Alkyl–\(\eta^2\)-alkene niobocene and tantalocene complexes with the allyldimethylsilyl–\(\eta^2\)-cyclopentadienyl ligand: synthesis, NMR studies and DFT calculations†

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Group 5 metal complexes \([\text{M}(\eta^2\text{C}_2\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}==\text{CH}_2\text{C}_5\text{H}_5})\text{X}] (\text{M} = \text{Nb}, \text{X} = \text{Me}, \text{CH}_3\text{Ph}, \text{CH}_3\text{SiMe}_3; \text{M} = \text{Ta}, \text{X} = \text{Me}, \text{CH}_3\text{Ph})\) and [Ta(\eta^2\text{C}_2\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}==\text{CH}_2\text{C}_5\text{H}_5)]X \((X = \text{Cl}, \text{Me}, \text{CH}_3\text{Ph}, \text{CH}_3\text{SiMe}_3)\) containing a chelating alkene ligand tethered to a cyclopentadienyl ring have been synthesized in high yields by reduction with Na/Hg \((X = \text{Cl})\) and alklylation with reductive elimination \((X = \text{alkyl})\) of the corresponding metal(\(\text{iv}\)) dichlorides \([\text{M}(\eta^2\text{C}_2\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}==\text{CH}_2\text{C}_5\text{H}_5})\text{Cl} 2\text{Cl}\] \((\text{M} = \text{Nb}, \text{X} = \text{Me}, \text{Ta}, \text{X} = \text{Me}, \text{Me}, \text{CH}_3\text{SiMe}_3, \text{M} = \text{Ta})\). These chloro– and alkyl–alkene coordinated complexes react with CO and isocyanides \([\text{CNBu}, \text{CN}(\text{2,6-Me}_2\text{C}_6\text{H}_3})\]) to give the ligand-substituted metal(\(\text{iii}\)) compounds and similar CO and CNR insertions have been extensively studied\(^1-3\) and the behaviour of \(\text{ansa}\)-metallocenes in comparison with their non-bridged systems has been reported recently\(^4\).

Related chloro–alkene group 5 metal(\(\text{iii}\)) compounds have occasionally been singularly isolated by reduction of dichloro-metallocenes in the presence of olefin,\(^5\) but relatively few alkyl–alkene compounds have been reported. Ligand promoted olefin insertion into the niobium–hydrido bond of permethylniobocene \([\text{NbCp}_2\text{SiMe}_3\text{CH}_2\text{CH}==\text{CH}_2\text{H}(\text{NbBu})]\) has been reported only for small ligands \((\text{CO}, \text{CNMe})\),\(^6\) whereas the related niobocene complexes have been shown to afford either ligand-trapped alkyl compounds,\(^5\text{c,}5\text{d}\) or the olefin substitution hydrido products.\(^5\text{e}\) Severe restrictions were also found for the permethyltantalocene complex\(^7\) whereas the related tantalocene \([\text{TaCp}_2\text{SiMe}_3\text{CH}_2\text{CH}==\text{CH}_2\text{H}(\text{NbBu})]\) compound reacted with excess ethylene to give the trapped ethyl–ethylene complex at elevated temperatures\(^8\) and similar CO and CNR promoted insertions have been shown to afford a group of ligand-trapped tantalocene alkyl \([\text{TaCp}_2\text{RL}]\) complexes.\(^9\)

Attempts to induce similar olefin insertion and to trap the resulting alkyl compounds failed when \(\text{ansa}\)-metallocene olefin hydrides were used.\(^6\text{a}\)

In this study we report the synthesis of the chloro– \([\text{TaCp}_2\text{SiMe}_3\text{CH}_2\text{CH}==\text{CH}_2\text{C}_5\text{H}_5})\text{Cl}\] and alkyl–alkene coordinated niobium and tantalum derivatives \([\text{M}(\eta^2\text{C}_2\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}==\text{CH}_2\text{C}_5\text{H}_5})\text{Cl}] (\text{M} = \text{Nb}, \text{Ta}; \text{R} = \text{H}, \text{Me})\), obtained from the dichloro metal(\(\text{iv}\)) compounds \([\text{M}(\eta^2\text{C}_2\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}==\text{CH}_2\text{C}_5\text{H}_5})\text{Cl}]\). The NMR behaviour of these compounds is compared with 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. ‡ NMR data of the dimethylsilylallyl moiety for complexes 4-12 in \text{CD}_2\text{Cl}_2 \text{at} 20 \text{°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(Ⅲ) complexes \([\text{M}(\eta^5-C_5\text{H}_5\text{Me}_2-(\text{CH}_2\text{=CH=CH}_2))\text{Cl}] \) (M = Nb, Ta, Cp = C_5\text{Me}_5, M = Ta) 3 were prepared previously by the reaction of the monocyclopentadienyl compounds with the corresponding lithium cyclopentadienides and simultaneous reduction with Na/Hg.\textsuperscript{11} Related reduction of toluene solutions of 1 and 2 with Na/Hg gave brown solids, presumably chloride bridged\textsuperscript{12} 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 \([\text{Ta}(\eta^5-C_5\text{Me}_5)\eta^1-\text{C}_2\text{H}_3\text{SiMe}_2-(\text{CH}_2\text{=CH=CH}_2))\text{Cl}] \) 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.

Addition of 1 equiv. of MgRCl (R = Me, CH\textsubscript{3}SiMe\textsubscript{3}) to the coordinated allyl group, nor could these species be observed spectroscopically. This reaction always resulted in formation of inseparable solids, presumably chlorine bridged\textsuperscript{12} 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 \([\text{Ta}(\eta^5-C_5\text{Me}_5)\eta^1-\text{C}_2\text{H}_3\text{SiMe}_2-(\text{CH}_2\text{=CH=CH}_2))\text{Cl}] \) 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.

\[ \text{Scheme 1} \]

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 alkylation 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, CH\textsubscript{3}Ph) or LiCH\textsubscript{3}SiMe\textsubscript{2} to toluene solutions of complexes 1–3 apparently did not allow isolation of the monoalkyl species with the free non-coordinated alkyl 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 alkylation agents, pure alkyl–alkene metal complexes \([\text{M}(\eta^5-C_5\text{H}_5\text{Me}_2-(\text{CH}_2\text{=CH=CH}_2))\text{R}] \) (M = Nb, R = Me 5, CH\textsubscript{3}Ph 6, CH\textsubscript{3}SiMe\textsubscript{2} 7; M = Ta, R = Me 8, CH\textsubscript{3}Ph 9 and \([\text{Ta}(\eta^5-C_5\text{Me}_5)\eta^1-\text{C}_2\text{H}_3\text{SiMe}_2-(\text{CH}_2\text{=CH=CH}_2))\text{Me}] \) 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(CH\textsubscript{3}Ph)\textsubscript{2}Cl and LiCH\textsubscript{3}SiMe\textsubscript{2} led to the formation of mixtures containing variable proportions of the chloro–alkene 4 and the corresponding alkyl–alkene complexes \([\text{Ta}(\eta^5-C_5\text{Me}_5)\eta^1-\text{C}_2\text{H}_3\text{SiMe}_2-(\text{CH}_2\text{=CH=CH}_2))\text{R}] \) (R = CH\textsubscript{3}Ph 11, CH\textsubscript{3}SiMe\textsubscript{2} 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 alkylation 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 alkylation 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 (CH\textsubscript{3}Ph and CH\textsubscript{3}SiMe\textsubscript{2}) and ring (C\textsubscript{6}H\textsubscript{5}Me\textsubscript{5}) substituents are present, and finally the chloro–alkene derivatives are easily alkylated. However formation of intermediate dialkyl complexes cannot be excluded.\textsuperscript{13}

Reactivity

All of the chloro–η\textsuperscript{3}-alkene 4 and alkyl–η\textsuperscript{3}-alkene complexes 5–12 described above react with CO and isocyanides CNBu and CN(2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{4})\textsubscript{2} to give the olefin substitution products as a new group of the very well known\textsuperscript{14} alkyl metal(Ⅲ) complexes \([\text{[M} \eta^5-\text{C}_5\text{H}_5\text{Me}_2-(\text{CH}_2\text{=CH=CH}_2))\text{X]} \) (M = Nb, R = H, X = CH\textsubscript{3}Ph, L = CO 13a, CNBu 13b; M = Ta, R = Me, X = CI, L = CO 14a, CNBu 14b, CN(2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{4}) 14c; X = Me, L = CO 14d; X = CH\textsubscript{3}Ph, L = CO 14e, CN(2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{4}) 14f; X = CH\textsubscript{3}SiMe\textsubscript{2}, L = CO 14g; L = CN(2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{4}) 14h) 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–14d and related chloro niobium(Ⅱ) derivatives (M = Nb, L = CO 13c, CNBu 13d) can also be obtained by reduction of the corresponding metal(Ⅲ) dichloro compounds with Na/Hg in the presence of the ligand. These compounds were characterized by elemental analysis and IR and \(^1\)H, \(^{13}\)C NMR spectroscopics. Full synthetic and structural data for compounds 13a–d and 14a–g are given in the ESI.\textsuperscript{1}

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 LiNH\textsubscript{2}Bu was monitored by \(^1\)H NMR spectroscopy in a Teflonvalved 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 \([\text{Ta} \eta^5-\text{C}_5\text{Me}_5] \eta^1-\text{C}_2\text{H}_3\text{SiMe}_2-(\text{CH}_2\text{=CH=CH}_2))\text{H(NH)(Bu)} \) 15. The \(^1\)H and \(^{13}\)C 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 (\( ^1\)H and \( ^{13}\)C\( (^1\)H)\)) for Me-Si groups and four (\( ^1\)H) and five (\( ^{13}\)C) signals for the silylated cyclopentadienyl ring. The hydride ligand is significantly shifted low field being observed as a singlet at \( \delta = 5.95 \) (see Experimental section). Although this is the region where the bridging Ta(\( \mu\)-H) hydride signals are observed for monocyclopentadienyln complexes containing bulky imido ligands,\(^{17} \) it was reported that this is also the region where the hydride signal of terminal Nb–H\(^-\) and Ta–H\(^-\) bonds are observed for this type of dicyclopentadienyl imido complexes. The difference between the \( ^{13}\)C quaternary and methyl carbon resonances of the tertbutylimido group is 30.8 ppm suggesting a linear disposition of the Nb–N–Bu ligand in complex 15.

**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–alkene (13, 14) niobocene and tantacone 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\( _5\)Si group and four multiplets (\( ^1\)H) and five signals (\( ^{13}\)C) for the ring system of the (\( ^{13}\)C-SiMe\(_3\)(allyl)) ligand. They also show one signal (\( ^1\)H, \( ^{13}\)C) for the (\( ^{13}\)C-H\(_3\)) (5–9, 13) and one singlet (\( ^1\)H) and two signals (\( ^{13}\)C) for the (\( ^{13}\)C-Me\(_3\)) ligands (4, 10–12, 14). In addition the expected singlets are observed for the Me–M (5, 8, 10, 14a), Me\( _5\)Si (7, 12, 14d), tBu (13b and 13d) and 2,6-Me\(_2\)-C\(_6\)H\(_4\) (14c, 14d, 14g) groups. The typical C\(_2\) local symmetry multiplets for C\(_6\)H\(_4\) and 2,6-Me\(_2\)-C\(_6\)H\(_4\) and the AB spin systems for the diastereotopic methylene protons of CH\(_2\)Ph and CH\(_2\)SiMe\(_2\) substituents were also observed in the \( ^1\)H NMR spectra.

**NMR studies related to the allylic Si–CH\(_2\)-CH=CH\(_3\) fragment.**

The most significant structural data are associated to the NMR behaviour observed for the Si–CH\(_2\)-CH=CH\(_3\) system. The \( ^1\)H NMR in CD\(_3\)OD for all complexes containing the free non-coordinated allylic moiety (Scheme 4, A) exhibit one multiplet at \( \delta = 5.6–5.9 \) (internal =CH\(^-\)), two multiplets at \( \delta = 4.9 \) (\( J_{\text{gem}} \approx 10 \) Hz, \( J_{\text{cis}} \approx 16 \) Hz, \( J_{\text{trans}} \approx 4 \) Hz) (terminal =CH\(^2\)H\(^2\)) and one doublet at \( \delta = 1.5–1.8 \) (\( J \approx 8 \) Hz) (SiCH\(_2\)H\(_2\)). This is consistent with the three \( ^{13}\)C signals observed at \( \delta = 134–136 \) (internal =CH\(_3\)), \( \delta = 113–114 \) (terminal =CH\(_2\)) and \( \delta = 25–26 \) (SiCH\(_3\)). The chemical shifts and coupling constants of these signals are very only slightly affected by the remaining substituents being almost the same for group 4 metal(iv)\(^{13} \) and for group 5 metal(\( \text{V}\)) 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 -CH=CH\(_2\) and Si–CH\(_2\) multiplets which appear at \( \delta = 2.5 \) and \( \delta = 1–4 \) 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 metalalyclop propane character reported\(^{13,16} \) for this type of compounds. Moreover, the direct C=H\(_2\) and C=H\(_2\) (\( J = 143–150 \) Hz) spin coupling constants found for the \( ^1\)H signals of the terminal and internal carbon atoms are also consistent with their sp\(^3\) hybridization, being smaller than the value reported\(^{17} \) for cyclo propane (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\(^{14} \) produce similar high-field shifts of the terminal =CH\(^2\)H\(_2\) olefinic protons whereas the internal =CH\(_2\) proton is remarkably shifted low-field to \( \delta = 7.30 \) ppm, demonstrating the high polarization of the olefinic system when it is coordinated to a d\(^{0}\) metal center.

The dichloro niobium(\( \text{V}\)) and tantalum(\( \text{V}\)) 1–3 and the dialky group 4 metal complexes \([\text{M}({\text{C}}_{5}{\text{R}}_{5})][\text{C}({\text{H}}_{3})_{2}\text{SiMe}_{3}\text{C}({\text{H}}_{3})\text{C}({\text{H}}_{2})\text{R}_{2}]\) 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 (C\(_2\)F\(_4\)) (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 enantiomericity 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.

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\(^4\) \(\text{IV}\) species\(^{13,16} \) this set of resonances has to be assigned to the averaged spectrum in the fast exchange regime occuring 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 \( ^1\)H NMR spectra of most of the d\(^2\) niobium(\( \text{III}\)) and tantalum(\( \text{III}\)) 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 but also prevented by formation of a rigid cyclic system with the cyclopentadienyl-pendant alkene. In addition a high barrier of activation 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 $^1$H and $^{13}$C 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.

Assignments of the signals observed in the $^1$H spectrum of complex 10 to the exo and endo stereoisomers was accomplished by NOE spectroscopy. Selective excitation (PGF WFG NOESY1D pulse sequence) of the Me-Ta resonance at $\delta$ 0.14 for the major stereoisomer (see Experimental section) afforded an enhancement in the two ring proton resonances at $\delta$ 4.48 and 5.11 of the $\eta^1$-C,H$_2$SiMe$_2$CH$_3$(C=CH$_2$) ligand and in one of the two terminal =CH$_2$ protons at $\delta$ 1.25. Similar excitation of the Me-Ta resonance at $\delta$ 0.33 for the minor component produced the enhancement in the resonances at $\delta$ 5.48 for only one of the ring protons, at $\delta$ 2.58 for one of the CH$_3$–Si protons and an almost insignificant enhancement in the resonance at $\delta$ 1.04 for one of the terminal =CH$_2$ 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 $^1$H 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 ($\lambda_{\text{H1-H2}}$) and $\gamma_{\text{H1-H2}}$, which mainly depend on the dihedral angles between the corresponding planes, whereas the negative values of the geminal $\gamma_{\text{H2-H3}}$ coupling constants and their chemical shifts are controlled by the electron-donor character of the ($\eta^1$-C$_3$H$_5$). $\gamma$'s and R' ligands. The short distances between the Me–Ta group and only one proton of the terminal CH$_3$ group observed for 10-exo in the NOESY spectra suggest that the C$_3$, C$_5$, Me and Ta atoms are not exactly coplanar.

Taking into account the large (more than two times) difference between the vicinal $\lambda_{\text{H1-H2}}$ 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 ($\lambda_{\text{H1-H2}}$ = 6.5 Hz) whereas the endo diastereomer would correspond to the major component ($\lambda_{\text{H1-H2}}$ = 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 $\eta^1$-C$_5$H$_5$ 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 reported previously that the geminal $\gamma_{\text{H1-H2}}$ 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 $^1$d$^3$ and $^2$d$^4$ silyl-bridged alkyl-alkene coordinated transition metal derivatives $[\text{M}(\eta^1$-C$_5$H$_5$)$\eta^1$-C$_2$H$_5$SiMe$_2$(CH$_3$-$\eta^2$-CH=CH$_2$)]$\text{CH}_3$]$\text{PH}$ with $\text{M} = \text{Sc, Zr, Hf, Nb}$ and $\text{Ta}$.

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*No local minimum could be found.

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 $^1$d$^3$ and $^2$d$^4$ silyl-bridged alkyl-alkene coordinated transition metal derivatives $[\text{M}(\eta^1$-C$_5$H$_5$)$\eta^1$-C$_2$H$_5$SiMe$_2$(CH$_3$-$\eta^2$-CH=CH$_2$)]$\text{CH}_3$]$\text{PH}$ with $\text{M} = \text{Sc, Zr, Hf, Nb}$ and $\text{Ta}$.

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

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

Fig. 2. Optimized geometries I(Sc,Bn)-exo and II(Sc,Bn)-endo of the scandium complex [Sc($\eta^1$-C$_5$H$_5$)$\eta^1$-C$_2$H$_5$SiMe$_2$(CH$_3$-$\eta^2$-CH=CH$_2$)]$\text{CH}_3$]$\text{PH}$. 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 model of the L$_3$M–olefin interaction involves $\sigma$-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 d$_0$ systems $\sigma$-donation is the only possible orbital interaction, whereas for d$_x$-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 d$_x$ 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 moieties 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 $[\text{M}(\eta^1$-C$_5$H$_5$)$\eta^1$-C$_2$H$_5$SiMe$_2$(CH$_3$-$\eta^2$-CH=CH$_2$)]$\text{CH}_3$]$\text{PH}$.

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 $\Delta E$ 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(Sc)–C1–C2–C3 is 56.8°.

Turning to the coordination geometries of the other d$_x$ 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
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 [Zr(η²-C₅H₅)(η²-C₅H₅SiMe₃(CH₂-η²-CH=CH₂)]²-CH₂Ph]²⁺.

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 [Nb(η²-C₅H₅)(η²-C₅H₅SiMe₃(CH₂-η²-CH=CH₂)]²-CH₂Ph]²⁺.

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 1a, 1b and 2a, of CₓMCₜ 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 p orbital of the olefin as the dative bond (LUMO for I(Sc,Zr) and HOMO for I(Nb)). The backbonding 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, (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 enantiomeric face. 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 enantiomeric face 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 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. 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).

Fig. 6 Optimized geometries II(Sc,Bn)-exo (η²) and IV(Sc,Bn)-endo (η²) of the scandium complex [Sc(η²-C₅H₅)(η²-C₅H₅SiMe₃(CH₂-η²-CH=CH₂)]²-CH₂Ph]²⁺.

Fig. 7 Optimized geometries II(Zr,Bn)-exo (η²) and III(Zr,Bn)-exo (η²) of the zirconium complex [Zr(η²-C₅H₅)(η²-C₅H₅SiMe₃(CH₂-η²-CH=CH₂)]²-CH₂Ph]²⁺.

The second highest filled molecular orbital of the niobium complex III(Nb,Bn)-exo depicted in Fig. 9 clearly shows the η¹-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
18.6 kcal mol\(^{-1}\) for Sc, Zr\(^{2+}\), Hf\(^{2+}\), Nb and Ta, respectively (Fig. 10).

Comparing the values for the \(d^8\) complexes, we see that the coordination of the olefin in I(Sc,Bn)-exo is really weak and not really preferred over the \(\eta^2\)-cooordination of the benzyl, and that the electrostatic contribution, which stabilizes the Zr\(^{2+}\)-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 \(\pi^*\) orbital.

The influence of the \(\eta^1\)-cooordination mode of the benzyl ligand has been studied comparing the previous results with DFT calculations for the methyl complexes [M(\(\eta^1\)-C\(_5\)H\(_5\))\(\eta^1\)-C\(_4\)H\(_8\)SiMe\(_2\)(CH\(_2\)-\(\eta^2\)-CH=CH\(_2\))CH\(_2\)SiMe\(_2\)]. Based on the very small thermodynamic energy differences between the exo and endo conformers (less than 0.6 kcal mol\(^{-1}\)), we observe higher relative energies between the coordinated and noncoordinated olefin states. In fact, a stabilizing influence of the \(\eta^1\)-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\(_2\)CSiMe\(_2\) or H\(_2\)C\(_2\)H groups. Consequently, \(\eta^1\) 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 [M(\(\eta^1\)-C\(_5\)H\(_5\))\(\eta^1\)-C\(_4\)H\(_8\)SiMe\(_2\)(CH\(_2\)-\(\eta^2\)-CH=CH\(_2\))CH\(_2\)SiMe\(_2\)] with M = Zr\(^{2+}\) and Hf\(^{2+}\), 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 decooordination 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 \(\eta^1\)-benzyllic 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.

Conclusions

The work presented herein outlines the synthesis of a new type of chloro- and alkyl-dicyclopentadienyl niobium and tantalum \(d^8\) complexes [M(\(\eta^1\)-C\(_5\)H\(_5\))\(\eta^1\)-C\(_4\)H\(_8\)SiMe\(_2\)(CH\(_2\)-\(\eta^2\)-CH=CH\(_2\))CH\(_2\)SiMe\(_2\)] (M = Nb, Ta; Cp = C\(_5\)H\(_5\), X = Cl, Me, CH\(_2\)Ph, CH\(_3\)SiMe\(_2\)) 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 [M(\(\eta^1\)-C\(_5\)H\(_5\))\(\eta^1\)-C\(_4\)H\(_8\)SiMe\(_2\)-(CH\(_2\)-\(\eta^2\)-CH=CH\(_2\))CH\(_2\)SiMe\(_2\)] (Cp = CH\(_2\)H, M = Nb) to the corresponding cationic group 4 metal complexes. The \(1^H\) NMR spectra of the related methyl substituted cationic species showed at 193 K the expected mixtures of exo-end diastereomers, but unfortunately the complexity of the spectra observed between 193 and 253 K prevented an assignment to the respective structures.

Table 2 Relative energies (kcal mol\(^{-1}\)) for different conformations of complexes [M(\(\eta^1\)-C\(_5\)H\(_5\))\(\eta^1\)-C\(_4\)H\(_8\)SiMe\(_2\)(CH\(_2\)-\(\eta^2\)-CH=CH\(_2\))CH\(_2\)SiMe\(_2\)] with M = Sc, Zr\(^{2+}\), Hf\(^{2+}\), Nb and Ta

<table>
<thead>
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<th>Conformation</th>
<th>M = Sc</th>
<th>Zr(^{2+})</th>
<th>Hf(^{2+})</th>
<th>Nb (5)</th>
<th>Ta (8)</th>
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<td>I(Me)-exo</td>
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<tr>
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<td>17.6</td>
<td>22.7</td>
<td>22.6</td>
</tr>
<tr>
<td>IV(Me)-openendo</td>
<td>4.1</td>
<td>15.6</td>
<td>16.7</td>
<td>21.6</td>
<td>22.1</td>
</tr>
</tbody>
</table>
conversion by alkene dissociation/association processes does not
result in formation of the imido hydride complex. Therefore formation of the imido hydride complex is not expected.

The solution was extracted into hexane and the residue was isolated by column chromatography on silica gel.

The NMR spectra were recorded at 20 °C on a 300-MHz spectrometer. Coupling constants are reported in Hz.

Chemical shifts were measured relative to the resonances of C$_6$D$_6$ and THF were distilled from Na/benzophenone
residue was extracted into hexane (50 cm$^3$) and cooled to −40 °C to give 5.60 g, 1.8 mmol (70%).

The solvent was removed under vacuum from the resulting brown 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) (0.61 g, 1.18 mmol, 65%) as a yellow green solid.

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

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(4-exo + 4-endo) (0.61 g, 1.18 mmol, 65%) as a yellow green solid.
The synthesis of all these compounds and full details of their structural characterization are given in the ESI.†

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References


