6.60%); δ_{H} (C_6D_6) 0.08, 0.10 (2s, $2 \times 3\text{H}$, SiMe_2), 1.16 (dd, $^2J = 14.0$ Hz, $^3J = 7.6$ Hz, 1H, SiCH_2), 1.30 (dd, $^2J = 4.8$ Hz, $^3J = 12.0$ Hz, 1H, =CH $_2$), 1.41 (dd, $^2J = 4.8$ Hz, $^3J = 11.3$ Hz, 1H, =CH $_2$), 2.08 (dd, $^2J = 14.0$ Hz, $^3J = 6.0$ Hz, 1H, SiCH_2), 2.27, 2.63 (2d, $^2J = 9.2$ Hz $2 \times 1\text{H}$, NbCH_2Ph), 2.40 (m, 1H, =CH), 4.39 (s, 5H, C_5H_5), 3.88, 4.53, 4.61, 5.62 (4m, $4 \times 1\text{H}$, C_5H_4) and 6.99–7.29 (m, 5H, NbCH_2Ph); δ_{C} (C_6D_6) -3.4 , 1.3 (SiMe_2), 28.1 (SiCH_2), 38.1 (=CH $_2$), 42.2 (=CH), 52.1 (NbCH_2Ph), 92.6, 100.9, 101.5, 117.8 (C_5H_4), 98.8 (C_5H_5), 107.0 (C_5H_4 *ipso*), 121.5, 126.2, 129.2 and 129.5 (NbCH_2Ph).

$[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\}\text{CH}_2\text{SiMe}_3]$ (**7**). A solution of $\text{Li}(\text{CH}_2\text{SiMe}_3)$ (0.24 g, 5.2 mmol) in hexane (20 cm 3) was added to a solution of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_2]$ (**1**) (1.00 g, 2.55 mmol) in toluene (30 cm 3) at -78 °C. The mixture was stirred for 16 h at room temperature. LiCl was separated by filtration and the solvent was removed under vacuum from the resulting brown solution. The residue was extracted into hexane (50 cm 3) and the solution was evaporated to obtain **7** (0.67 g, 1.65 mmol, 65%) as a foamy brown solid (Found: C, 56.18; H, 7.72%. $\text{C}_{19}\text{H}_{31}\text{NbSi}_2$ requires C, 55.86; H, 7.65%); δ_{H} (C_6D_6) -0.6 , -0.15 (2d, $^2J = 13.4$ Hz, $2 \times 1\text{H}$, $\text{NbCH}_2\text{SiMe}_3$), 0.09, 0.14 (2s, $2 \times 3\text{H}$, SiMe_2), 0.18 (s, 9H, SiMe_3), 1.10 (dd, $^2J = 14.7$ Hz, $^3J = 8.7$ Hz, 1H, SiCH_2), 1.29 (dd, $^2J = 5.1$ Hz, $^3J = 11.7$ Hz, 1H, =CH $_2$), 1.42 (dd, $^2J = 5.1$ Hz, $^3J = 9.1$ Hz, 1H, =CH $_2$), 2.10 (dd, $^2J = 14.7$ Hz, $^3J = 6.9$ Hz, 1H, SiCH_2), 2.45 (m, 1H, =CH), 4.52 (s, 5H, C_5H_5), 3.70, 4.72(2) and 5.6 (4m, $4 \times 1\text{H}$, C_5H_4); δ_{C} (C_6D_6) -5.9 ($\text{NbCH}_2\text{SiMe}_3$), -3.6 , 2.0 (SiMe_2), 4.6 ($\text{NbCH}_2\text{SiMe}_3$), 27.9 (SiCH_2), 44.6 (=CH $_2$), 53.4 (=CH), 91.2, 101.1, 105.5, 117.4 (C_5H_4), 97.5 (C_5H_5) and 100.2 (C_5H_4 *ipso*).

$[\text{Ta}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{-}\eta^2\text{-CH}=\text{CH}_2)\}\text{R}]$ (R = Me **8**, CH_2Ph **9**). A solution of MgCl_2 (R = Me 1.40 cm 3 , 4.16 mmol; R = CH_2Ph 2.08 cm 3 , 4.06 mmol) in THF was added at -78 °C to a solution of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}_2]$ (**2**) (1.00 g, 2.08 mmol) in toluene (50 cm 3) The mixture was stirred for 16 h at room temperature. MgCl_2 was separated by filtration and the solvent was removed under vacuum from the resulting brown solution. The residue was extracted into hexane (30 cm 3) and the solution was evaporated and cooled to give **8** (0.42 g, 1.24 mmol, 60%) or **9** (0.51 g, 1.24 mmol, 60%) as foamy brown solids. (**8**): (Found: C, 45.52; H, 5.51%. $\text{C}_{16}\text{H}_{23}\text{SiTa}$ requires C, 45.28; H, 5.46%); δ_{H} (C_6D_6) 0.11, 0.17 (2s, $2 \times 3\text{H}$, SiMe_2), 0.37 (s, 3H, TaMe), 1.15 (dd, $^2J = 14.7$ Hz, $^3J = 7.2$ Hz, 1H, SiCH_2), 0.93 (dd, $^2J = 6.9$ Hz, $^3J = 10.8$ Hz, 1H, =CH $_2$), 1.32 (dd, $^2J = 6.9$ Hz, $^3J = 9.9$ Hz, 1H, =CH $_2$), 2.68 (dd, $^2J = 14.7$ Hz, $^3J = 7.5$ Hz, 1H, SiCH_2), 1.97 (m, 1H, =CH), 4.45 (s, 5H, C_5H_5) and 3.82, 4.58, 4.64, 5.28 (4m, $4 \times 1\text{H}$, C_5H_4); δ_{C} (C_6D_6) -7.0 (TaMe), -3.3 , 2.1 (SiMe_2), 29.2 (SiCH_2), 35.2 (=CH $_2$), 38.4 (=CH), 91.2, 98.9, 99.5, 120.3 (C_5H_4), 97.7 (C_5H_5) and 106.4 (C_5H_4 *ipso*).

(**9**): (Found: C, 53.09; H 5.55%. $\text{C}_{22}\text{H}_{27}\text{SiTa}$ requires C, 52.80; H, 5.44%); δ_{H} (C_6D_6) 0.09, 0.10 (2s, $2 \times 3\text{H}$, SiMe_2), 0.91 (dd, $^2J = 6.6$ Hz, $^3J = 10.8$ Hz, 1H, =CH $_2$), 1.25 (dd, $^2J = 6.6$ Hz, $^3J = 10.2$ Hz, 1H, =CH $_2$), 1.36 (dd, $^2J = 14.7$ Hz, $^3J = 6.0$ Hz, 1H, SiCH_2), 2.08 (m, 1H, =CH), 4.43 (s, 5H, C_5H_5), 2.34, 2.68 (2d,

$^2J = 11.5$ Hz 2×1 H, TaCH₂Ph), 2.56 (dd, $^2J = 14.7$ Hz, $^3J = 7.2$ Hz, 1H, SiCH₂), 3.88, 4.53(2), 5.67, (4m, 4×1 H, C₅H₄) and 6.9–7.4 (m, 5H, TaCH₂Ph); δ_C (C₆D₆) –3.2, 1.6 (SiMe₂), 29.2 (SiCH₂), 35.7 (=CH₂), 38.1 (TaCH₂Ph), 42.0 (=CH), 92.3, 99.0, 100.1, 98.0 (C₅H₄), 108.1 (C₅H₄ *ipso*), 121.8 (C₅H₅), 126.1–129.2, (CH₂Ph) and 141.8 (TaCH₂Ph *ipso*).

[Ta(η^5 -C₅Me₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}R] (R = Me **10**, CH₂Ph **11**). **Method 1.** A solution of MgClR (R = Me 1.82 cm³, 5.46 mmol; R = CH₂Ph 2.73 cm³, 5.46 mmol) in THF was added at –78 °C to a solution of [Ta(η^5 -C₅Me₅){ η^5 -C₅H₄SiMe₂(CH₂CH=CH₂)}Cl] (**3**) (1.00 g, 1.82 mmol) in toluene (50 cm³). The mixture was stirred for 16 h at room temperature. MgCl₂ was separated by filtration and the solvent was removed under vacuum from the resulting brown solution. The residue was extracted into hexane (30 cm³) and the solution was evaporated and cooled to give a mixture of (**10-endo** + **10-exo**) (0.48 g, 1.36 mmol, 75%) or (**11**) (0.78 g, 1.36 mmol, 75%) as green solids. (**10**): (Found: C, 51.16; H, 6.80%. C₂₁H₃₃SiTa requires C, 51.00; H, 6.73%). (**10-exo**): δ_H (C₆D₆) 0.07 (dd, $^2J = 7.7$ Hz, $^3J = 11.0$ Hz, 1H, =CH₂), 0.10, 0.16 (2s, 2×3 H, SiMe₂), 0.14 (s, 3H, TaMe), 1.04 (m, 1H, =CH), 1.42 (s, 15H, C₅Me₅), 1.25 (dd, $^2J = 7.7$ Hz, $^3J = 11.2$ Hz, 1H, =CH₂), 2.15 (dd, $^2J = 15.1$ Hz, $^3J = 5.2$ Hz, 1H, SiCH₂), 2.40 (dd, $^2J = 15.1$ Hz, $^3J = 7.7$ Hz, 1H, SiCH₂) and 4.48, 4.55, 4.65, 5.11 (4m, 4×1 H, C₅H₄); δ_C (C₆D₆) –0.2 (TaMe), –0.1, 0.01 (SiMe₂), 10.5 (C₅Me₅), 30.2 (SiCH₂), 38.7 (=CH), 40.7 (=CH₂), 96.5, 98.7, 103.6, 107.3 (C₅H₄), 103.0 (C₅Me₅) and 115.2 (C₅H₄ *ipso*).

(**10-endo**): δ_H (C₆D₆) 0.18, 0.23 (2s, 2×3 H, SiMe₂), 0.26 (dd, $^2J = 7.1$ Hz, $^3J = 11.3$ Hz, 1H, =CH₂), 0.33 (s, 3H, TaMe), 0.45 (m, 1H, =CH), 1.04 (dd, $^2J = 7.1$ Hz, $^3J = 10.6$ Hz, 1H, =CH₂), 1.39 (s, 15H, C₅Me₅), 2.58 (dd, $^2J = 14.8$ Hz, $^3J = 4.9$ Hz, 1H, SiCH₂), 3.38 (dd, $^2J = 14.8$ Hz, $^3J = 2.9$ Hz, 1H, SiCH₂) and 4.25, 4.38, 5.48, 5.98 (4m, 4×1 H, C₅H₄); δ_C (C₆D₆) –2.81 (TaMe), 0.43, 2.09 (SiMe₂), 10.53 (C₅Me₅), 25.9 (SiCH₂), 30.6 (=CH₂), 40.5 (=CH), 92.1, 103.6, 112.7, 123.9 (C₅H₄), 103.4 (C₅Me₅) and 95.2 (C₅H₄ *ipso*).

(**11**): (Found: C 56.72, H 6.35%. C₂₇H₃₇SiTa requires C, 56.83; H, 6.54%); δ_H (C₆D₆) –0.10, 0.02 (2s, 2×3 H, SiMe₂), 0.36 (dd, $^2J = 6.9$ Hz, $^3J = 10.7$ Hz, 1H, =CH₂), 1.21 (dd, $^2J = 6.9$ Hz, $^3J = 10.6$ Hz, 1H, =CH₂), 1.17 (m, 1H, =CH), 1.39 (s, 15H, C₅Me₅), 1.69, 1.88 (2d, $^2J = 7.8$ Hz, 2×1 H, TaCH₂Ph), 1.75 (dd, $^2J = 15.3$ Hz, $^3J = 4.9$ Hz, 1H, SiCH₂), 3.20 (dd, $^2J = 15.3$ Hz, $^3J = 2.9$ Hz, 1H, SiCH₂), 4.11, 4.59, 4.82, 5.12 (4m, 4×1 H, C₅H₄) and 7.32–7.42 (m, 5H, TaCH₂Ph); δ_C (C₆D₆) –1.8, –0.5 (SiMe₂), 10.8 (C₅Me₅), 25.3 (TaCH₂Ph), 29.3 (SiCH₂), 39.3 (=CH₂), 42.3 (=CH), 95.1, 102.4, 104.9, 112.0 (C₅H₄), 104.7 (C₅Me₅), 123.0 (C₅H₄ *ipso*) and 121.4 (TaCH₂Ph).

Method 2. A solution of MgClCH₂Ph (0.5 cm³, 1.0 mmol) in THF was added to a solution of [Ta(η^5 -C₅Me₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}Cl] (**4**) (0.50 g, 0.97 mmol) at –78 °C and the mixture was stirred for 16 h at room temperature. MgCl₂ was separated by filtration and the solvent was removed under vacuum from the resulting brown solution. The residue was extracted into hexane (50 cm³) and the solution was concentrated to 10 cm³ and cooled at –40 °C to give **11** (0.39 g, 0.70 mmol, 70%) as a green solid.

[Ta(η^5 -C₅Me₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}CH₂SiMe₃] **12**. **Method 1.** A solution of Li(CH₂SiMe₃) (0.25 g, 2.72 mmol) in hexane (20 cm³) was added to a solution of [Ta(η^5 -C₅Me₅){ η^5 -C₅H₄SiMe₂(CH₂CH=CH₂)}Cl] (**3**) (0.5 g, 0.908 mmol) in toluene (30 cm³) at –78 °C. The mixture was stirred for 16 h at room temperature. LiCl was separated by filtration and the solvent was removed under vacuum from the resulting brown solution. The residue was extracted into hexane (50 cm³) and the solution was evaporated and cooled to obtain **12** (0.51 g, 0.59 mmol, 65%) as a brown solid (Found: C, 51.13; H, 7.38%. C₂₄H₄₁Si₂Ta requires C, 50.87; H, 7.29%); δ_H (C₆D₆) –1.12, 0.76 (2d, $^2J = 11.0$ Hz, 2×1 H, TaCH₂SiMe₃), 0.00 (m, 2H, =CH₂), 0.16, 0.20 (2s, 2×3 H, SiMe₂), 0.48 (s, 9H, SiMe₃), 0.90 (m, 1H, =CH), 1.37 (s, 15H, C₅Me₅), 2.20 (dd, $^2J = 15.2$ Hz, $^3J = 6.2$ Hz, 1H, SiCH₂), 2.54 (dd,

$^2J = 15.2$ Hz, $^3J = 4.6$ Hz, 1H, SiCH₂), 4.62(2) and 5.27, 5.46 (4m, 4×1 H, C₅H₄); δ_C (C₆D₆) –1.5, –0.1 (SiMe₂), –0.4 (TaCH₂SiMe₃), 5.5 (TaCH₂SiMe₃), 11.2 (C₅Me₅), 30.7 (SiCH₂), 36.1 (=CH₂), 40.1 (=CH), 97.4, 100.8, 102.4, 107.7 (C₅H₄), 105.1 (C₅Me₅) and 118.1 (C₅H₄ *ipso*).

Method 2. A solution of Li(CH₂SiMe₃) (0.091 g, 0.97 mmol) in hexane (20 cm³) was added to a solution of [Ta(η^5 -C₅Me₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}Cl] (**4**) (0.5 g, 0.97 mmol) in hexane (30 cm³) at –78 °C. The mixture was stirred for 16 h at room temperature. LiCl was separated by filtration and the solvent was removed under vacuum from the resulting brown solution to obtain **12** (0.55 g, 0.73 mmol, 75%) as a foamy brown solid.

[M(η^5 -C₅R₅){ η^5 -C₅H₄SiMe₂(CH₂-CH=CH₂)}XL] **13a–13d**, **14a–14g**. The synthesis of all these compounds and full details of their structural characterization are given in the ESI.†

[Ta(η^5 -C₅Me₅){ η^5 -C₅H₄SiMe₂(CH₂-CH=CH₂)}H(N^tBu)] **15**. C₆D₆ (0.4 cm³) was added to a mixture of LiN^tBu (4.6 mg, 0.116 mmol) and [Ta(η^5 -C₅Me₅){ η^5 -C₅H₄SiMe₂(CH₂- η^2 -CH=CH₂)}Cl] (**4**) (30 mg, 0.058 mmol) into a NMR tube. After 24 h at room temperature **15** was the unique product in solution. δ_H (C₆D₆) 0.45, 0.44 (2s, 2×3 H, SiMe₂), 1.14 (s, 9H, CMe₃), 1.86 (d, $^3J = 8.4$ Hz, 2H, SiCH₂), 1.95 (s, 15H, C₅Me₅), 4.73, 5.44, 5.75, 6.11 (4m, 4×1 H, C₅H₄), 4.98 (m, 2H, =CH₂), 5.91 (m, 1H, =CH) and 5.95 (s, 1H, TaH); δ_C (C₆D₆) –1.4, –1.5 (SiMe₂), 12.9 (C₅Me₅), 25.6 (SiCH₂), 113.3 (=CH₂), 97.7, 106.1, 109.8, 110.8 (C₅H₄), 135.5 (=CH), 113.4 (C₅Me₅) and 115.5 (C₅H₄ *ipso*).

Computational details

Density functional theory (DFT) calculations were performed with the TURBOMOLE program package, version 5.5.²⁴ The Vosko–Wilk–Nusair²⁵ local density approximation (LDA) and the generalized gradient approximation (GGA) with corrections for exchange and correlation according to Becke²⁶ and Perdew²⁷ (BP86) were used for all calculations. The TURBOMOLE approach to DFT GGA calculations is based on the use of Gaussian-type-orbitals (GTO) as basis functions. Geometries were optimized within the framework of the RI-J approximation²⁸ using accurate triple- ζ valence basis sets augmented by one polarization function TZV(P)²⁹ for all elements. Relativistic effective core potentials were employed to model the energetically deep-lying and chemically mostly inert 1s–3d core electrons of the zirconium and niobium atoms, and 1s–4f core electrons of the hafnium and tantalum atoms. Single-point calculations with the ESCF program³⁰ of the same TURBOMOLE package have followed the geometry optimizations to check the instability of the models and no negative eigenvalues were found. Optimized geometries and final energies are presented in the ESI.†

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