Journal of Organometallic Chemistry, 358 (1988) 169–183
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Reactions of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[Si(SiMe_3)_3]X$ (X = Cl, Me) complexes with carbon monoxide and the isocyanide $2,6\text{-}Me_2C_6H_3NC$. Crystal structure of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl$

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(Received May 23rd, 1988)

Abstract

The new tris(trimethylsilyl)silylzirconium derivative $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[Si(SiMe_3)_3]Cl$ (**1**) is prepared by reaction of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)ZrCl_2$ with $(THF)_3LiSi(SiMe_3)_3$. Mixed alkyl/silyl complex $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[Si(SiMe_3)_3]Me$ (**2**) is obtained after treatment of **1** with MeMgBr. Reactions of compounds **1** and **2** with carbon monoxide and $2,6\text{-}Me_2C_6H_3NC$ are described. Carbon monoxide inserts cleanly into the Zr–Si bond of **1**, giving the η^2-silaacyl $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[\eta^2\text{-}COSi(SiMe_3)_3]Cl$ (**3**). The reaction of **2** with CO proceeds via the intermediate $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[\eta^2\text{-}COSi(SiMe_3)_3]Me$ (**4**) to the enolate hydride $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[OC(=CH_2)Si(SiMe_3)_3]H$ (**5**). A mechanism for this rearrangement is proposed. This chemistry contrasts with that previously observed for $(\eta^5\text{-}C_5H_5)_2Zr[Si(SiMe_3)_3]Me$, which reacts with CO to cleanly give the stable acyl $(\eta^5\text{-}C_5H_5)_2Zr[Si(SiMe_3)_3](\eta^2\text{-}COMe)$. Methyl iodide and compound **5** react to give the iodide $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[OC(=CH_2)Si(SiMe_3)_3]I$ (**6**) and methane. The reaction of **5** with 2 equivalents of HCl provides a new synthetic route to an acylsilane, $MeCOSi(SiMe_3)_3$. Reactions of **1** and **2** with the isocyanide $2,6\text{-}Me_2C_6H_3NC$ give the insertion products $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl$ (**7**) and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Me]Si(SiMe_3)_3$ (**8**), respectively. Steric crowding in these compounds is evidenced by restricted rotation about the N–C(xylyl) bonds. An X-ray crystal structure of **7** has been determined. Crystals of **7** are monoclinic, $P2_1/c$, with a 18.276(6) Å, b 9.993(3) Å, c 21.550(5) Å, β 106.25(3)°; V 3779(2) Å^3, $Z = 4$, R_F 6.63%, R_{wF} 6.48%.

0022-328X/88/$03.50

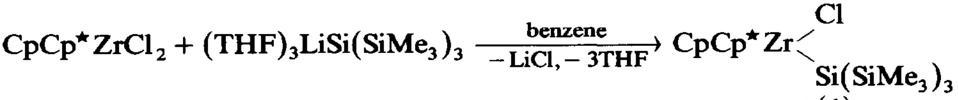
Introduction

Early transition metal silyl compounds are proving to have a rich reaction chemistry that is distinct from that of late transition metal silyl derivatives [1–16]. For example, early transition metal (d^0) silyl complexes are reactive toward insertions of unsaturated substrates into their M–Si bonds, whereas late metal silyls typically are not [3,12–16]. We are interested in the factors that influence this insertion chemistry, and have observed that the reactivity of early metal–silicon bonds varies considerably as the metal, and substituents at both the metal and silicon, are changed. Here we describe some insertion chemistry that has been observed for the mixed-ring zirconium silyls $CpCp^{\star}Zr[Si(SiMe_3)_3]Cl$ and $CpCp^{\star}Zr[Si(SiMe_3)_3]Me$ ($Cp = \eta^5\text{-}C_5H_5$; $Cp^{\star} = \eta^5\text{-}C_5Me_5$). These complexes differ markedly from the closely related species $Cp_2Zr[Si(SiMe_3)_3]Cl$ and $Cp_2Zr[Si(SiMe_3)_3]Me$ [12b] in their reactivities toward unsaturated compounds.

Results and discussion

Synthesis and characterization of tris(trimethylsilyl)silyl derivatives of (cyclopentadienyl)(pentamethylcyclopentadienyl)zirconium

The mixed-ring dichloride $CpCp^{\star}ZrCl_2$ reacts with $(THF)_3LiSi(SiMe_3)_3$ to afford the silylzirconium **1** in reasonable yield (eq. 1).



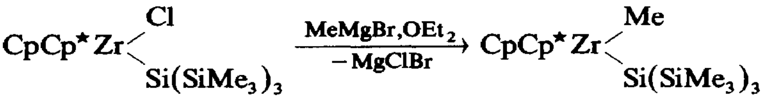
$$\mathrm{CpCp^{\star}ZrCl_2 + (THF)_3LiSi(SiMe_3)_3 \xrightarrow[-LiCl,\,-3THF]{benzene} CpCp^{\star}Zr\!\left\langle\begin{array}{l}Cl\\ Si(SiMe_3)_3\end{array}\right.} \tag{1}$$

(1)

Compound **1**, which was characterized by NMR, IR, and elemental analysis, has properties similar to the related silyls $Cp_2Zr(SiMe_3)Cl$ [11a] and $Cp_2Zr[Si(SiMe_3)_3]Cl$ [12b]. Like the latter two compounds, **1** is pentane soluble and red in color. NMR data for new compounds are given in Table 1.

Attempts were made to prepare other silyl derivatives of the type $CpCp^{\star}Zr(SiMe_3)X$ ($X = Cl$ or $Si(SiMe_3)_3$) by reactions of $CpCp^{\star}ZrCl_2$ and **1**, respectively, with $Al(SiMe_3)_3 \cdot OEt_2$ in benzene-d_6. However, after 2 days ^1H NMR spectra showed that no reactions had occurred.

The orange alkyl silyl derivative **2** was obtained in high yield by addition of one equivalent of MeMgBr to **1** in diethyl ether (eq. 2).



$$\mathrm{CpCp^{\star}Zr\!\left\langle\begin{array}{l}Cl\\ Si(SiMe_3)_3\end{array}\right. \xrightarrow[-MgClBr]{MeMgBr,OEt_2} CpCp^{\star}Zr\!\left\langle\begin{array}{l}Me\\ Si(SiMe_3)_3\end{array}\right.} \tag{2}$$

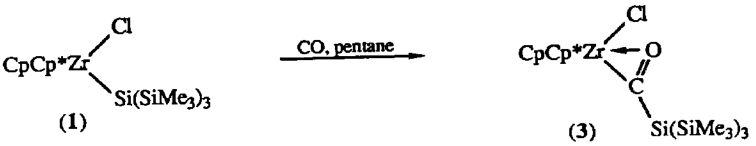
(1) **(2)**

In the solid state this compound is reasonably stable at room temperature for indefinite periods, but it was observed to slowly decompose in benzene-d_6 solution, producing the silane $HSi(SiMe_3)_3$ (by ^1H NMR). Although mixed alkyl/silyl complexes are in general rare [1,17], a number of related derivatives of zirconium are known [11b,12b,16,18].

Reactions of compounds 1 and 2 with carbon monoxide

When a pentane solution of **1** is stirred under 100 psi of CO for 1 h, a pink precipitate is formed. This solid is easily separated from the solvent by filtration.

Subsequent cooling of the filtrate to $-45\,^{\circ}\mathrm{C}$ provides pink crystals with spectroscopic properties that are identical to those of the precipitate, identified as the silaacyl complex **3** (eq. 3).



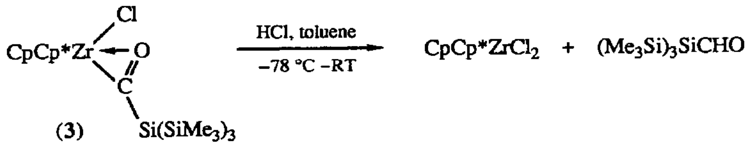
(3)

When this reaction was monitored by ^{13}C NMR using labeled ^{13}CO, three minor ^{13}CO-incorporation products were observed in addition to **3**, which was formed in over 70% yield. The side products in this reaction were not identified. Although **3** is stable indefinitely as a solid, it decomposes in solution over the course of a few days. There is also an apparent sensitivity to room light, since solutions of **3** undergo accelerated decomposition in the presence of light. Disilyl ketones are also known to be light sensitive in solution [19].

The unusual bright pink color of **3** is similar to that of the previously reported silaacyl $Cp_2Zr(\eta^2\text{-COSiMe}_3)Cl$ [12a,b]. Spectroscopic properties for **3** are also analogous to those observed for $Cp_2Zr(\eta^2\text{-COSiMe}_3)Cl$. ^{13}C-labeling studies revealed a relatively weak peak in the infrared spectrum of **3** at 1440 cm^{-1} that can be attributed to the $\nu(C{=}O)$ stretch. This carbonyl stretching frequency seems low relative to analogous zirconium acyls (1500–1550 cm^{-1}) [20], however it is close to values observed for other known η^2-silaacyls (1462–1503 cm^{-1}) [12,13,15,16]. The ^{13}C NMR shift of the carbonyl carbon of **3** (δ 382.79) is also characteristic of an η^2-silaacyl ligand in a d^0 transition metal complex [12,13,15,16].

Curiously, the silyl $Cp_2Zr[Si(SiMe_3)_3]Cl$ does not undergo an insertion reaction with CO to an appreciable extent under comparable conditions [12b]. A possible explanation for this difference in reactivity between **1** and $Cp_2Zr[Si(SiMe_3)_3]Cl$ is that increased steric interactions about the metal center promote CO insertion into the Zr–Si bond of **1**. A similar effect has been observed for $Cp_2Zr[CH(SiMe_3)_2]Me$, insertion of CO occurring exclusively into the bulkier Zr–C bond [20j].

Note that recently, silaacyl **3** was used in the synthesis of the first stable formylsilane, $(Me_3Si)_3SiCHO$ (eq. 4) [15].



(4)

When a pentane solution of **2** is stirred under 90 psi of CO an immediate color change from orange to pink occurs. This pink color is remarkably similar to that observed for **3**. Over the course of 1 h the initial pink color fades to afford the final beige product $CpCp^{\star}Zr[OC({=}CH_2)Si(SiMe_3)_3]H$ (**5**). This reaction was monitored by low temperature ^{13}C NMR, using ^{13}CO (ca. 1 atm) and dichloromethane-d_2 solvent. Incorporation of ^{13}CO was detected upon warming the sample to $-50\,^{\circ}\mathrm{C}$. At this temperature the new zirconium complex exhibited a singlet at δ -0.32 that can be assigned to a methyl ligand, ZrMe. This argues against initial insertion into the Zr–C bond, since this would be expected to give a doublet at ca. δ 2.2 for the

(Continued on p. 174)

Table 1

NMR data for new compounds

Compound	$^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR [a]		$^1\mathrm{H}$ NMR [b]		$^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR [c]	
$\mathrm{CpCp^*Zr[Si(SiMe_3)_3]Cl}$	$\mathit{Si}(\mathrm{SiMe_3})_3$	−87.30	$\mathrm{Si(CH_3)_3}$	0.50	$\mathrm{Si(CH_3)_3}$	6.54
(1)	$\mathrm{Si}(\mathit{Si}\mathrm{Me_3})_3$	−6.03	$\mathrm{C_5(CH_3)_5}$	1.83	$\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$	13.70
			$\mathrm{C_5H_5}$	6.04	$\mathrm{C_5H_5}$	113.55
					$\mathit{C}_5\mathrm{(CH_3)_5}$	122.95
$\mathrm{CpCp^*Zr[Si(SiMe_3)_3]Me}$	$\mathit{Si}(\mathrm{SiMe_3})_3$	−105.72	$\mathrm{ZrCH_3}$	−0.43	$\mathrm{Si(CH_3)_3}$	6.38
(2) [d]	$\mathrm{Si}(\mathit{Si}\mathrm{Me_3})_3$	−6.34	$\mathrm{Si(CH_3)_3}$	0.22	$\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$	13.49
			$\mathrm{C_5(CH_3)_5}$	2.04	$\mathrm{ZrCH_3}$	48.58
			$\mathrm{C_5H_5}$	6.12	$\mathrm{C_5H_5}$	112.11
					$\mathit{C}_5\mathrm{(CH_3)_5}$	120.46
$\mathrm{CpCp^*Zr[\eta^2\text{-}COSi(SiMe_3)_3]Cl}$			$\mathrm{Si(CH_3)_3}$	0.29	$\mathrm{Si(CH_3)_3}$	1.98
(3)			$\mathrm{C_5(CH_3)_5}$	1.73	$\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$	12.19
			$\mathrm{C_5H_5}$	5.70	$\mathrm{C_5H_5}$	110.58
					$\mathit{C}_5\mathrm{(CH_3)_5}$	117.26
					ZrCOSi	382.79
$\mathrm{CpCp^*Zr[\eta^2\text{-}COSi(SiMe_3)_3]Me}$			$\mathrm{ZrCH_3}$	−0.32	$\mathrm{Si(CH_3)_3}$	1.72
(4) [e]			$\mathrm{Si(CH_3)_3}$	0.30	$\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$	11.51
			$\mathrm{C_5(CH_3)_5}$	1.66	$\mathrm{ZrCH_3}$	18.61
			$\mathrm{C_5H_5}$	5.33	$\mathrm{C_5H_5}$	107.65
					$\mathit{C}_5\mathrm{(CH_3)_5}$	113.23
					ZrCOSi	395.36
$\mathrm{CpCp^*Zr[OC({=}CH_2)Si(SiMe_3)_3]H}$			$\mathrm{Si(CH_3)_3}$	0.35	$\mathrm{Si(CH_3)_3}$	1.74
(5)			$\mathrm{C_5(CH_3)_5}$	1.89	$\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$	12.19
			$\mathrm{CH_2}$	4.22, 4.34	$\mathrm{CH_2}$	103.71
			(^1J(C–H) 9.0, 6.3 Hz)		$\mathrm{C_5H_5}$	108.73
			ZrH	5.85	$\mathit{C}_5\mathrm{(CH_3)_5}$	118.37
			$\mathrm{C_5H_5}$	5.98	ZrOCSi	171.48

$\mathrm{CpCp^{*}Zr[OC({=}CH_2)Si(SiMe_3)_3]I}$	$Si(CH_3)_3$	0.38	$Si(CH_3)_3$	1.98
(6)	$C_5(CH_3)_5$	1.86	$C_5(\mathit{CH}_3)_5$	13.30
	CH_2	4.27, 4.32	CH_2	105.29
	C_5H_5	6.18	C_5H_5	113.37
			$\mathit{C}_5(CH_3)_5$	122.59
			ZrOCSi	173.34
$\mathrm{CpCp^{*}Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl}$	$Si(CH_3)_3$	0.27	$Si(CH_3)_3$	4.24
(7)	$C_5(CH_3)_5$	1.84	$C_5(\mathit{CH}_3)_5$	13.40
	$C_6H_3(C\mathit{H}_3)_2$	2.06, 2.50	$C_6H_3(\mathit{C}H_3)_2$	21.83, 23.06
	C_5H_5	5.91	C_5H_5	111.32
	C_6H_3	6.88(m)	C_6H_3	126.17, 129.65, 133.28, 147.79
			$\mathit{C}_5(CH_3)_5$	118.55
			ZrCNSi	272.40
$\mathrm{CpCp^{*}Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)CH_3]Si(SiMe_3)_3}$	$Si(CH_3)_3$	0.48	$Si(CH_3)_3$	7.82
(8)			$C_5(\mathit{CH}_3)_5$	13.47
	$C_6H_3(C\mathit{H}_3)_2$	1.68, 1.97	$C_6H_3(\mathit{C}H_3)_2$	18.84, 21.67, 23.68
			$NC\mathit{C}H_3$	
	NCH_3	2.08		
	$C_5(CH_3)_5$	1.75	C_5H_5	106.95
	C_5H_5	5.64	C_6H_3	125.62, 129.00, 131.44, 145.78
	C_6H_3	6.88(m)		
			$\mathit{C}_5(CH_3)_5$	116.48
			ZrCNSi	242.93

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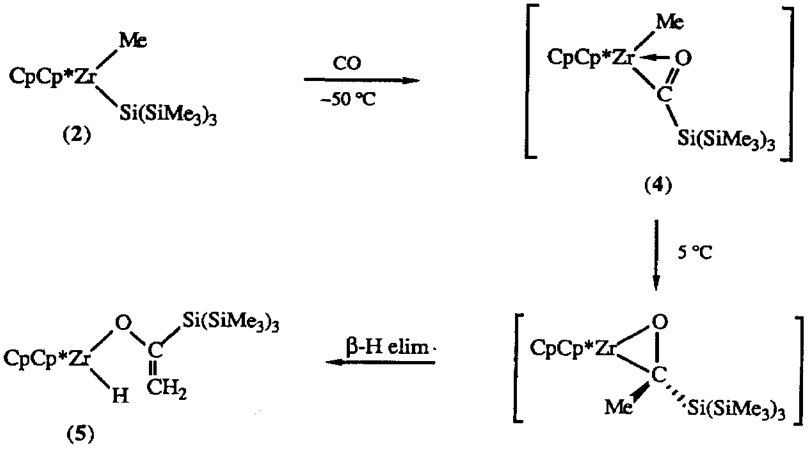
[a] Shifts in ppm, referenced to $SiMe_4$ (0.00 ppm) at 59.6 MHz and 22° C in benzene-d_6, except as noted. [b] Shifts in ppm, referenced to $SiMe_4$ (0.00 ppm) at 300 MHz and 22° C in benzene-d_6, except as noted. [c] Shifts in ppm, referenced to $SiMe_4$ (0.00 ppm) at 75.5 MHz and 22° C in benzene-d_6, except as noted. [d] NMR spectra taken in dichloromethane-d_2. [e] NMR spectra taken in dichloromethane-d_2 at -50° C.



Scheme 1

Zr(η^2-^{13}COMe) group [12b]. Consistent with the formation of an η^2-silaacyl group is the observation of a peak at δ 395.36 in the ^{13}C NMR spectrum ($-50\,^\circ$C) that corresponds to the incorporated ^{13}CO. This chemical shift is at much lower field (by ca. 70 ppm) than that of η^2-alkylacyls [20], but is in agreement with known early transition metal η^2-silaacyls [12,13,15,16]. The observations above provide good evidence for $\mathrm{CpCp^{\star}Zr[\eta^2\text{-}COSi(SiMe_3)_3]Me}$ (**4**) as an intermediate in the formation of **5**. Warming the sample to 5 °C resulted in extensive conversion of **4** to the final product **5**. No other intermediates were observed during this reaction.

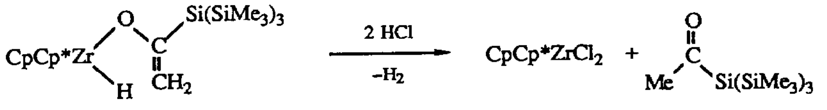
Enolate hydride **5** was isolated as beige crystals from pentane. Spectroscopic properties for **5** are similar to corresponding properties for the related compound $\mathrm{Cp_2^{\star}Zr[OC({=}CH_2)SiMes_2H]H}$ (Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$) [16]. The ^{1}H NMR spectrum of **5** exhibits a singlet at δ 5.98 (5 H, Cp), a singlet at δ 5.85 (1 H, ZrH), a singlet at δ 1.89 (15 H, Cp*), a singlet at δ 0.35 (27 H, $\mathrm{Si(SiMe_3)_3}$), and two singlets at δ 4.34 (1 H) and 4.22 (1 H) attributed to the vinylic hydrogens. When ^{13}CO is used to form **5**, the latter two resonances are split into doublets exhibiting coupling constants ^2J(C–H) of 6.3 and 9.0 Hz, respectively. The infrared spectrum of **5** contains bands at 1580 (Zr–H), 1540 (C=C), 1350 (C–Si), and 1180 (C–O) cm^{-1}. In ^{13}C-labeled **5**, the last three bands shift to 1520, 1340 and 1155 cm^{-1}, respectively.

A proposed mechanism for formation of **5** from **2** and CO is given in Scheme 1. The initially formed η^2-silaacyl complex undergoes a carbon–carbon coupling reaction within the coordination sphere of the metal forming an acylsilane adduct of zirconium. Finally, β-hydrogen elimination in this intermediate provides the enolate hydride **5**. Similar rearrangements have been observed in the reactions of $\mathrm{Cp_2^{\star}\overline{ZrCH_2CH_2CH_2CH_2}}$ [20c] and $\mathrm{Cp_2^{\star}Zr(SiMes_2H)Me}$ [16] with CO.

It is of interest to note here that in other analogous alkyl/silyl-zirconocene derivatives $\mathrm{Cp_2Zr(SiR_3)R'}$, e.g. $\mathrm{Cp_2Zr(SiMe_3)Me}$, preferential CO insertion into the Zr–C bond occurs [18]. For the closely related compound $\mathrm{Cp_2Zr[Si(SiMe_3)_3]Me}$, insertion of CO affords the acyl $\mathrm{Cp_2Zr[Si(SiMe_3)_3](\eta^2\text{-}COMe)}$ exclusively, and the latter compound is stable indefinitely in solution [12b]. Presently, preferential CO insertion into the Zr–Si bond of a mixed alkyl/silyl complex has been observed only for 2 and $Cp^*_2Zr(SiMes_2H)Me$ [16]. In addition, in these cases the insertion reaction is rapidly followed by rearrangement to an enolate hydride derivative. A common feature of the latter two compounds is the presence of pentamethylcyclopentadienyl ligands, which are more sterically demanding and more electron donating than a cyclopentadienyl ligand. Whatever the reason for the greater reactivity of the mixed alkyl/silyl complexes possessing Cp^* ligands, it seems clear that relatively simple changes in substituents in these systems can drastically alter the observed chemistry. Note that for the alkyl/germyl titanocene derivative $Cp_2Ti(GePh_3)Me$, CO insertion into the Ti–C bond occurs, giving $Cp_2Ti(GePh_3)(\eta^2\text{-}COMe)$ [21].

Reaction of 5 with methyl iodide produces $CpCp^*Zr[OC(=CH_2)Si(SiMe_3)_3]I$ (6) with evolution of methane (by ^1H NMR). As expected, 6 exhibits a ^1H NMR spectrum that is similar to that for 5, with the notable absence of a resonance due to ZrH.

Treatment of 5 with 2 equivalents of HCl gas affords the acylsilane $MeCOSi(SiMe_3)_3$ in near quantitative yield by ^1H NMR (eq. 5).



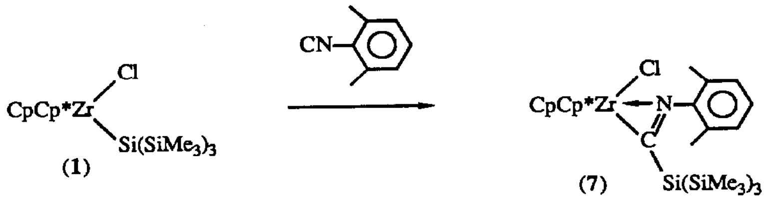
(5)

(5)

NMR resonances for $MeCOSi(SiMe_3)_3$ were compared to those of an authentic sample [22]. Thus, η^2-silaacyl complexes provide a new synthetic route to acylsilanes, which are important intermediates in organic synthesis [23]. Presently relatively few methods are available for the synthesis of acylsilanes. Note that the method of eq. 5 represents the zirconium-mediated conversion of silyllithium, Grignard reagent, and CO to an acylsilane.

Reactions of compounds 1 and 2 with 2,6-$Me_2C_6H_3NC$

Insertion of the isocyanide 2,6-$Me_2C_6H_3NC$ into the Zr–Si bond of 1 occurs readily to form the η^2-iminosilaacyl 7 (eq. 6).



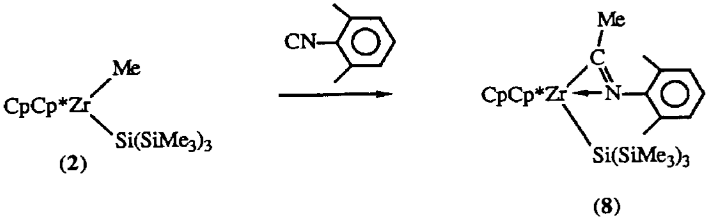
(1) (7)

(6)

The two xylyl methyl groups of 7 are inequivalent by ^1H NMR (δ 2.06 and 2.50), and no coalescence of the two peaks was observed up to 80 °C. This is consistent with a high degree of steric crowding in the molecule, leading to restricted rotation about the nitrogen–xylyl bond (see description of the structure of 7 below). In the less hindered dicyclopentadienyl compound $Cp_2Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl$ the xylyl methyl groups are equivalent at room temperature by ^1H NMR [12b]. In contrast, $Cp^*_2Zr[C(N\text{-}2,6\text{-}Me_2C_6H_3)Me]Me$ appears to be so crowded that the iminoacyl group is forced to bond in an η^1-coordination mode [24]. Restricted rotation in the germyl derivative $Cp_3U[C(N\text{-}2,6\text{-}Me_2C_6H_3)GePh_3]$ has also been observed [25].

The imine carbon of 7 resonates at δ 272.40 (^{13}C NMR), which is in close agreement (± 5 ppm) with other recently discovered iminosilaacyls [12b]. The $\nu(C{=}N)$ stretching frequency ($1530\ cm^{-1}$) is slightly shifted to longer wavelength relative to the similar, less hindered iminosilaacyls $Cp_2Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl$ ($1555\ cm^{-1}$) and $Cp_2Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)SiMe_3]Cl$ ($1558\ cm^{-1}$) [12b].

In sharp contrast to isoelectronic carbon monoxide, $2,6\text{-}Me_2C_6H_3NC$ inserts exclusively into the Zr–C bond of 2 to afford $CpCp^{*}Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Me]Si(SiMe_3)_3$ (8) in 60% yield (eq. 7).



(7)

The chemical shift for the iminoacyl methyl protons (δ 2.08) in the ^1H NMR spectrum, and the ^{13}C NMR chemical shift for the iminoacyl carbon (δ 242.93) are in agreement with other alkyliminoacyl complexes [20j,24,26,27]. The low frequency $\nu(C{=}N)$ stretch ($1580\ cm^{-1}$) observed in the infrared spectrum of **8** is consistent with η^2-coordination of the iminoacyl [20j,24,26,27]. As a solid, **8** has a half-life of about 6 weeks, decomposing to an unidentified mixture of products.

The difference in reactivity between CO and CNR toward **2** seems surprising since these substrates are isoelectronic. Presently we do not fully understand this discrepancy, but an explanation based on steric effects can be made. In sterically congested mixed alkyl/silyl complexes, insertion of CO into the Zr–Si bond can be preferred if this accomplishes relief of steric strain. Since the isocyanide $2,6\text{-}Me_2C_6H_3NC$ contains a relatively bulky xylyl group, insertion into the Zr–Si bond of **2** might not relieve steric stress to the same extent as the analogous reaction with CO. Thus, the small steric relief that might be attained by insertion of CNR into the Zr–Si bond may be offset by the electronic preference for insertion into the Zr–C bond of **2**.

Description of the structure of $CpCp^{*}Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl$ *(7)*

In order to better understand electronic and steric factors, the X-ray crystal structure of 7 was determined. The molecular structure is shown in Fig. 1 with the atom labeling scheme. Crystal and data collection parameters are summarized in Table 2. Tables 3 and 4 list positional parameters and bond distances and angles, respectively. The structure consists of well-separated molecules with no abnormally short intermolecular contacts.

The imino nitrogen and carbon atoms of the iminosilaacyl ligand are both bonded directly to the zirconium atom. Bond angles within the Zr–N(1)–C(16) triangle are similar ($\pm 4°$) to the corresponding values obtained for η^2-iminoacyls [26] and for the η^2-silaacyl $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$ [12a,b]. The Zr–C(16) bond length of 2.309(10) Å is somewhat greater than values observed for Zr–C(iminoacyl)

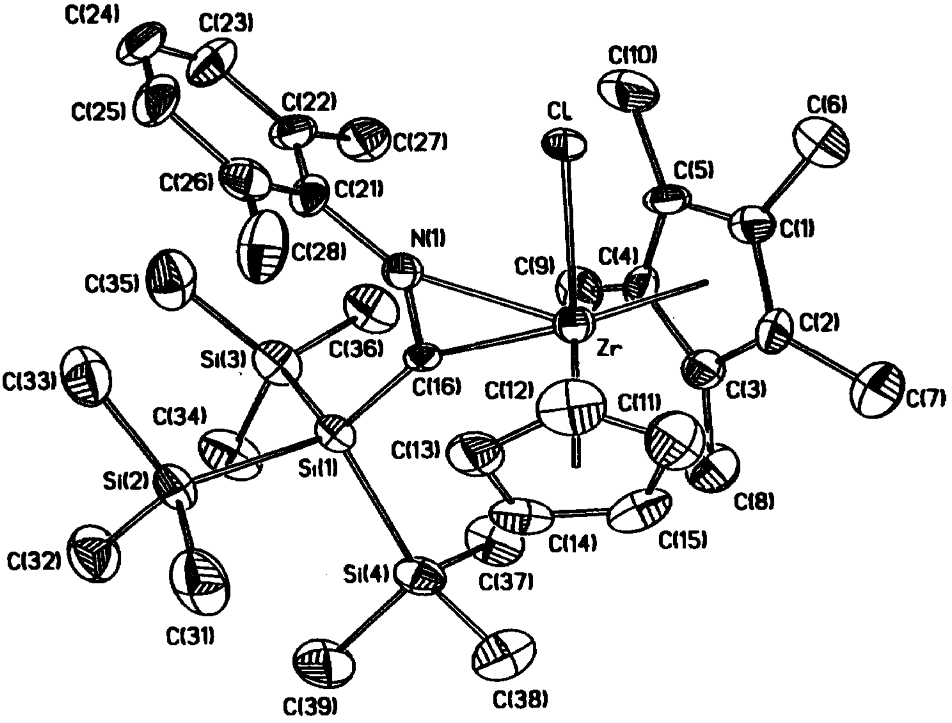


Fig. 1. ORTEP view of $CpCp^{*}Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl$ (7).

distances (2.23–2.25 Å) [26b,28]. The Zr–C(iminoacyl) distance in the closely related $Cp_2Zr[\eta^2\text{-}C(NMe)CHPh_2]Me$ is 2.247(5) Å [28]. The Zr–N(1) distance (2.249(8) Å) and the C(16)–N(1) distance (1.320(12) Å) of 7 are also slightly longer

Table 2

Crystal data collection and refinement for 7

(a) Crystal parameters			
formula	$C_{33}H_{56}ClNSi_4Zr$	β, deg	106.25 (3)
crystal system	monoclinic	V, Å^3	3779 (2)
space group	$P2_1/c$	Z	4
a, Å	18.276 (6)	crystal dimens, mm	0.22 × 0.31 × 0.38
b, Å	9.993 (3)	D(calcd), g cm^{-3}	1.24
c, Å	21.550 (5)	μ(Mo-K_α), cm^{-1}	5.0
(b) Data collection			
temp., °C	23	scan speed, deg min^{-1}	variable, 6–20
radiation, λ	Mo-K_α (0.71073 Å)	unique data	4940 (5449 collected)
monochromator	graphite	unique data obsd	3017, $5\sigma(F_o)$
diffractometer	Nicolet R3m/μ	std rflns	3 stds/197 rflns
2θ scan range, deg	4–45	scan technique	Wyckoff
(c) Refinement			
data/parameter	8.3	$(\Delta\rho)$max, eÅ^{-3}	1.02 (near Cp)
GOF	1.344	R_F, %	6.63
Δ/σ	0.023	R_{wF}, %	6.48

Table 3

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U^a
Zr	5331.8(5)	532(1)	1025.0(4)	31.0(3)
Cl	3526(1)	1672(2)	−63(1)	28.3(8)
Si(1)	2043(2)	1347(3)	2130(1)	32(1)
Si(2)	2137(2)	3595(3)	2504(1)	41(1)
Si(3)	707(2)	856(3)	1906(2)	49(1)
Si(4)	2590(2)	−50(3)	3047(1)	46(1)
C(1)	3633(5)	−1483(11)	298(4)	43(4)
C(2)	3999(5)	−1900(10)	920(5)	44(4)
C(3)	3474(5)	−1951(10)	1297(5)	40(4)
C(4)	2739(5)	−1629(10)	870(5)	37(4)
C(5)	2839(6)	−1333(10)	269(4)	42(4)
C(6)	3947(7)	−1466(13)	−279(5)	72(6)
C(7)	4795(6)	−2460(13)	1133(6)	73(6)
C(8)	3624(6)	−2541(11)	1964(5)	58(5)
C(9)	2013(6)	−1832(10)	1042(5)	52(5)
C(10)	2212(6)	−1057(12)	−350(5)	66(5)
C(11)	4956(6)	768(12)	1458(5)	61(5)
C(12)	4714(6)	2061(11)	1320(5)	57(5)
C(13)	4278(5)	2462(13)	1723(5)	51(5)
C(14)	4260(5)	1404(11)	2132(4)	49(4)
C(15)	4680(5)	363(12)	1982(5)	55(5)
C(16)	2566(5)	1173(9)	1461(4)	26(3)
C(21)	1954(6)	2813(10)	546(5)	37(4)
C(22)	1205(6)	2417(11)	225(5)	43(4)
C(23)	719(7)	3321(12)	−121(5)	62(5)
C(24)	932(7)	4600(13)	−194(5)	67(6)
C(25)	1672(8)	4976(12)	86(5)	57(5)
C(26)	2197(6)	4082(10)	456(5)	46(4)
C(27)	934(6)	967(11)	252(5)	54(5)
C(28)	3003(6)	4550(10)	750(6)	66(5)
C(31)	3150(6)	4083(12)	2872(6)	73(6)
C(32)	1620(7)	3858(12)	3125(5)	68(6)
C(33)	1674(7)	4809(11)	1851(5)	64(5)
C(34)	449(6)	776(13)	2687(5)	75(6)
C(35)	88(6)	2200(12)	1443(6)	76(6)
C(36)	404(6)	−812(11)	1521(5)	65(5)
C(37)	2165(7)	−1792(11)	2916(5)	66(5)
C(38)	3641(6)	−229(12)	3310(6)	69(5)
C(39)	2368(7)	673(13)	3774(5)	78(6)
N(1)	2494(4)	1823(7)	913(3)	31(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

than the corresponding values for η^2-iminoacylzirconium complexes (by ca. 0.02–0.04 Å). This could be a result of the greater steric congestion in 7. The Si(1)–C(16) bond length of 1.949(11) Å is only slightly (0.02 Å) longer than the value obtained for the η^2-silaacyl $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$ [12a,b]. The 2,6-$Me_2C_6H_3$ group is twisted by 67.4° out of the plane of the η^2-iminosilaacyl.

The average Zr–Cp(centroid) distance (2.267(11) Å) is approximately the same as those found in sterically hindered zirconocene derivatives [29]. Substitution of one η^5-C_5H_5 ligand for the larger η^5-C_5Me_5 ligand would be expected to lead to a larger

Table 4

Selected bond distances and angles for 7

(a) Bond distances (Å)			
Zr–Cl	2.604(2)	N(1)–C(16)	1.320(12)
Zr–N(1)	2.249(8)	C(16)–Si(1)	1.949(11)
Zr–C(16)	2.309(10)	Si(1)–Si(2)	2.377(4)
Zr–CNT(1) [a]	2.279(11)	Si(1)–Si(3)	2.403(4)
Zr–CNT(2) [a]	2.254(11)	Si(1)–Si(4)	2.397(4)
N(1)–C(21)	1.465(12)		
(b) Bond angles (deg)			
CNT(1)–Zr–CNT(2)	126.7(3)	Cl–Zr–N(1)	82.1(2)
Cl–Zr–CNT(1)	102.0(2)	Cl–Zr–C(16)	115.7(2)
Cl–Zr–CNT(2)	102.7(2)	N(1)–Zr–C(16)	33.6(3)
C(16)–Zr–CNT(1)	107.6(3)	Zr–C(16)–N(1)	70.7(5)
C(16)–Zr–CNT(2)	102.9(2)	Zr–N(1)–C(16)	75.7(5)
N(1)–Zr–CNT(1)	117.4(3)	Zr–N(1)–C(21)	150.0(7)
N(1)–Zr–CNT(2)	112.3(3)	Zr–C(16)–Si(1)	156.2(4)

[a] CNT(1) = centroid of C(1)–C(5); CNT(2) = centroid of C(11)–C(15).

centroid–Zr–centroid angle. However, the 126.7(3)° angle observed for 7 is near to the lowest value found for Cp_2ZrX_2 systems (126–132°) [29]. The less obtuse angle observed for 7 is probably the result of steric interactions attributed to the bulky $Si(SiMe_3)_3$ group and to the xylyl methyl groups, which are constrained to point toward the Cp and Cp* ligands. Evidence for such repulsive interactions are found in two particularly short H ··· H separations: 1.83 Å between hydrogens on C(28) and C(13), and 2.04 Å between hydrogens on C(38) and H(8).

The Zr–Cl bond length, 2.605(2) Å, is quite long compared to Zr–Cl bonds in other $Cp_2Zr(X)Cl$ structures [29]. This distance is considerably longer than typical values such as 2.44 Å in Cp_2ZrCl_2 [30], 2.441(10) Å in $(CH_2)_3(\eta^5\text{-}C_5H_4)_2ZrCl_2$ [31], 2.447(1) Å in $(\eta^5\text{-}C_5H_4SiMe_3)_2Zr[CH(SiMe_3)_2]Cl$ [32] and 2.480(1) Å in $Cp_2Zr(CPh{=}CMe_2)Cl$ [33], and even greater than the longest values observed, e.g., 2.536(1) Å in $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$ [12b], 2.531(2) Å in $Cp_2Zr(CPh_2OMe)Cl$ [34] and 2.545(1) Å in $Cp_2Zr[CH(SiMe_3)(C_{14}H_9)]Cl$ ($C_{14}H_9$ = anthracen-9-yl) [35]. It therefore seems that severe steric crowding has greatly influenced the bonding parameters in this molecule.

Other attempted reactions

No reaction was observed between **1** and acetylene (excess, benzene-d_6, 90 °C, 1 day), phenylacetylene (1 equivalent, benzene-d_6, 1 day), trimethylphosphine (1 equivalent, benzene-d_6, 1 day), or benzonitrile (1 equivalent, benzene-d_6, 1 day). Reaction with 4-methoxybenzonitrile (1 equivalent, pentane, 1 day) occurred to give two products which could not be separated or characterized. In contrast, $Cp_2Zr[Si(SiMe_3)_3]Cl$ does not react with 4-methoxybenzonitrile [12b]. Reactions of **1** that gave mixtures of uncharacterized products include those with carbon dioxide (excess, benzene-d_6, 5 days), phenylisocyanate (1 equivalent, benzene-d_6, 1 day), t-butyl isocyanide (1 equivalent, benzene-d_6, 1 day), and acetonitrile (1 equivalent, benzene-d_6, 1 day).

Conclusion

As observed with **1** and **2**, early transition metal (d^0) silyl complexes exhibit increased reactivity toward insertion of unsaturated substrates relative to late transition metal silyls. This increased M–Si bond activity can be attributed to the lack of π-bonding between a d^0 metal center and silicon [1d,12]. Replacement of a Cp ligand in $Cp_2Zr[Si(SiMe_3)_3]Cl$ with a Cp* ligand results in activation of the Zr–Si bond toward insertion of carbon monoxide. This single ligand substitution also changes the selectivity of CO insertion in mixed alkyl/silyl complexes. Thus, it appears that the insertion chemistry of zirconium silyl complexes can be greatly influenced by rather subtle changes in the electronic and steric environment of the metal center. The Zr–Si bond "activation" described here has provided a new synthetic route to an acylsilane (eq. 5), and the synthesis of the first stable formylsilane (eq. 4) [15].

Experimental

All manipulations were conducted under an inert atmosphere of nitrogen or argon. All solvents were distilled from sodium benzophenone ketyl before use, except dichloromethane which was distilled from calcium hydride. $CpCp^*ZrCl_2$ [36] and $Al(SiMe_3)_3 \cdot OEt_2$ [37] were prepared according to the literature procedures. The compound $(THF)_3LiSi(SiMe_3)_3$ was prepared by the literature procedure [38] with the modification that halide-free MeLi (Aldrich) was used. If MeLi complexed with LiBr is used, some bromide becomes complexed with the $(THF)_3LiSi(SiMe_3)_3$ and partial halogen exchange with **1** is observed. The acylsilane $MeCOSi(SiMe_3)_3$ was prepared by the method of Brook [22]. The compounds MeMgBr (Aldrich), $2,6\text{-}Me_2C_6H_3NC$ (Fluka), and $ZrCl_4$ (Aesar) were used as received. Elemental analyses were performed by Galbraith microanalytical laboratories.

Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a GE QE-300 instrument at 300 and 75.5 MHz, respectively. $^{29}Si\{^1H\}$ NMR spectra were recorded at 59.6 MHz on the GE QE-300, and an INEPT sequence was employed to enhance the signals [39].

*CpCp*Zr[Si(SiMe₃)₃]Cl (1).* A 250 ml round flask was charged with $CpCp^*ZrCl_2$ (7.88 g, 21.8 mmol), $(THF)_3LiSi(SiMe_3)_3$ (10.25 g, 21.8 mmol), and 200 ml of benzene. The reaction mixture was stirred for 12 h and the volatiles were then removed by vacuum transfer. The desired reaction product was isolated from the residue by applying successive pentane extractions until addition of solvent no longer gave a red solution. The combined extracts were concentrated and cooled (−45 °C) to give three crops of red crystalline **1** (7.77 g) in 62% yield (m.p. 122 °C dec.). Anal. Found: C, 49.94; H, 7.99. $C_{24}H_{47}ClSi_4Zr$ calcd.: C, 50.16; H, 8.24%. IR (Nujol, CsI, cm^{-1}): 1250m sh, 1235m, 1070w, 1025m, 1015m, 905vw, 860m sh, 830s, 800m, 745w sh, 730m, 675m sh, 670m, 620m, 405w, 365m, 340m, 310vw, 270w.

*CpCp*Zr[Si(SiMe₃)₃]Me (2).* Compound **1** (1.00 g, 1.74 mmol) was dissolved in diethyl ether (30 ml) and cooled to −78 °C. To this stirred solution was added 3.6 ml of 0.48 *M* MeMgBr (1.73 mmol) in diethyl ether. The reaction mixture was allowed to slowly warm to room temperature over 2 h with stirring. The solution was evaporated to dryness and the product extracted with pentane (3 × 20 ml). The combined pentane extracts were concentrated to ca. 30 ml and cooled to −45 °C.

Two crops of orange crystalline **2** were isolated to give an overall yield of 82% (0.793 g). Compound **2** is stable indefinitely as a solid at room temperature (m.p. 78 °C dec), but gradually decomposes in solution to produce $HSi(SiMe_3)_3$ (by ^1H NMR). Anal. Found: C, 53.93; H. 9.28. $C_{25}H_{50}Si_4Zr$ calcd.: C, 54.18; H, 9.09%. IR (Nujol, CsI, cm^{-1}): 1250w sh, 1230s, 1120m, 1070w, 1025m, 1015m, 900w sh, 830s br, 670s, 620s, 400m br, 380w sh, 360m.

$CpCp^\star Zr[\eta^2\text{-}COSi(SiMe_3)_3]Cl$ (3). A pressure bottle containing **1** (2.10 g, 3.65 mmol) dissolved in pentane (50 ml) was pressurized with CO (100 psi) and allowed to stir for 30 min. The pink precipitate was isolated by filtration and dried under vacuum to provide 0.95 g of **3**. An additional 0.60 g of crystalline **3** was obtained by concentration and cooling (−45 °C) of the filtrate. Overall yield of **3** (m.p. 115 °C dec) was 71%. Anal. Found: C, 49.77; H, 8.08. $C_{25}H_{47}ClOSi_4Zr$ calcd.: C, 49.83; H, 7.86%. IR (Nujol, CsI, cm^{-1}): ν(C=O) 1440 cm^{-1}.

$CpCp^\star Zr[OC(=CH_2)Si(SiMe_3)_3]H$ (5). A pressure bottle containing an orange solution of **2** (0.26 g, 0.47 mmol) in pentane (25 ml) was pressurized with CO (90 psi) and stirred. The solution immediately became pink and then gradually turned beige after 1 h. The solution was transferred to a Schlenk tube, concentrated, and cooled to −78 °C. Crystals of beige **5** were then isolated by filtration in 48% yield (0.13 g). Anal. Found: C, 53.33; H, 8.71. $C_{26}H_{50}OSiZr$ calcd.: C, 53.64; H, 8.66%. IR (Nujol, CsI, cm^{-1}): 1580m br, 1540m, 1350m, 1250w sh, 1240s, 1180s, 1000s, 860w sh, 830s, 790s, 740w, 685m, 660w, 620m, 580m br, 485m, 445m, 420w, 365m, 310w.

Reaction of 5 with MeI. To an NMR tube containing 0.028 g (0.048 mmol) of **5** in benzene-d_6 was added 3 μl (0.048 mmol) of MeI. An immediate reaction was observed to give methane and $CpCp^\star Zr[OC(=CH_2)Si(SiMe_3)_3]I$ (**6**) cleanly by ^1H NMR.

Reaction of 5 with HCl. To an NMR tube containing 0.028 g (0.048 mmol) of **5** in benzene-d_6 was added 2 equivalents of HCl gas by vacuum transfer. As monitored by ^1H NMR, the reaction proceeded nearly quantitatively to $CpCp^\star ZrCl_2$ and the acylsilane $MeCOSi(SiMe_3)_3$. For the acylsilane, resonances were observed at δ 0.22 (27 H, $SiMe_3$) and δ 2.13 (3 H, Me).

$CpCp^\star Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl$ (7). To a flask containing 1.36 g (2.37 mmol) of **1** and 0.31 g (2.37 mmol) of $2,6\text{-}Me_2C_6H_3NC$ was added 30 ml of benzene with stirring. The solution immediately became dark green. After stirring for 2 h the volatiles were removed by vacuum transfer and the residue was washed with cold pentane (−78 °C, 2 × 10 ml). The yellow product was then dissolved in pentane, filtered, and cooled (−45 °C) to give 2 crops (1.27 g) of yellow, crystalline **7** in 76% yield (m.p. 153 °C dec). Anal. Found: C, 55.70; H, 7.96. $C_{33}H_{56}ClNSi_4Zr$ calcd.: C, 56.16; H, 8.00%. IR (Nujol, CsI, cm^{-1}): 1530w, 1505w, 1255w sh, 1240m, 1140w, 1085w, 1070vw sh, 1015w, 855m sh, 825s, 800m, 790m, 765m, 680w, 620w, 600w sh, 495w, 470vw, 455vw, 410vw, 390vw, 350w, 330w, 315vw, 280w.

$CpCp^\star Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Me]Si(SiMe_3)_3$ (8). Benzene (15 ml) was added to a flask containing **2** (0.458 g, 0.825 mmol) and $2,6\text{-}Me_2C_6H_3NC$ (0.108 g, 0.824 mmol). The mixture was stirred for 1.5 h and then evaporated to dryness. The product was extracted into pentane (30 ml) and crystallized by concentration and cooling (−45 °C). Thermally unstable, pale yellow crystals of **8** were isolated in 60% yield (0.399 g, m.p. 118 °C dec). IR (Nujol, CsI, cm^{-1}): 1595m, 1580m, 1340w, 1250w sh, 1230m, 1160m, 1120m, 1090m, 1020m sh, 1015m, 855m sh, 825s, 790m, 765m, 660m, 615m, 395m, 350w, 325m.

Collection of diffraction data for 7. A yellow crystal of 7 was sealed in a glass capillary under argon. Based on systematic absences, 7 was found to crystallize in monoclinic $P2_1/c$. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $20° \leq 2\theta \leq 25°$. The parameters used during the collection of diffraction data are contained in Table 2. Correction for absorption was not needed (μ 5.0 cm^{-1}, regular crystal shape); a correction for a 3% linear decay in intensity was applied.

Solution and refinement of 7. The structure 7 was solved via heavy-atom methods which located the Zr atom. The remaining non-hydrogen atoms were found from subsequent difference Fourier syntheses and were refined anisotropically. Hydrogen atom positions were calculated (d(C–H) 0.96 Å, μ 1.2 times U_{iso} for the carbon to which it was attached). The final difference Fourier syntheses showed only a diffuse background. An inspection of F_o vs. F_c values and trends based upon sin θ, Miller index or parity group failed to reveal any systematic errors in the data. All computer programs used in the data collection and refinement are contained in the Nicolet XRD (Madison, WI) program packages P3, SHELXTL (version 5.1) and XP. SHELXTL served as the source for the neutral atom scattering factors. Supplementary material consisting of a list of observed and calculated structure factors, tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates can be obtained from the authors.

Acknowledgement

This research was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF under Grant Number AFOSR-85-0228. The U. S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. We thank John Arnold for obtaining the ^{29}Si NMR data.

References

1 Reviews: (a) C.S. Cundy, B.M. Kingston and M.F. Lappert, Adv. Organomet. Chem., 11 (1973) 253; (b) B.J. Aylett, Adv. Inorg. Chem. Radiochem., 25 (1982) 1; (c) J.A. Gladysz, Acc. Chem. Res., 17 (1984) 326; (d) T.D. Tilley, in S. Patai and Z. Rappoport (Eds.), The Chemistry of Organosilicon Compounds, Wiley, New York, in press.

2 B.M. Kingston and M.F. Lappert, J. Chem. Soc., Dalton Trans., (1972) 69.

3 K. Tamao, M. Akita, R. Kanatani, N. Ishida and M. Kumada, J. Organomet. Chem., 226 (1982) C9.

4 G. Hencken and E. Weiss, Chem. Ber., 106 (1973) 1747.

5 (a) L. Rösch, G. Altnau, W. Erb, J. Pickardt and N,. Bruncks, J. Organomet. Chem., 197 (1980) 51; (b) L. Rösch and G. Altnau, Angew. Chem. Int. Ed. Engl., 20 (1981) 582.

6 M.S. Holtman and E.P. Schram, J. Organomet. Chem., 187 (1980) 147.

7 G.A. Razuvaev, V.N. Latyaeva, L.I. Vyshinskaya, A.V. Malysheva and G.A. Vasil'eva, Dokl. Akad. Nauk SSSR, 237 (1977) 605.

8 M.D. Curtis, L.G. Bell and W.M. Butler, Organometallics, 4 (1985) 701.

9 (a) J.F. Harrod and S.S. Yun, Organometallics, 6 (1987) 1381; (b) C.T. Aiken, J.F. Harrod and E. Samuel, J. Am. Chem. Soc., 108 (1986) 4059.

10 (a) D.H. Berry and J.H. Mitstifer, J. Am. Chem. Soc., 109 (1987) 3777; (b) D.H. Berry and Q. Jiang, ibid., 109 (1987) 6270.

11 (a) T.D. Tilley, Organometallics, 4 (1985) 1452; (b) J. Arnold, D.N. Shina, T.D. Tilley and A.M. Arif, ibid., 5 (1986) 2037; (c) J. Arnold, T.D. Tilley, A.L. Rheingold and S.J. Geib, ibid., 6 (1987) 473.

12 (a) T.D. Tilley, J. Am. Chem. Soc., 107 (1985) 4084; (b) B.K. Campion, J. Falk and T.D. Tilley, ibid., 109 (1987) 2049; (c) J. Arnold, H.-G. Woo, T.D. Tilley, A.L. Rheingold and S.J. Geib, Organometallics, in press.

13 (a) J. Arnold and T.D. Tilley, J. Am. Chem. Soc., 107 (1985) 6409; (b) J. Arnold, T.D. Tilley and A.L. Rheingold, ibid., 108 (1986) 5355; (c) J. Arnold, T.D. Tilley, A.L. Rheingold and S.J. Geib, J. Chem. Soc., Chem. Commun., (1987) 793; (d) J. Arnold, T.D. Tilley, A.L. Rheingold and S.J. Geib, Inorg. Chem., 26 (1987) 2556; (e) J. Arnold, T.D. Tilley, A.L. Rheingold, S.J. Geib and A.M. Arif, J. Am. Chem. Soc., in press.

14 J. Arnold and T.D. Tilley, J. Am. Chem. Soc., 109 (1987) 3318.

15 F.H. Elsner, H.-G. Woo and T.D. Tilley, J. Am. Chem. Soc., 110 (1988) 313.

16 D.M. Roddick and T.D. Tilley, Organometallics, in press.

17 A.J. Blakeney and J.A. Gladysz, Inorg. Chim. Acta, 53 (1980) L25.

18 B.K. Campion, D. Alvarez and T.D. Tilley, manuscript in preparation.

19 A.G. Brook, P.F. Jones and G.J.D. Peddle, Can. J. Chem., 46 (1968) 2119.

20 (a) J.A. Marsella, J.C. Huffman, K.G. Caulton, B. Longato and J.R. Norton, J. Am. Chem. Soc., 104 (1982) 6360; (b) J.A. Marsella, K.G. Moloy and K.G. Caulton, J. Organomet. Chem., 201 (1980) 389; (c) J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, J. Am. Chem. Soc., 100 (1978) 2716; (d) G. Fachinetti, C. Floriani, F. Marchetti and S. Merlino, J. Chem. Soc., Chem. Commun., (1976) 522; (e) C.A. Bertelo and J. Schwartz, J. Am. Chem. Soc., 97 (1975) 228; (f) D.B. Carr and J. Schwartz, ibid., 101 (1979) 3521; (g) G. Fachinetti, G. Fochi and C. Floriani, J. Chem. Soc., Dalton Trans., (1977) 1946; (h) G. Erker and F. Rosenfeldt, Angew. Chem., Int. Ed. Engl., 17 (1978) 605; (i) J. Jeffrey, M.F. Lappert, N.T. Luong-Thi, M. Webb, J.L. Atwood and W.E. Hunter, J. Chem. Soc., Dalton Trans., (1981) 1593; (j) M.F. Lappert, N.T. Luong-Thi and C.R.C. Milne, J. Organomet. Chem., 174 (1979) C35.

21 J.F. Harrod, A. Malek, F.D. Rochon and R. Melanson, Organometallics, 6 (1987) 2117.

22 A.G. Brook, J.W. Harris, J. Lennon and M. El Sheikh, J. Am. Chem. Soc., 101 (1979) 83.

23 (a) D. Seyferth and R.M. Weinstein, J. Am. Chem. Soc., 104 (1982) 5534; (b) H.J. Reich and M.J. Kelley, ibid., 104 (1982) 1119; (c) A.G. Brook, Adv. Organomet. Chem., 7 (1968) 95; (d) E. Colvin, Silicon in Organic Synthesis, Butterworths, London, 1981; (e) W.P. Weber, Silicon Reagents for Organic Synthesis, Springer-Verlag, Berlin, 1983, and ref. therein.

24 P.T. Wolczanski and J.E. Bercaw, J. Am. Chem. Soc., 101 (1979) 6450.

25 M. Porchia, F. Ossola, G. Rossetto, P. Zanella and N. Brianese, J. Chem. Soc., Chem. Commun., (1987) 550.

26 (a) S.L. Latesky, A.K. McMullen, G.P. Niccolai, I.P. Rothwell and J.C. Huffman, Organometallics, 4 (1985) 1896; (b) L.R. Chamberlain, L.D. Durfee, P.E. Fanwick, L. Kobriger, S.L. Latesky, A.K. McMullen, I.P. Rothwell, K. Folting, J.C. Huffman, W.E. Streib and R. Wang, J. Am. Chem. Soc., 109 (1987) 390.

27 K.H. den Haan, G.A. Luinstra, A. Meetsma and J.H. Teuben, Organometallics, 6 (1987) 1509.

28 D.J. Cardin, M.F. Lappert and C.L. Raston, Chemistry of Organo-Zirconium and -Hafnium Compounds, Wiley, New York, 1986, p. 223.

29 Ref. 28, pp. 70–72.

30 K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton and G.V. Rees, Acta Crystallogr. B, 30 (1974) 2290.

31 C.H. Saldarriaga-Molina, A. Clearfield and I. Bernal, Inorg. Chem., 13 (1974) 2880.

32 M.F. Lappert, P.I. Riley, P.I.W. Yarrow, J.L. Atwood, W.E. Hunter and M.J. Zaworotko, J. Chem. Soc., Dalton Trans., (1981) 814.

33 C.J. Cardin, D.J. Cardin, D.A. Morton-Blake, H.E. Parge and A. Roy, J. Chem. Soc., Dalton Trans., (1987) 1641.

34 G. Erker, U. Dorf, J.L. Atwood and W.E. Hunter, J. Am. Chem. Soc., 108 (1986) 2251.

35 C.L. Raston and A.H. White, unpublished work cited in: M.E. Silver, O. Eisenstein and R.C. Fay, Organometallics, 2 (1983) 44.

36 P.T. Wolczanski and J.E. Bercaw, Organometallics, 1 (1982) 793.

37 L. Rösch and G. Altnau, J. Organomet. Chem., 195 (1980) 47.

38 G. Gutekunst and A.G. Brook, J. Organomet. Chem., 225 (1982) 1.

39 T.A. Blinka, B.J. Helmer and R. West, Adv. Organomet. Chem., 23 (1984) 193.