Zirconium complexes of a cyclopentadienyl-amido ligand with a pendant amine donor via amine and alkane elimination

Ying Mu, Warren E. Piers, Donald C. MacQuarrie, and Michael J. Zaworotko

Abstract: Zirconium complexes of the multidentate ligand $CpH^{NMe}SiN(H)R$ (SiNR = -$SiMe_2$N-*t*-butyl; NMe = -$CH_2CH_2NMe_2$, **1**) were prepared and characterized via amine and alkane elimination procedures. Reaction of **1** with $Zr(NMe_2)_4$ gave a mixture of bis-amido complexes **2** in which the ligand was 1,2 and 1,3 substituted. This mixture was converted to the analogous dichlorides **3** using $Me_2NH{\cdot}HCl$ and 1,3-**3** was purified at this stage; alternatively, 1,3-**3** was obtained in one pot from **1** and $Zr(NMe_2)_4$ in ≈70% yield. Conversion of 1,3-**3** to dimethyl compound $(Cp^{NMe}SiNR)Zr(CH_3)_2$, 1,3-**4**, was accomplished via reaction of the dichloride with methyllithium; methide abstraction with the Lewis acids $B(C_6F_5)_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$ generated the cationic alkyls $[(Cp^{NMe}SiNR)Zr(CH_3)]^+[R'B(C_6F_5)_3]^-$ (R′ = CH_3, **6a**; C_6F_5, **6b**), which were characterized by NMR spectroscopy. Zirconium complexes containing **1** ligated as its 1,2 isomer were obtained from alkane elimination reactions between **1** and in situ prepared R_nZrCl_{4-n} (R = CH_3, n = 3; R = CH_2SiMe_3, n = 2). 1,2-**3** and the methyl chloride complex 1,2-$(Cp^{NMe}SiNR)Zr(CH_3)Cl$, **5**, were obtained in 18 and 30% yield, respectively. Complex **5** was characterized by X-ray crystallography (monoclinic, space group $P2_1/a$, a = 9.6951(10) Å, b = 14.3794(16) Å, c = 14.364(3) Å, V = 1990.3(5) Å^3, Z = 4, R = 0.046, R_w = 0.041.)

Key words: amine elimination, Cp-amido, zirconium complexes.

Résumé : On a préparé les complexes de zirconium du ligand multidentate $CpH^{NMe}SiN(H)R$ (SINR = -$SiMe_2$N-*t*-butyl; NME = -$CH_2CH_2NME_2$, **1**), et on les a caractérisés via les procédés d'élimination d'amine et d'alcane. La réaction du composé **1** avec le $Zr(NMe_2)_4$ donne un mélange de complexes bis-amido dans lequel le ligand est substitué en 1,2 et 1,3. On a transformé le mélange en dichlorures correspondants **3** en utilisant le $Me_2NH{\cdot}HCl$ et on a purifié à ce stade le composé 1,3-**3**. On a obtenu alternativement le composé 1,2-**3** dans un seul récipient à partir du composé **1** et du $Zr(NMe_2)_4$ avec un rendement de 70%. On a transformé le composé 1,3-**3** en composé diméthylé $(Cp^{NMe}SiNR)Zr(CH_3)_2$ via la réaction du dichlorure avec le méthyllithium; l'abstraction d'un méthylure par un acide de Lewis $B(C_6F_5)_3$ et par $[Ph_3C]^+[B(C_6F_5)_4]^-$ a généré les alkyles cationiques $[Cp^{NMe}SiNR)Zr(CH_3]^+[R'B(C_6F_5)_3]^-$ (R′ = CH_3, **6a**; C_6F_5, **6b**) que l'on a caractérisés par la spectroscopie de RMN. Les complexes de zirconium contenant le composé **1** lié comme son isomère 1,2 sont obtenus à partir d'une réaction d'élimination d'alcane entre le composé **1** et le R_nZrCl_{4-n} (R = CH_3, n = 3; R = CH_2SiMe_3, n = 2) préparé in situ. On a obtenu le composé 1,3-**3** et le complexe de chlorure de méthyle 1,2-$(Cp^{NMe}SiNR)Zr(CH_3)Cl$, **5**, avec respectivement des rendements de 18 et 30%. Le complexe **5** est caractérisé par cristallographie de rayons X (groupe d'espace monoclinique $P2_1/a$, a = 9,6951(10) Å, b = 14,3794(16) Å, c = 14,364(3) Å, V = 1990,3(5) Å^3, Z = 4, R = 0,046, R_w = 0,041.)

Mots clés : élimination d'amine, Cp-amido, complexes de zirconium.

[Traduit par la rédaction]

Introduction

The impact of metallocene-based catalyst technology on the polyolefin industry has been substantial in the past five years and continues to expand (1). Deployment of these catalysts on an industrial scale has necessitated the synthesis of complex (and temperamental!) organometallic compounds on a multi-kilogram scale, a non-trivial technological achievement and one that continues to be developed by a number of specialty chemical companies. New methods for ligand attachment are thus of considerable current interest.

Traditional methodology for attaching cyclopentadienyl, *ansa*-type bis-cyclopentadienyl and constrained geometry cyclopentadienyl-amido type ligands, involves generation of a group 1 or 2 metal salt of the ligand, followed by a salt elimination reaction with a suitable group 3 or 4 metal halide. Although this strategy undeniably works for the majority of catalyst targets, it suffers from some disadvantages. In some instances, the dimetal salt of the desired ligand is unstable or formed in low yields. This is particularly the case for Cp-amido type ligands, which may be prone to Si–N bond cleav-

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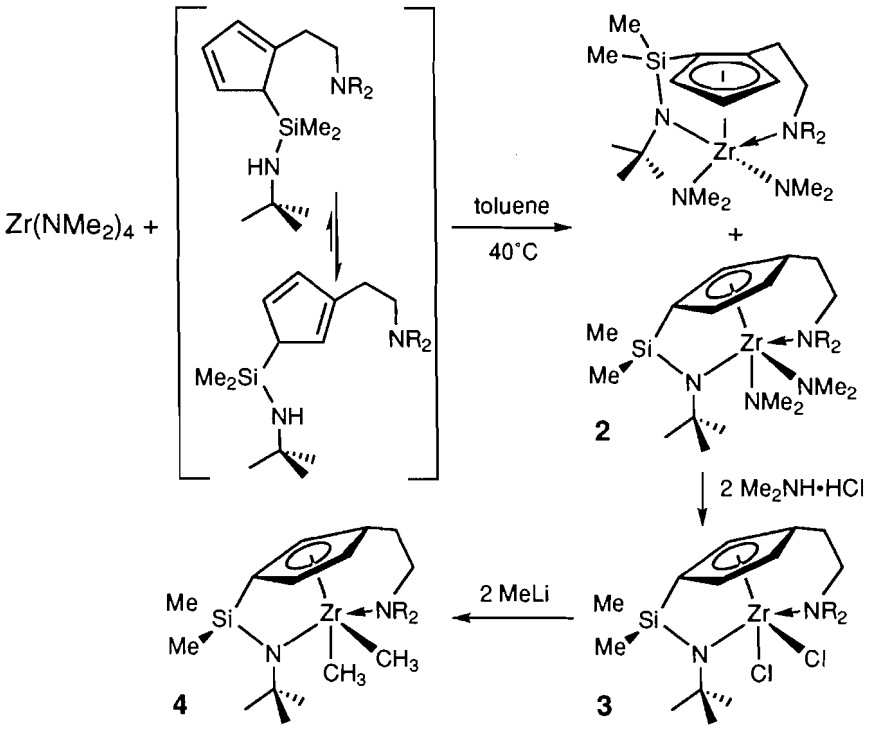
Scheme 1.



age upon treatment with alkyllithium deprotonating agents. The subsequent reaction with transtion metal halides is sensitive to several variables in reaction conditions, such as temperature, the concentration of donor solvents, and the nature of the group 1 or 2 metal employed. Thus, specific conditions are required for attachment of different ligands where more general procedures would be desirable. Finally, the eliminated salts MX_n are sometimes difficult to remove completely from the products.

To alleviate these problems, alternative strategies for ligand attachment have recently been reported. Taking a cue from some chemistry reported in the 60s by Chandra and Lappert (2), Teuben and co-workers (3) used amine elimination rather than salt elimination as a means to coordinate Cp-amido type ligands to group 4 metals. Other examples (4) of this method of ligand attachment have been reported since then, the most significant being the synthesis by Jordan and co-workers of *rac*-(EBTHI)Zr(NMe_2)$_2$ via reaction between diproteo ethylenebis(tetrahydroindenyl) and Zr(NMe_2)$_4$ (5). In a nice exhibition of synthetic ingenuity, the eliminated amine was allowed to remain in the reaction long enough to convert the kinetic products of the reaction to the thermodynamic (and desired) racemic product thus circumventing the problem of having to separate out the *meso* isomer.

While amine elimination is a promising method, potential problems associated with complete removal of eliminated amine persist. We have thus recently begun to examine alkane elimination as an alternative to the salt or amine elimination strategies described above. Although some examples of alkane elimination have been reported (6), this method has not been widely explored, perhaps because homoleptic alkyl complexes of early transition metals are somewhat unstable (7). We found that attachment of the tridentate Cp-amido ligand 1,3-CpH^{NMe}SiN(H)R (SiNR = -$SiMe_2$N-*t*-butyl; NMe = -$CH_2CH_2NMe_2$, **1**) to scandium via alkane elimination from in situ generated Sc(CH_2SiMe_3)$_3$·2THF was facile (8). In this paper, we describe the synthesis of organozirconium derivatives of **1** via both amine and alkane elimination.

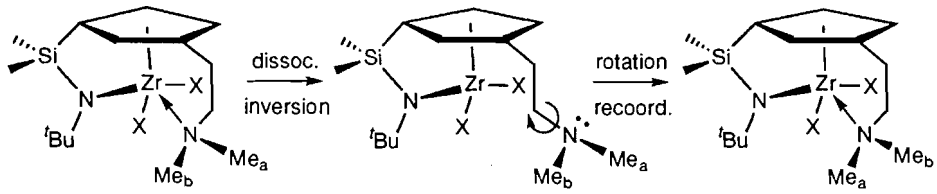
Results and discussion

Ligand attachment via amine elimination

The ligand **1** was prepared as described in detail previously (8). ^{1}H NMR spectra of these ligands are complex due to the presence of two isomers arising from 1,5-silatropic shifts (9) (Scheme 1) as well as various isomers of both 1,3 and 1,2 substitution arising from 1,2 prototropic shifts (10) (not shown in the scheme). For **1**, the ratio of 1,3:1,2 isomers was determined to be ≈7:3. Ligand **1** was found to be sensitive to heat and moisture, precluding purification by distillation or column chromatography. In addition, attempted deprotonation with the usual reagents (*n*-BuLi, KH, i-PrMgBr) did not lead to pure salts of the ligands, preventing the use of traditional salt elimination reactions for ligand attachment.

The rate of interconversion of the substitutional isomers, as well as the rates of reaction for each of the isomers with deprotonating agents, will dictate which isomer will bind to a metal. In scandium complexes of **1**, the 1,3 isomer attached almost exclusively. In contrast, the 1,2 isomer was active to a degree in amine elimination reactions between **1** and Zr(NMe_2)$_4$; this chemistry is summarized in Scheme 1. The bis-amide derivatives 1,2-**2** and 1,3-**2** were formed in a ≈1:9 ratio as an orange oil and were inseparable. Conversion of the bis-amides to the analogous dichlorides was carried out using Me_2NH·HCl (3). At this stage, the 1,3 isomer of **3** could be purified by recrystallization, since the dichlorides were white crystalline solids.

Scheme 2.



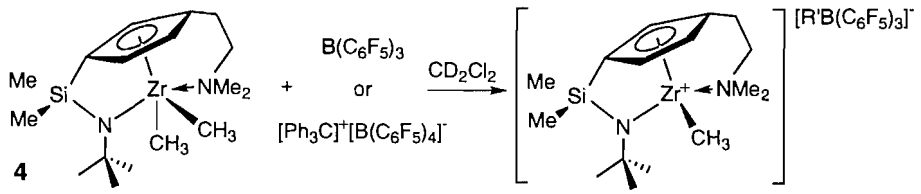
Complete removal of dimethylamine was affected by heating the crude solid product under dynamic vacuum for a brief period. Alkylation of the dichloride 1,3-(Cp^{NMe}SiNR)$ZrCl_2$ with methyllithium proceeded smoothly to yield 1,3-(Cp^{NMe}SiNR)$Zr(CH_3)_2$, 1,3-**4**.

Since the bis-amido complexes **2** were not readily purified, the stepwise procedure from $Zr(NMe_2)_4$ dichloride 1,3-**3** was adapted to a "one-pot" process that dispensed with isolation of the amido intermediates (see Experimental). Yields of 1,3-(Cp^{NMe}SiNR)$ZrCl_2$ from $Zr(NMe_2)_4$ and diproteo ligand **1** were in the 65–75% range and, by ^1H NMR spectroscopy, contained < 2% isomeric 1,2-**3**.

Table 1 gives ^1H and $^{13}C\{^1H\}$ NMR data for new, isolated compounds. The geometry about the zirconium center in these complexes cannot be deduced from this data. We presume, based on models and the solid state structure of the scandium hydride dimer [(Cp^{NMe}SiNR)ScH]$_2$ (8), that an approximately trigonal bypyramidal geometry is present. Because of the planar chirality associated with the unsymmetrical disubstitution of the Cp ring, groups with the same connectivity are diastereotopic in complexes 1,3-**2**, **3**, and **4**, with the exception of the N-methyl groups on the pendant amine arm of the ligand. In each case, a single resonance for these groups was observed in both the ^1H and the $^{13}C\{^1H\}$ NMR spectra at room temperature. This suggests that the amine is either not coordinated to zirconium in these complexes, or undergoes a rapid equilibration process on the NMR time scale. Since the amine arm of the 1,3-substituted ligand does coordinate in related scandium complexes, we favor the latter explanation; a plausible process which exchanges the N-methyl groups (but not the other diastereotopic groups in the molecule) is shown in Scheme 2. Dissociation of the amine, followed by inversion at nitrogen (a low barrier process) (11), bond rotation about C—N, and recoordination of the amine exchanges the N methyl groups.

Since amine dissociation is likely a chemically significant process in these compounds, it is perhaps surprising that dimethyl complex 1,3-**4** reacts rapidly with the Lewis acid activators $B(C_6F_5)_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$ to effect methide abstraction (12) and produce the cationic alkyls [(Cp^{NMe}SiNR)$Zr(CH_3)]^+[R'B(C_6F_5)_3]^-$ (R' = CH_3, **6a**; C_6F_5, **6b**) as shown in eq. [1]. Cations **6a** and **6b** are isoelectronic with the neutral scandium alkyl derivative supported by 1,3-**1**, which we

[1]



recently reported (8). The chemical shift for the zirconium methyl groups (0.56 and 0.57 ppm for **6a** and **6b**, respectively) are characteristic of cationic zirconium methyl groups (13); other ligand signals also shift downfield relative to those in **4** as a consequence of bonding to the more electropositive zirconium center. Interestingly, only one diastereomeric cation is produced, suggesting that either one of the two diastereotopic methyl groups was abstracted preferentially or that the resulting methyl cation mixture rapidly isomerizes to one diastereomer.

The cations **6a** and **6b** were stable for a few hours in CD_2Cl_2 before decomposition became apparent. The NMR tube scale reactions were quite clean but attempts to isolate these compounds in preparative scale reactions led to oily materials with complex NMR spectra. Since neither **3** nor **4** exhibited significant activity towards propene polymerization upon activation with MAO,[3] the chemistry of these cations was not pursued further.

[3] Y. Mu, I. Munro, and W.E. Piers, unpublished results.

Ligand attachment via alkane elimination

Our success in the use of alkane elimination protocols for generation of organoscandium complexes led us to develop procedures for ligand attachment to zirconium via this strategy. In the reactions we explored, the zirconium-containing products isolated incorporated ligand **1** as its 1,2-substituted isomer. In situ generated R_nZrCl_{4-n} (R = CH_3, n = 3; R = CH_2SiMe_3, n = 2) was allowed to react with the diproteo ligand **1** as a mixture of its 1,2 and 1,3 substituted isomers. Yields of pure products were quite low and 1,3 products were observed only as minor components of the crude product mixture. These poor yields may be a reflection of the thermal instability of the in situ generated zirconium alkyls; for example, when solutions of the methyl reagent were allowed to warm to temperatures above 0°C, discolouration ensued as the reagent decomposed. It is unclear why the 1,2 isomer of the ligand **1** appears to react faster with these zirconium alkyls than the 1,3 substituted species.

Compounds 1,2-**3** and **5** were identified by their distinct

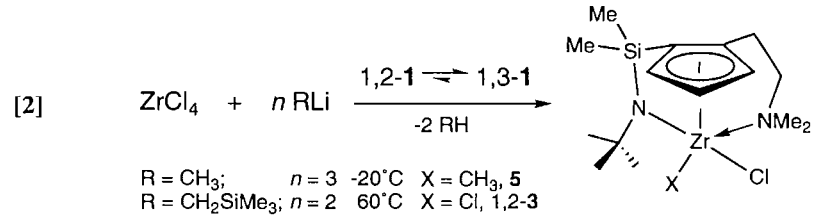
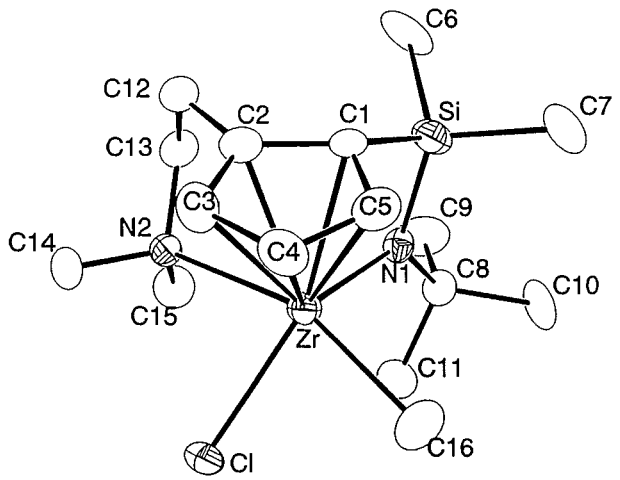


Fig. 1. ORTEP drawing of 1,2-($Cp^{NMe}SiNR$)$Zr(CH_3)Cl$, **5**.



NMR spectra and by an X-ray structural determination of methyl chloride **5**. An ORTEP diagram of the molecular structure of **5** is shown in Fig. 1 and crystal data, atomic coordinates, and selected metrical data are given in Tables 2–4, respectively. If the centroid of the cyclopentadienyl donor is viewed as occupying one coordination site, the geometry about zirconium in this complex is closest to being square pyramidal, although the chlorine ligand tilts ≈25–30° out of the basal plane. This geometry is favoured by the 1,2 substitution on the cyclopentadienyl ring since the N1-Zr-N2 angle is 91.98(23)° compared to N_{amido}-Sc-N_{amine} angles of 111.74(17)° and 116.41(12)° in approximately trigonal-bipyramidal scandium complexes of 1,3-**1**. No disorder between the chloride and the methyl ligands was observed, nor was there any spectroscopic evidence for an isomer of **5** in which these ligands exchange positions.

The zirconium chlorine (14) and zirconium carbon (15) bonds in **5** are comparable to analogous bonds in Cp_2ZrX_2 compounds. The Zr—N_{amide} distance of 2.078(6) Å is much shorter than the Zr—N_{amine} length of 2.603(7) Å. While the former is within the expected range (2.00–2.08 Å) for zirconium amido nitrogen bond lengths (16), the latter is longer than normal (cf. the Zr—N distance of 2.434(3) Å in (η^8-COT)(η^4-COT)$Zr(NH_3)$ (17) and 2.421(9) Å in a zirconium complex containing a pendant pyrrolidine donor (4a)). This is suggestive of a very weak donor bond between zirconium and the amine ligand and is consistent with the observed equilibration of the diastereotopic N-methyl groups via the process given above in Scheme 2.

In conclusion, amine elimination is an effective means of attaching the tridentate ligand $Cp(H)^{NMe}SiN(H)R$ to zirconium, yielding predominately complexes of the 1,3 isomer of the ligand. On the other hand, the products isolated from the alkane elimination reactions are 1,2-isomer ligated complexes. The poor yields of the latter reactions suggest that more well-defined and stable alkane derivatives of zirconium may be required to improve efficiency.

Experimental

General

General techniques, drying of solvents, and analytical tools employed were as described previously (4*a*). All materials were purchased from Aldrich and used as recieved or purified by standard procedures (18). $Zr(NMe_2)_4$ (19), $B(C_6F_5)_3$ (20), and $Ph_3CB(C_6F_5)_4$ (21) were synthesized according to published procedures. Microanalytical data were obtained from Oneida Research Services, Inc., One Halsey Road, Whitesboro, NY 13492; however, like others (22), we found it difficult to obtain satisfactory analysis of carbon in these zirconium complexes due, presumably, to incomplete combustion.

Synthesis of ($Cp^{NMe}SiNR$)$Zr(NMe_2)_2$, 1,3-2

$CpH^{NMe}SiN(H)R$ (2.32 g, 8.7 mmol) in 25 mL of toluene was added to a solution of $Zr(NMe_2)_4$ (2.33 g, 8.7 mmol) in 10 mL of toluene at −78°C. The reaction mixture was allowed to warm to room temperature and then stirred at 40°C for 1 h. Solvent was removed and the residue was heated at 80°C under vacuum for several hours to remove the lower boiling-point impurities. [($Cp^{NMe}SiNR$)$Zr(NMe_2)_2$] (3.66 g, 8.2 mmol, 94%) was obtained as a yellowish oil that was >95% pure by ^1H NMR.

Synthesis of ($Cp^{NMe}SiNR$)$ZrCl_2$, 1,3-3

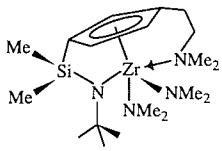
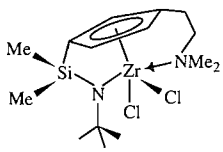
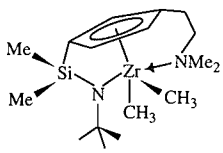
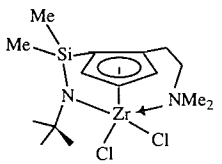
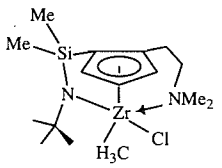
Method A

($Cp^{NMe}SiNR$)$Zr(NMe_2)_2$ (3.66 g, 8.2 mmol) was dissolved in 40 mL of THF. Anhydrous $Me_2NH{\cdot}HCl$ (1.35 g, 16.5 mmol) was added to the solution at −78°C. The mixture was allowed to warm to room temperature and stirred until the solid $Me_2NH{\cdot}HCl$ disappeared. The volatile materials were removed in vacuo and the residue was extracted with 50 mL of toluene. Insoluble materials were removed by filtration and the toluene was removed to give the crude product as an off-white solid. Pure product (2.74 g, 6.42 mmol, 77.8%) was obtained by recrystallization from hexane.

Method B

$ZrCl_4$ (2.62 g, 11.2 mmol) and $LiNMe_2$ (2.30 g, 45 mmol) were combined in a flask and 50 mL of Et_2O at was added by vacuum transfer at −78°C. The mixture was allowed to warm to room temperature and stirred for 3 h at which time the mixture was cooled again to −78°C. A solution of CpH^{NMe}-SiN(H)R (3.00 g, 11.26 mmol) in 20 mL of toluene was added

Table 1. ^1H and $^{13}C\{^1H\}$ NMR data for isolated new compounds.[a]

Compound	No.	^1H and NMR data δ(ppm)	Assignment	J(Hz)	$^{13}C\{^1H\}$ NMR data δ(ppm)	Assignment
	1,3-**2**	6.33, 6.10, 6.00 (m, 3H)	Cp*H*	2.4, 2.0	128.3, 118.3, 118.0,	
		2.84, 2.81 (s, 12H)	$ZrN(CH_3)_2$		115.4, 112.5	Cp*C*
		2.80, 2.70 (m, 2H)	NCH_2		60.9	NCH_2
		2.45, 2.15 (m, 2H)	NCH_2CH_2		56.1	$NC(CH_3)_3$
		2.12 (s, 6H)	CH_3NCH_2		45.3	$(CH_3)_2NCH_2$
		1.28 (s, 9H)	$NC(CH_3)_3$		43.9, 43.6	$ZrN(CH_3)_2$
		0.57, 0.53 (s, 6H)	$SiCH_3$		34.6	$NC(CH_3)_3$
					27.3	NCH_2CH_2
					2.4, 2.1	$Si(CH_3)_2$
	1,3-**3**	6.42, 6.39, 6.13 (m, 3H)	Cp*H*	2.6, 2.2	134.6, 122.1, 121.3,	
		3.48 (ddd, 1H)	NCH_2	12.4, 12.4, 6.4	121.1, 112.2	Cp*C*
		2.11 (ddd, 1H)	NCH_2	6.2, 1.2	61.8	NCH_2
		2.21 (ddd, 1H)	NCH_2CH_2	12.4, 12.4, 6.4	58.8	$NC_2(CH_3)_3$
		1.49 (ddd, 1H)	NCH_2CH_2	6.2, 1.2	47.4	$(CH_3)_2NCH_2$
		2.09 (s, 6H)	CH_3NCH_2		32.6	$NC(CH_3)_3$
		1.55 (s, 9H)	$NC(CH_3)_3$		24.7	NCH_2CH_2
		0.57, 0.45 (s, 6H)	$SiCH_3$		2.5, 0.4	$Si(CH_3)_2$
	1,3-**4**	6.28, 6.11, 6.10 (m, 3H)	Cp*H*	2.6, 2.2	132.3, 120.2, 117.3,	
		2.99 (ddd, 1H)	NCH_2	12.0, 12.0, 6.4	114.8, 107.2	Cp*C*
		2.22 (ddd, 1H)	NCH_2	6.4, 1.6	62.8	NCH_2
		2.31 (ddd, 1H)	NCH_2CH_2	12.0, 12.0, 6.0	56.5	$NC(CH_3)_3$
		1.57 (ddd, 1H)	NCH_2CH_2	6.0, 1.6	47.1	$(CH_3)_2NCH_2$
		1.86 (s, 6H)	CH_3NCH_2		33.7	$NC(CH_3)_3$
		1.49 (s, 9H)	$NC(CH_3)_3$		31.8, 30.4	$ZrCH_3$
		0.53, 0.52 (s, 6H)	$SiCH_3$		25.4	NCH_2CH_2
		0.00, -0.14 (s, 6H)	$ZrCH_3$		3.2, 1.1	$Si(CH_3)_2$
	1,2-**3**	6.62, 6.43, 5.95 (m, 3H)	Cp*H*		134.9, 126.8, 120.1,	
		3.02 (ddd, 1H)	NCH_2		118.6, 107.6	Cp*C*
		2.31 (ddd, 1H)	NCH_2		64.0	NCH_2
		2.14 (ddd, 1H)	NCH_2CH_2		58.0	$NC(CH_3)_3$
		1.55 (ddd, 1H)	NCH_2CH_2		49.0	$(CH_3)_2NCH_2$
		2.09 (s, 6H)	CH_3NCH_2		31.8	$NC(CH_3)_3$
		1.34 (s, 9H)	$NC(CH_3)_3$		26.0	NCH_2CH_2
		0.45, 0.27 (s, 6H)	$SiCH_3$		3.7, 2.5	$Si(CH_3)_2$
	1,2-**5**	6.32, 6.29, 5.81 (m, 3H)	Cp*H*		132.6, 122.7, 117.7	
		2.89 (ddd, 1H)	NCH_2		(2C), 106.6	Cp*C*
		2.41 (ddd, 1H)	NCH_2		62.5	$NC(CH_3)_3$
		2.24 (ddd, 1H)	NCH_2CH_2		56.4	NCH_2
		1.60 (ddd, 1H)	NCH_2CH_2		47.7	$(CH_3)_2NCH_2$
		2.05 (s, 6H)	CH_3NCH_2		35.0	$ZrCH_3$
		1.27 (s, 9H)	$NC(CH_3)_3$		32.9	$NC(CH_3)_3$
		0.37, 0.31 (s, 6H)	$SiCH_3$		26.1	NCH_2CH_2
		0.67 (s, 3H)	$ZrCH_3$		3.8, 2.6	$Si(CH_3)_2$

[a]All spectra recorded in C_6D_6.

via syringe. The mixture was allowed to warm to room temperature and then stirred at 40°C for 1 h. Solvent was removed and the residue was heated at 80°C for several hours to remove volatile materials. The residue was redissolved in THF (50 mL) and anhydrous $Me_2NH{\cdot}HCl$ (1.84 g, 22.5 mmol) was added at −78°C. The mixture was stirred at room temperature until the solid $Me_2NH{\cdot}HCl$ disappeared and was worked up as described above. Yield from $ZrCl_4$, 3.31 g, 7.8 mmol, 69%. Anal. calcd. for $C_{15}H_{28}N_2SiCl_2Zr$: C 42.23, H 6.62, N 6.57; found: C 41.37, H 6.61, N 6.37.

Table 2. Summary of data collection and structure refinement details for 1,2-($Cp^{NMe}SiNR$)$Zr(CH_3)Cl$, **5**.

Empirical formula	$C_{16}H_{31}N_2SiClZr$	d_{calc}, g cm^{-3}	1.36
fw	406.19	μ, cm^{-1}	0.73
Crystal system	Monoclinic	*h, k, l* ranges	−10, 10; 0, 15; 0, 15
Space group	$P\ 2_1/a$	No. unique reflections	2608
Crystal dimensions, mm	0.15 × 0.30 × 0.40	No. observed reflections	1573
Temp, °C	21	($I > 3.0\sigma$)	
a, Å	9.6951(10)	No. of parameters	190
b, Å	14.3794(16)	*k* value	0.000050
c, Å	14.364(3)	Min/Max transmission	0.902/0.998
β, °	96.308(15)	Max residual density, e Å^{-3}	0.410
V, Å^3	1990.3(5)	Min residual density, e Å^{-3}	−0.370
Z	4	*R*, R_w	0.046, 0.041
F(000)	848	Goodness of fit	1.78

Table 3. Atomic parameters *x, y, z* and B_{iso} for 1,2-($Cp^{NMe}SiNR$)$Zr(CH_3)Cl$, **5**.

Atom	*x*	*y*	*z*	B_{iso}[a]
Zr	0.699 94(9)	0.542 58(6)	0.315 80(6)	2.97(4)
Cl	0.746 78(24)	0.581 99(15)	0.487 13(14)	3.89(11)
Si	0.719 5(3)	0.478 66(19)	0.114 63(18)	4.34(14)
N1	0.828 9(6)	0.507 4(4)	0.214 9(4)	3.0(3)
N2	0.726 7(7)	0.378 6(5)	0.392 4(5)	3.3(4)
C1	0.557 2(8)	0.492 6(7)	0.173 6(6)	3.2(4)
C2	0.514 7(8)	0.437 3(7)	0.247 7(6)	3.5(5)
C3	0.446 1(9)	0.492 2(8)	0.307 1(7)	4.3(5)
C4	0.443 5(9)	0.584 7(7)	0.273 1(7)	4.2(5)
C5	0.511 4(9)	0.583 5(7)	0.191 6(7)	4.5(5)
C6	0.710 6(10)	0.568 6(8)	0.017 4(6)	7.2(7)
C7	0.731 3(10)	0.360 7(8)	0.062 0(6)	6.5(6)
C8	0.981 5(9)	0.521 3(6)	0.219 6(6)	3.9(5)
C9	1.017 0(10)	0.598 7(8)	0.153 8(6)	6.2(6)
C10	1.058 6(9)	0.432 1(7)	0.200 5(8)	6.4(6)
C11	1.033 8(8)	0.554 6(7)	0.320 1(6)	4.6(5)
C12	0.539 8(9)	0.334 6(7)	0.264 5(6)	4.3(5)
C13	0.684 0(9)	0.312 9(6)	0.312 7(7)	4.0(5)
C14	0.871 6(9)	0.356 0(6)	0.429 8(6)	4.5(5)
C15	0.638 7(9)	0.360 2(6)	0.469 4(6)	4.1(5)
C16	0.734 9(9)	0.700 8(6)	0.302 7(7)	5.3(5)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Synthesis of ($Cp^{NMe}SiNR$)$Zr(CH_3)_2$, 1,3-4

($Cp^{NMe}SiNR$)$ZrCl_2$ (1.2 g, 2.8 mmol) was suspended in Et_2O (60 mL) and MeLi (4.0 mL of a 1.4 M solution in Et_2O, 5.6 mmol) was added via syringe at −78°C. The mixture was stirred at −78°C for 4 h, then warmed slowly to room temperature. The solvent was removed and the product was extracted with hexanes. Insoluble materials were filtered off and the extract was reduced in volume to 2–3 mL and cooled to −40°C for several hours to precipitate the product. The pure product (0.74 g, 1.9 mmol, 69%) was obtained by cold filtration as an off-white crystalline solid. Anal. calcd. for $C_{17}H_{34}N_2SiZr$: C 52.93, H 8.88, N 7.26; found: C 52.32, H 8.74, N 7.23.

In situ generation of [($Cp^{NMe}SiNR$)ZrMe]$^+$[$MeB(C_6F_5)_3$]$^-$, 6a

($Cp^{NMe}SiNR$)$Zr(CH_3)_2$ (25 mg 0.065 mmol) and $B(C_6F_5)_3$ (33 mg, 0.065 mmol) were loaded into a 5 mm NMR tube and dissolved in CD_2Cl_2 (≈0.8 mL). ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded. ^1H NMR (CD_2Cl_2, ppm): 7.03 (m, 1H, ^3J = 2.6 Hz, ^4J = 2.2 Hz, 1H of C_5H_3), 6.42 (m, 1H, C_5H_3), 6.30 (m, 1H, ^4J = 2.2 Hz, C_5H_3), 3.28 (ddd, 1H, ^2J = 13.0 Hz, ^3J = 9.6 Hz, ^3J = 5.2 Hz, NCH_2CH_2), 3.12 (ddd, 1H, ^3J = 5.0 Hz, NCH_2CH_2), 3.01 (ddd, 1H, ^2J = 15.4 Hz, NCH_2CH_2), 2.93 (ddd, 1H, ^2J = 15.4 Hz, NCH_2CH_2), 2.50 (s, 6H, $N(CH_3)_2$), 1.54 (s, 9H, $NC(CH_3)_3$), 0.56 (s, 3H, $ZrCH_3$), 0.47 (br, 3H,

Table 4. Slected bond distances and angles for 1,2-($Cp^{NMe}SiNR$)$Zr(CH_3)Cl$, **5**.

	Bond lengths (Å)		
Zr—Cl	2.5175(23)	Zr—C16	2.311(9)
Zr—N1	2.078(6)	Zr—N2	2.603(7)
Zr—C1	2.446(8)	C1—C2	1.425(13)
Zr—C2	2.467(8)	C2—C3	1.385(14)
Zr—C3	2.555(9)	C3—C4	1.418(15)
Zr—C4	2.567(9)	C4—C5	1.405(15)
Zr—C5	2.481(9)	C1—C5	1.414(14)
Zr—Cp_{cent}	2.1981(9)		
	Bond angles (°)		
Cl-Zr-N1	132.76(17)	Zr-N1-Si	106.0(3)
Cl-Zr-N2	77.98(16)	Zr-N1-C8	127.4(5)
Cl-Zr-C16	81.1(3)	Si-N1-C8	125.5(5)
N1-Zr-N2	91.98(23)	Zr-N2-C13	103.9(5)
N1-Zr-C16	94.5(3)	Zr-N2-C14	113.5(5)
N2-Zr-C16	156.6(3)	Zr-N2-C15	115.8(5)
N1-Si-C1	93.8(3)	C13-N2-C14	107.9(6)
N1-Si-C6	114.9(4)	C13-N2-C15	108.6(6)
Cp_{cent}-Zr-N1	101.0	Cp_{cent}-Zr-N2	96.3
Cp_{cent}-Zr-C16	104.5	Cp_{cent}-Zr-Cl	125.8

BCH_3), 0.46 (s, 6H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm): 137.4, 124.2, 121.7, 120.2, 108.6 (C_5H_3), 70.3 (NCH_2CH_2), 57.9 ($NCMe_3$), 44.7, 44.2 (NMe_2), 39.8 (Zr*Me*), 33.9 (B*Me*), 33.0 ($NCMe_3$), 25.1 (NCH_2CH_2), 1.04, 0.02 ($SiMe_2$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, ppm, referenced to $BF_3{\cdot}Et_2O$ at 0.0 ppm): −13.4. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, ppm, referenced to at 0.0 ppm): −165.1 (t, ^3J = 23 Hz, *p*-C_6F_5), −167.7 (t, *m*-C_6F_5), −133.1 (d, ^3J = 22 Hz, *o*-C_6F_5).

In situ generation of $[(Cp^{NMe}SiNR)ZrMe]^+[B(C_6F_5)_4]^-$, 6b

($Cp^{NMe}SiNR$)$Zr(CH_3)_2$ (25 mg, 0.065 mmol) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (63 mg, 0.065 mmol) were loaded into a 5 mm NMR tube and dissolved in CD_2Cl_2 (≈0.8 mL). ^1H NMR (CD_2Cl_2, ppm): δ 7.03 (m, 1H, ^3J = 2.6 Hz, ^4J = 2.2 Hz, C_5H_3), 6.43 (m, 1H, C_5H_3), 6.31 (m, 1H, ^4J = 2.2 Hz, C_5H_3), 3.29 (ddd, 1H, ^2J = 13.0 Hz, ^3J = 9.6 Hz, ^3J = 5.2 Hz, NCH_2CH_2), 3.12 (ddd, 1H, ^3J = 5.2 Hz, ^3J = 5.0 Hz, NCH_2CH_2), 3.01 (ddd, 1H, ^2J = 15.4 Hz, NCH_2CH_2), 2.93 (ddd, 1H, NCH_2CH_2), 2.50 (s, 6H, $N(CH_3)_2$), 1.55 (s, 9H, $NC(CH_3)_3$), 0.57 (s, 3H, $ZrCH_3$), 0.47 (s, 6H, $Si(CH_3)_2$). Partial ^1H NMR (CD_2Cl_2, ppm, −40°C): 2.48, 2.46 (s, 6H, $N(CH_3)_2$), 0.42, 0.40 (s, 6H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm): 137.4, 124.2, 121.7, 120.2, 108.6 (C_5H_3), 70.3 (NCH_2CH_2), 57.9 ($NCMe_3$), 44.6, 44.1 (NMe_2), 39.8 (Zr*Me*), 33.0 ($NCMe_3$), 25.0 (NCH_2CH_2), 1.00, −0.07 ($SiMe_2$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, ppm): −15.1 ($B(C_6F_5)_4^-$). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): −163.2 (t, ^3J = 19.4 Hz, *p*-C_6F_5), −167.2 (t, *m*-C_6F_5), −133.2 (d, ^3J = 19.4 Hz, *o*-C_6F_5).

Synthesis of 1,2-($Cp^{NMe}SiNR$)$Zr(CH_3)Cl$, 5

$ZrCl_4(THF)_2$ (0.30 g 0.80 mmol) and solid MeLi (0.05 g, 2.4 mmol) were combined in a flask and Et_2O (30 mL) was vacuum transferred in at −78°C. The mixture was warmed to −20°C and stirred for 1 h. A solution of $CpH^{NMe}SiN(H)R$ (0.21 g, 0.80 mmol) in hexanes (10 mL) was added via syringe at −20°C. The mixture was slowly warmed to 0°C and stirred for 30 min, then warmed to room temperature. The solvent was removed and the residue was extracted with hexanes. The extract was reduced in volume to 2–3 mL and cooled to −40°C; the yellowish crystalline product (98 mg, 0.24 mmol, 30%) was collected via filtration and dried in vacuo. Anal. calcd. for $C_{16}H_{31}ClN_2SiZr$: C 47.31, H 7.69, N 6.90; found: C 47.99, H 7.98, N 6.70.

Synthesis of 1,2-($Cp^{NMe}SiNR$)$ZrCl_2$, 1,2-3

$ZrCl_4(THF)_2$ (0.10 g, 0.27 mmol) and solid $TMSCH_2Li$ (0.05 g, 0.53 mmol) were combined in a flask and Et_2O (20 mL) was vacuum transferred in at −78°C. The mixture was allowed to warm to room temperature and stirred for 1 h. The Et_2O was removed in vacuo and replaced with toluene (20 mL) and the undissolved solids were removed by filtration. A solution of $CpH^{NMe}SiN(H)R$ (71 mg, 0.27 mmol) in 5 mL of toluene was added via syringe. The mixture was stirred at 60°C for 1 h, during which period a white precipitate formed. The solution was concentrated and a few mL of hexanes were added; the white solid was collected on a frit and dried under vacuum (20 mg, 0.05 mmol, 18%). Anal. calcd. for $C_{15}H_{28}Cl_2N_2SiZr$: C 42.23, H 6.62, N 6.57; found: C 41.85, H 6.76, N 6.42.

X-ray crystallographic analysis of 1,2-($Cp^{NMe}SiNR$)$Zr(CH_3)Cl$, 5

Single crystals were mounted in thin-walled glass capillaries and placed on an Enraf Nonius CAD-4 diffractometer. Unit cell dimensions were determined via least-squares refinement of the setting angles of 24 high-angle reflections and intensity data were collected using the ω-2θ scan mode. Data were corrected for Lorentz, polarization, and absorption effects but not for extinction. Pertinent data collection and structure refinement parameters are presented in Table 2. The structure was solved using direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters. Aryl and methylene hydrogen atoms were placed in calculated postions (D_{C-H} = 1.00 Å). Methyl hydrogen atoms were located via difference Fourier map inspection. Hydrogen atoms were given isotropic temperature factors based upon the atom to which they are bonded, and fixed during least-squares refinement. A weighting scheme based upon counting statistics was used with the weight modifier k in kF_o^2 being determined via evaluation of variation in the standard reflections that were collected during the course of data collection. Neutral atom scattering factors were taken from *International tables for X-ray crystallography* (23). Values of R and R_w are given by $R = (F_o - F_c)/EF_o$ and $R_w = [E(w(F_o - F_c))^2/E(wF_o^2)]^{1/2}$. All crystallographic calculations were conducted with the PC version of the NRCVAX program package (24) locally implemented on an IBM compatible 80486 computer. Anisotropic thermal parameters and hydrogen atom parameters are available as supplementary material.[4]

[4] Copies of material on deposit may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. The table of hydrogen atom parameters has also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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