Intramolecular coordination of an alkene to a mixed dicyclopentadienyl benzyl zirconium cation studied by NMR spectroscopy

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Benzylation of [Zr(η^5-C_5H_5){η^5-$C_5H_4SiMe_2(CH_2CH{=}CH_2)$}$Cl_2$] 1 yields [Zr(η^5-$C_5H_5$){η^5-$C_5H_4SiMe_2$-$(CH_2CH{=}CH_2)$}$(CH_2C_6H_5)_2$] 2, which reacts with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ to generate the same cation, 3$^+$, which has been fully characterised by ^{1}H, ^{13}C NMR and ^{1}H DNMR spectroscopy.

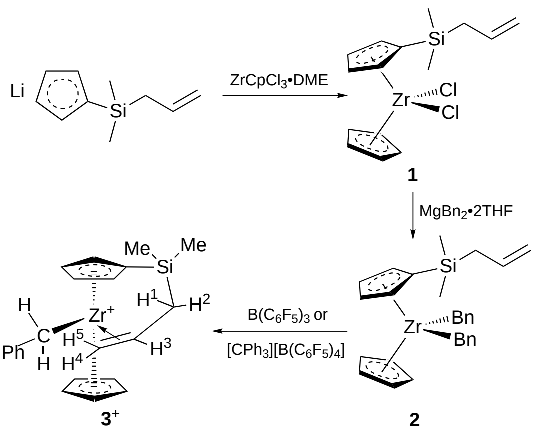
It is generally accepted[1] that a cationic 14-electron alkyl dicyclopentadienylzirconium complex of the type $[ZrCp_2R]^+$ stabilized by coordinative contact with a counter-ion $[R\text{-MAO}]^-$ (MAO = methylalumoxane), $[RB(C_6F_5)_3]^-$ or $[B(C_6F_5)_4]^-$ provides a route to $[ZrCp_2R(\text{alkene})]^+$, a productive, active, cationic polymerization catalyst. Numerous synthetic studies involving the characterization of dicyclopentadienyl alkyl cationic group 4 metal complexes and their catalytic activity in Ziegler–Natta polymerization processes, have recently been reported.[2] Many structural techniques have been used to investigate the formation of cationic species of this type and various theoretical methods[3] have been applied to calculate the kinetic and thermodynamic parameters of their transition states and intermediate species.

However, in spite of the many attempts made,[4] the crucial cationic d^0 metal–alkene complex has only been observed and studied by X-ray diffraction[5] in the zirconium complex $[ZrCp_2(OCMe_2CH_2CH_2CH{=}CH_2)]^+$, in which the alkenic double bond shows a rather weak interaction with the metal center. The isolation of dimethyl titanium[6a] and zirconium[6b] complexes containing the 1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl ligand has been reported, for which extensive low temperature NMR studies were unable to detect the alkene-coordinated metal complex. An yttrium pentenyl chelate has also been studied,[7] where the exchange between the diastereotopic C_5H_4Me ligands is proposed to occur *via* rapid and reversible alkene dissociation followed by rate limiting inversion of the pyramidal d^0 yttrium center. A related compound reported by Erker[8] was isolated by reaction of the butadiene zirconium complex $[ZrCp_2(C_4H_6)]$ with $B(C_6F_5)_3$, resulting in the formation of a betaine system in which an anionic allyl system is coordinated to the dicyclopentadienyl zirconium cation.

In order to favour alkene coordination we decided to synthesize zirconium complexes containing the more electron-withdrawing di(methyl)(allyl)silyl(cyclopentadienyl) ligand to create a more acidic metal center with a slightly longer and more fluxional pendant chain, owing to the bulkier silicon atom.

As shown in Scheme 1 the dichloro complex [Zr(η^5-C_5H_5){η^5-$C_5H_4SiMe_2(CH_2CH{=}CH_2)$}$Cl_2$] **1** was prepared† by reaction of the lithium salt of di(methyl)(allyl)silylcyclopentadiene[9] with stoichiometric amounts of $ZrCpCl_3\cdot$DME. Treatment of **1** with $MgBn_2\cdot2THF$ yielded the dibenzyl complex **2**.

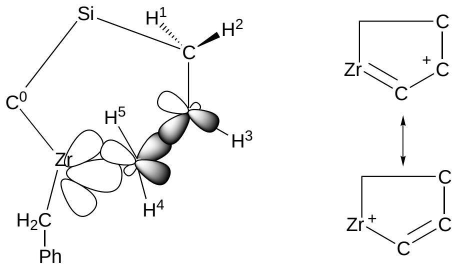
NMR spectra recorded after mixing 1 equiv. of either $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ with 1 equiv. of complex **2** in CD_2Cl_2 at −70 °C demonstrate the formation of the same 14-electron cationic species **3**$^+$. Characteristic methylene resonances of Ph_3CCH_2Ph (δ 3.90) and non-coordinated $[PhCH_2B(C_6F_5)_3]^-$ (δ 2.70, br) were observed, respectively.



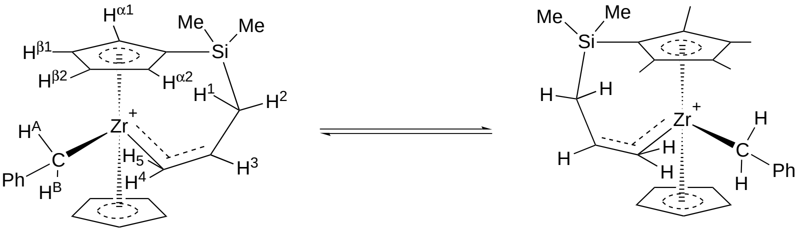
Scheme 1

Stabilization of this 14-electron cationic zirconium species is usually achieved by benzallylic coordination of the benzyl ligand, evidenced by the loss of the C_{2v} symmetry of the phenyl ring and a substantial difference between the ^{1}H chemical shifts for the two methylenic protons ($\Delta\delta$ = 2.80 ppm) observed[1c] in the solid by X-ray analysis and in solution by NMR spectroscopy at low temperatures. However, this behaviour is not observed in the ^{1}H NMR spectra of **3**$^+$ at 203 K which shows C_{2v} symmetry for the phenyl ring, an AB spin system (δ_{av} 3.13, $\Delta\delta$ = 0.27 ppm) for the two diastereotopic methylenic protons, two SiMe signals at δ 0.31 and 0.59, and four resonances at δ 5.74, 6.13, 6.35, 7.10 due to the CpSi ring protons, consistent with an asymmetric species. The ^{1}H NMR spectra of **3**$^+$ did not show a typical vinylic signal between δ 4.9 and 5.6, but instead five new multiplets were observed at δ 1.81, 2.05, 2.13, 2.78, 7.30. Table 1 summarizes the chemical shifts and proton–proton coupling constants for the allyl chain protons of complexes **2** and **3**$^+$.

All of the spin–spin coupling constants for H^3, H^4 and H^5 in complexes **2** and **3**$^+$ are very similar indicating that the sp^2 character of the alkenic carbon atoms is not lost. However the H^3 signal is shifted [$\Delta\delta = \delta(\mathbf{3}^+) - \delta(\mathbf{2})$] to low field ($\Delta\delta$ = +1.58 ppm) whereas the terminal H^4 and H^5 signals are displaced to high field ($\Delta\delta$ = −2.08 and −2.83 ppm, respectively); the CH_2Si resonance is split and also displaced to low field ($\Delta\delta$ = +0.38, +0.46 ppm). Similar behaviour is



Scheme 2



Scheme 3

Table 1 Important ^1H NMR data for complexes **2** and **3**$^+$ in CD_2Cl_2 at 203 K

	δ(SSCC, *J*/Hz)	
Assignment	**2**	**3**$^+$
H^1, H^2	1.66	2.05, 2.13
	(H^1, H^2–H^3 8.0)	(H^1–H^2 11.5)
		(H^1–H^3 10.5)
		(H^2–H^3 5.2)
H^3	5.72	7.30
	(H^3–H^4 10.5)	(H^3–H^4 8.80)
	(H^3–H^5 16.3)	(H^3–H^5 16.5)
H^4	4.86	2.78
	(H^4–H^5 3.8)	(H^4–H^5 4.0)
H^5	4.83	1.81

observed in the ^{13}C NMR spectra which show $\Delta\delta(CH{=}CH_2) = +36.2$, $\Delta\delta(CH{=}CH_2) = -22.7$, $\Delta\delta(CH_2Si) = +2.8$ and $\Delta\delta(C_{Cp}) = -3.1$ ppm. Displacement of the terminal alkenic CH_2 moiety signals to high field is consistent with its coordination to the metal atom. This interaction is stronger than that reported by Wu and Jordan[5] and may be interpreted as the result of the interaction of the σ-bonding alkene orbital with the vacant $2a_1$ zirconium orbital and simultaneous overlapping of the HOMO π alkene orbital with the vacant zirconium orbital of the same symmetry, b_2.

As shown in Scheme 2 these interactions result in delocalized electron density in the Zr–C–C system, similar to that observed for classical allyl cations, which is favoured by the known silicon effect[9] and can be described in terms of the resonance structures of Scheme 2, where the terminal alkenic carbon is in a well known pentacoordinate situation.[10] This description is consistent with the observed displacement of the CH= and $SiCH_2$ resonances to low field and of CH_2= resonances to high field.

Variable temperature ^1H NMR spectra show dynamic behaviour which implies an interchange between the signals of the CH_2Ph, CH_2Si, $(CH_3)_2Si$ and the $H^{\alpha1}$–$H^{\alpha2}$ and $H^{\beta1}$–$H^{\beta2}$ protons of the C_5H_4R ring, with little exchange in the Zr–C–C system. The assignment of the $H^{\alpha1}$–$H^{\alpha2}$ and $H^{\beta1}$–$H^{\beta2}$ signals was made from the results of saturation transfer experiments at 253 K and the spin–lattice relaxation time T_1 values measured at -213 K ($H^{\alpha1}$: δ 6.30, $T_1 = 1.67$ s; $H^{\alpha2}$: $\delta = 6.10$, $T_1 = 1.61$ s; $H^{\beta1}$: $\delta = 7.10$, $T_1 = 0.96$ s; $H^{\beta2}$: $\delta = 5.70$, $T_1 = 1.26$ s). The signal at δ 7.10 is assigned to the $H^{\beta1}$ proton located near the C_5H_5 moiety since is well known that proton relaxation times depend mainly on the number of adjacent protons and their distances. The $SiCH_2$ resonance is observed at 263 K as one doublet (^3J 8.3 Hz) due to spin–spin coupling with H^3. Coalescences of the $SiMe_2$ and CH_2Ph resonances are observed at 253 K with the same $\Delta G^\ddagger = 11.7$ kcal mol^{-1} (1 cal = 4.184 J) calculated for the collapse of two equally populated singlets and for an AB spin system, respectively. This indicates that both are associated with a unique dynamic process involving interconversion between two enantiomers through a transition state with C_s symmetry.

The kinetic parameters for the process shown in Scheme 3 ($\log A = 14.4 \pm 0.5$, $E_a = 13.4 \pm 0.54$ kcal mol^{-1}, $\Delta H^\ddagger = 12.9 \pm 0.53$ kcal mol^{-1}, $\Delta S^\ddagger = 5.0 \pm 2.3$ cal K^{-1} mol^{-1} and $\Delta G^\ddagger_{298\,K} = 11.4$ kcal mol^{-1}) obtained from ^1H DNMR data for exchange of the $SiMe_2$ groups are consistent with an intramolecular process with negligible variation of entropy and are in good agreement with theoretical data reported by Bercaw and coworkers[11] for $[MCp_2Me]^+$.

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Footnotes and References

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† Complex **1** was isolated *via* treatment of a THF solution of $(C_5H_5)SiMe_2CH_2CH{=}CH_2$ (8.46 g, 42.0 mmol) with a 1.6 M solution of buthyllithium in hexane (28 ml, 45.0 mmol) for 3 h, and addition of the resulting solution to a suspension of $Zr(C_5H_5)Cl_3{\cdot}DME$ (14.9 g, 42 mmol) in THF (80 ml) and stirring for 18 h at room temp. Complex **2** was prepared as a yellow solid (yield 84%) by stirring a mixture of **1** (853 mg, 2.18 mmol) and $MgBn_2{\cdot}2THF$ (920 mg, 2.62 mmol) in diethyl ether (100 ml) for 18 h at room temp.

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