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STRUCTURE AND REACTIVITY OF $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$: AN UNUSUAL SILANIMINE CARBONYL COMPLEX WITH EXTENSIVE σ–π* BACK-BONDING*

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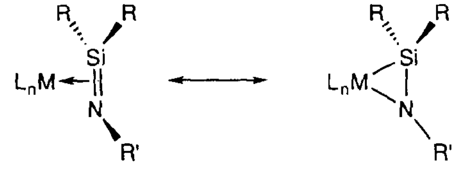
Abstract—The carbonyl silanimine complex $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**) has been prepared by ligand substitution on the phosphine derivative, $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(PMe_3)$ (**1**) and by generation of the alkyl derivative $Cp_2Zr(CH_2SiMe_3)(N^tBuSiMe_2H)$ under a carbon monoxide atmosphere. Most aspects of the spectroscopic properties and structural parameters are consistent with the formulation of **2** as a zirconium (IV) metallacycle, containing a Zr—Si—N three-membered ring and a linear, terminal carbonyl ligand. However, the carbonyl stretching frequency for **2** is observed at 1797 cm^{-1} in the infrared, much lower than expected for a zirconium (IV) complex, and indeed, lower than any other zirconocene carbonyl. ZINDO molecular orbital calculations indicate that the origin of this anomalously low stretching band is donation of electron density into the CO π* orbital directly from an orbital on the adjacent silicon center, i.e. σ–π* back-bonding. Consistent with this picture, the formally non-bonding Si···C distance in **2** (2.347(7) Å) is much longer than a typical single bond (*ca* 1.87 Å), but in the range observed for delocalized organic π-ligands bonded to silicon. Although the bond between the silicon and carbonyl ligand is not fully formed in the ground state of **2**, thermolysis in the presence of PMe_3 yields the five-membered metallacycle *cyclo*-$Cp_2Zr[OC({=}PMe_3)SiMe_2N^tBu]$ (**3**), resulting from CO insertion into the Zr—Si bond and formation of a cyclic silaacyl, followed by attack of phosphine at the electrophilic acyl carbon.



As part of our on-going investigations of metal complexes of unsaturated silicon ligands we recently reported the synthesis, structure and reactivity of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(PMe_3)$ (**1**, Cp ≡ $\eta^5\text{-}C_5H_5$), the first example of a η^2-silanimine ($R_2Si{=}NR'$) complex.[1–3] Silaolefin complexes, in general, exhibit bonding modes illustrated by the extreme resonance forms of the Dewar-Chatt-Duncanson model developed for complexes of unsaturated carbon ligands. Structural studies of **1** indicate the silanimine is an excellent π-acceptor ligand and is best described by the zirconium(IV), metallacyclic bonding extreme. In our original report it was briefly noted that the phosphine ligand in **1** can be displaced with carbon monoxide to yield the carbonyl adduct $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**). Complex **2** is unusual in that carbon monoxide does not generally bind to an electron-deficient, formally d^0, metal center as would appear to be present in **2**. In this contribution we present structural, spectroscopic, and chemical evidence that **2** does indeed contain a terminal carbonyl ligand, which is bound quite tightly to the complex, despite the electron-poor zirconium center. Furthermore, molecular orbital calculations

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[*] In honor of the 50th birthday of Professor John E. Bercaw—colleague, mentor and friend.

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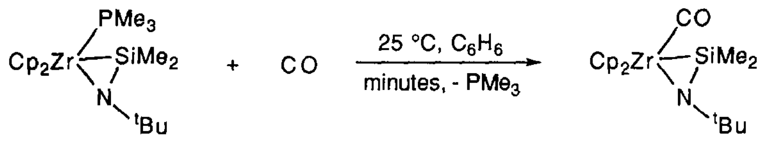
support the proposal that this unexpected stability arises from donation of electron density directly from the silanimine ligand into the π^* orbital of the carbonyl.

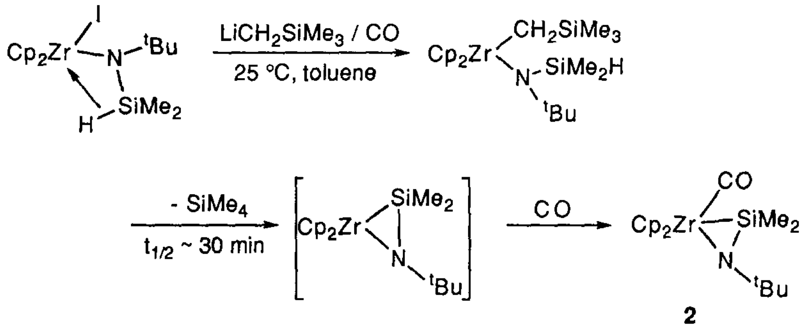
RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (2)

Benzene solutions of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(PMe_3)$ (**1**) react immediately with carbon monoxide (1 atm, 25°C) to yield the simple ligand substitution product, $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ [**2**, eq. (1)]. This carbonyl complex can also be directly formed by the generation of the alkyl derivative $Cp_2Zr(CH_2SiMe_3)(N^tBuSiMe_2H)$ under a carbon monoxide atmosphere [eq. (2)]. In both instances, **2** is formed by the trapping of the $16e^-$ intermediate, $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)$, with CO. Compound **2** has been prepared in 73% isolated yield by the method of eq. (1), and in 61% yield by the route shown in eq. (2).

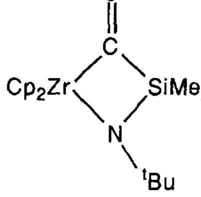


1 **2** (1)



2 (2)

A priori, alternative structures can be reasonably considered for **2**. In particular, a four-membered ring complex such as *cyclo*-$Cp_2Zr[C({=}O)SiMe_2N^tBu]$ (**A**) might arise from insertion of carbon monoxide into the Zr—Si bond. Tilley and coworkers have demonstrated that CO insertion into early metal–silyl bonds to yield acyclic silaacyl complexes is quite facile.[4] However, the spectroscopic data for **2** are most consistent with its characterization as the simple carbonyl adduct. The ^1H NMR spectrum of **2** consists of three singlets for the Cp (δ 5.30), ^tBu (δ 1.05), and $SiMe_2$ (δ 0.26) groups.



A

Coupling between the $SiMe_2$ protons and the carbonyl carbon is not observed in the ^1H NMR spectrum of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(^{13}CO)$, prepared by the reaction of **1** with ^{13}CO. Structure **A** would be expected to display a ^{13}C–^1H coupling ($^3J_{CH}$) of *ca* 2 Hz, as is observed in labeled silaacyls such as $Cp_2Zr(\eta^2\text{-}^{13}COSiMe_3)(Cl)$ ($^3J_{CH} = 1.8$ Hz).[4b] A peak at δ 290.7 in the $^{13}C\{^1H\}$ NMR spectrum of **2** is assigned to the carbonyl carbon and a singlet at δ −69.9 is observed in the $^{29}Si\{^1H\}$ NMR spectrum of **2**. Significantly, the ^{29}Si resonance appears as a doublet ($J_{SiC} = 24.1$ Hz) in the labeled adduct, **2**–^{13}CO. Typical values of $^1J_{SiC}$ for sp^3-hybridized carbon are much larger (50–60 Hz) and even greater values would be expected for a sp^2-hybridized carbon in an acyl. For example, the five-membered ring compound *cyclo*-$Cp_2Zr(OC({=}O)SiMe_2N^tBu)$ exhibits $^1J_{SiC} = 88.4$ Hz.[2] Thus, the value of 24.1 Hz is clearly not consistent with a normal single bond between the silicon and carbonyl carbon as in **A**.

Although the NMR data presented above is consistent with the formulation of **2** as a silanimine complex containing a terminal carbonyl, the infrared spectrum is more ambiguous and rather surprising. Specifically, the carbonyl ligand in **2** exhibits a strong band at 1797 cm^{-1} in the infrared spectrum (benzene solution). This band shifts upon isotopic substitution to 1756 cm^{-1} for **2**–^{13}CO [$\nu(^{12}CO)/\nu(^{13}CO) = 1.023$]. This appears to be the lowest energy carbonyl stretch reported for any zirconocene carbonyl complex. Electron deficient ("d^0") zirconium carbonyls exhibit stretches at energies that are, in general, only slightly lower than that of free CO (2143 cm^{-1}). The first example of a zirconium(IV) carbonyl complex, the thermally unstable $Cp^*_2Zr(H)_2(CO)$ ($Cp^* \equiv \eta^5\text{-}C_5Me_5$), was described by Bercaw and co-workers in 1978 and exhibits a CO stretch at 2044 cm^{-1}.[5] Only a few other examples of zirconium(IV) have been subsequently reported, and these complexes also exhibit $\nu(CO)$ in the relatively high energy range 2152–2006 cm^{-1}.[6] Furthermore, $\nu(CO)$ in **2** is significantly lower than the values observed for zirconium(II) carbonyls (e.g. $Cp_2Zr(CO)_2$, $\nu(CO) = 1975$, 1885 cm^{-1} and $Cp_2Zr(CO)(PMe_3)$, $\nu(CO) = 1853$ cm^{-1}).[7,8]

However, the value observed for **2** is still *ca* 300 cm^{-1} higher than would be expected for a silaacyl complex, such as **A**. The only known η^1-silaacyl, *fac*-$Re(CO)_3(diphos)(\eta^1\text{-}COSiPh_3)$[9] (diphos = $Ph_2PCH_2CH_2PPh_2$), exhibits a C=O stretch at 1490 cm^{-1}. Several examples of early metal complexes containing η^2-silaacyl ligands have been reported[4] and display C=O stretches at energies comparable to the η^1-complex, e.g. $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$ (1489 cm^{-1}),[4a] $Cp_2Zr(\eta^2\text{-}COSiMe_3)(OSO_2CF_3)$ (1500 cm^{-1})[4b] and $Cp^*TaCl_3(\eta^2\text{-}COSiMe_3)$ (1462 cm^{-1}).[4d] In addition, known silaacyl complexes have chemical shifts above 340 ppm for the acyl carbon in the ^{13}C NMR spectrum, much further downfield than the shift of δ 290.7 observed for **2**. Examples include *fac*-$Re(CO)_3(diphos)(\eta^1\text{-}COSiPh_3)$ (δ 340.1),[9] $Cp^*TaCl_3(\eta^2\text{-}COSiMe_3)$ (δ 351.1),[4d] $CpCp^*Zr[\eta^2\text{-}COSi(SiMe_3)_3]Cl$ (δ 382.79)[4c] and $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$ (δ 391.6).[4a]

The CO stretching frequency for **2** falls in an ambiguous range: much too low for an electron deficient carbonyl, but much too high for an acyl. Fortunately, further information regarding the structure of **2** has been obtained from a single crystal X-ray diffraction study.

Molecular structure of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**)

An ORTEP drawing of **2** is shown in Fig. 1 and crystallographic data and selected bond distances

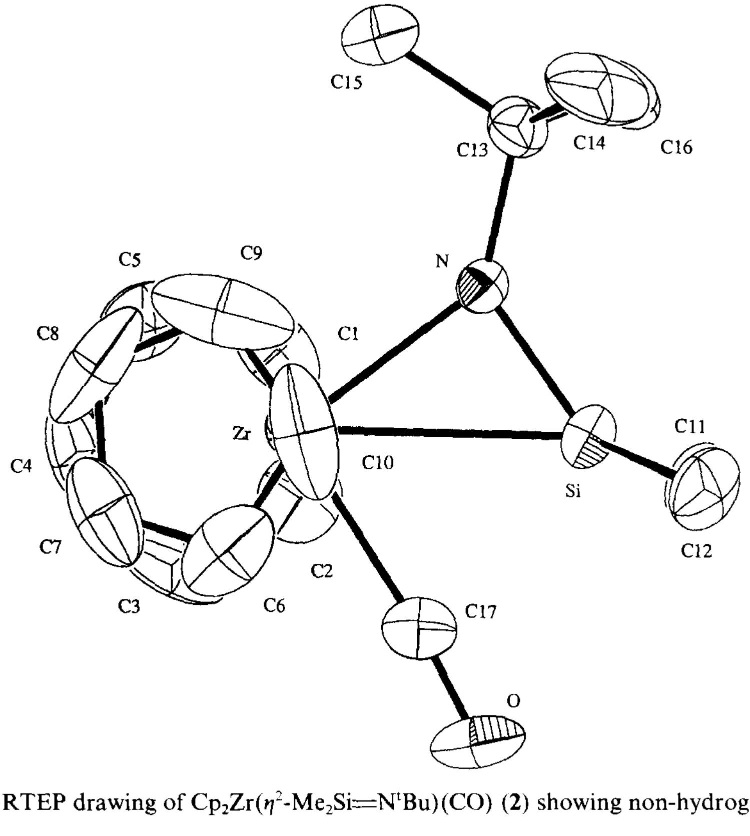


Fig. 1. ORTEP drawing of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**) showing non-hydrogen atoms.

Table 1. Crystallographic data for $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**)

Formula	$C_{17}H_{25}NOSiZr$
Formula weight	378.70
Crystal dimensions	0.15 × 0.20 × 0.33 mm
Crystal class	Orthorhombic
Space group	$P2_12_12_1$ (#19)
Z	4
Cell constants:	
a	8.601(1) Å
b	8.660(1) Å
c	24.995(3) Å
V	1861.7(7) $Å^3$
μ	6.42 cm^{-1}
D(calc)	1.351 g cm^{-3}
F(000)	784
Radiation	Mo-K_α (λ = 0.71073 Å)
θ range	2.0–27.5°
Scan mode	ω–2θ
h, *k*, *l* collected	+11, +11, ±32
No. reflections measured	2479
No. unique reflections	2452
No. reflections used in refinement	1727 ($I > 3\sigma$)
No. parameters	190
Data/parameter ratio	9.1
R_1	0.032
R_2	0.038
GOF	1.152

Table 2. Selected bond distances (Å) in **2**[a]

Zr—Si	2.706(1)	C13—C16	1.534(8)
Zr—N	2.162(4)	Zr—C1	2.535(5)
Zr—C17	2.145(5)	Zr—C2	2.527(6)
Si—C11	1.880(7)	Zr—C3	2.510(6)
Si—C12	1.854(7)	Zr—C4	2.508(7)
Si···C17	2.347(7)	Zr—C5	2.503(7)
Si—N	1.661(4)	Zr—C6	2.523(7)
C17—O	1.162(7)	Zr—C7	2.489(7)
N—C13	1.478(6)	Zr—C8	2.478(7)
C13—C14	1.520(8)	Zr—C9	2.493(8)
C13—C15	1.523(9)	Zr—C10	2.514(7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

and angles are given in Tables 1–3. Carbonyl adduct **2** adopts the expected bent metallocene geometry with three atoms (N, Si, C17) bound to zirconium in the equatorial plane, and with nitrogen in the "outer" position. The centroid—Zr—centroid angle of 132.4° is similar to the value observed in **1** (129.6°) and a variety of other zirconocene complexes.[10] However, the angle subtended at zirconium by the N and C17 atoms [93.7(2)°] is considerably smaller than that found for a number of similar compounds having three atoms bound to zirconium in the equatorial wedge.[11] The analogous angle in **1** (P—Zr—N) is much larger at 117.0°, due in part to the large size of the phosphine compared with the carbonyl ligand in **2**. The nitrogen atom in **2** adopts a planar geometry, a feature common to many metal amides, and to silyl amides in particular. Interestingly, because the nitrogen lone pair is perpendicular to the vacant valence orbitals on zirconium,[12] the planarity at nitrogen can not be readily ascribed to N → Zr π-donation. However, both the steric bulk of the t-butyl group and the electropositive nature of zirconium and silicon would encourage planarity at nitrogen. It is important to note that the location of the t-butyl group in the Zr—Si—N plane is inconsistent with the zirconium(II), silanimine formulation, but does support the metallacyclic structure.

The Zr—N distance in **2** is nearly identical to that observed in **1** [2.162(4) *vs* 2.167(3) Å]. The Zr—Si bond length of 2.706(1) Å is somewhat longer than the distance of 2.654(1) Å for **1**. Both

Table 3. Selected bond angles (°) in **2**[a]

Cp1—Zr—Cp2	132.4	N—Si—C12	120.5(2)
Zr—C17—O	173.4(5)	Zr—N—Si	89.1(2)
C17—Zr—Si	55.8(1)	Zr—N—C13	139.8(3)
C17—Zr—N	93.7(2)	Si—N—C13	131.1(3)
Si—Zr—N	37.9(1)	N—C13—C14	109.4(4)
Zr—Si—N	53.0(1)	N—C13—C15	110.0(4)
Zr—Si—C11	124.1(2)	N—C13—C16	109.7(5)
Zr—Si—C12	122.9(2)	C14—C13—C15	109.0(6)
C11—Si—C12	106.7(3)	C14—C13—C16	111.0(5)
N—Si—C11	121.4(3)	C15—C13—C16	107.6(5)

[a] Cp1 and Cp2 refer to the centroids of the Cp rings. Numbers in parentheses are estimated standard deviations in the least significant digits.

of these Zr—Si distances, however, are relatively short compared with simple silyl complexes of zirconium [d(Zr—Si) = 2.707–2.815 Å].[13] In addition, the Si—N distance of 1.661(4) Å is slightly shorter than that found in **1** [1.687(3) Å]. The Si—N distance still falls within the range observed for Si—N single bonds in a variety of Si—N compounds (1.64–1.80 Å).[14] Free silanimines and their Lewis base adducts show much shorter Si=N bond lengths [e.g. $^tBu_2Si{=}NSi^tBu_3$, d(Si=N) = 1.568(3) Å].[15] In comparison to **1**, the longer Zr—Si and shorter Si—N distances in **2** suggest a somewhat smaller degree of π-back-bonding from the metal to the silanimine fragment, consistent with the greater π-acidity of carbonyl compared with trimethylphosphine. However, the metrical parameters for the three-membered rings of **1** and **2** suggest that the metallacyclic, zirconium(IV), resonance form dominates the bonding in both of the η^2-silanimine complexes.

The carbonyl ligand of **2** exhibits a nearly linear Zr—C—O angle [173.4(5)°], with the oxygen bent very slightly away from the Si—N fragment. The formally non-bonding contact between the carbonyl carbon and the silicon, d(C17—Si), is 2.347(7) Å, much too long to be considered a normal Si—C single bond (*ca* 1.82–1.90 Å [14]), as would be expected in a cyclic structure such as **A**. The Zr—C17 distance of 2.145(5) Å is somewhat short, but falls within the range observed in structurally characterized zirconium carbonyls (2.133–2.25 Å).[16] Similarly, the C—O bond length in **2** [1.162(7) Å] is not unusually long for a zirconium carbonyl (1.116–1.183 Å).[16]

Taken separately or together, the geometrical parameters are clearly indicative of formulation of **2** as a terminal carbonyl complex. Indeed, the general trends [relatively short d(Zr—C) and long d(C—O)] are consistent with a fairly tight binding of CO to the zirconium center, as is observed in zirconium(II) and zirconium(0) complexes. However, the geometry of the Zr—Si—N fragment favor the view of **2** as a zirconium(IV), metallacyclic compound rather than as an η^2-Si=N complex. The origins of the anomalous aspects of **2** are addressed in the following section.

Origin of π-back-bonding to the carbonyl ligand

Compound **2** presents something of a paradox when viewed in terms of the traditional bonding schemes of organometallic chemistry. The extremely low ν(CO) suggests extensive delocalization of electron density into the π^* orbital of the carbonyl ligand, which is usually associated with donation of π electrons from the metal to the carbonyl. Furthermore, by the usual logic applied, the fact that ν(CO) for **2** is $>50\ cm^{-1}$ lower than in $Cp_2Zr(PMe_3)(CO)$ would seem to indicate that the $Me_2Si{=}N^tBu$ ligand is a significantly better electron donor (towards the metal) than PMe_3.

The proposition that the silanimine is a strong net electron donor, however, is not reasonable in light of what is known about silaolefins in general,[17] and their metal complexes, in particular. The relatively poor p–π overlap in multiple bonds to silicon results in a very strong preference of silicon for sp^3 hybridization. In addition, silicon is a very electropositive element. Both factors lead to the result that free stable silaolefins are much more strongly electrophilic than their carbon analogs in virtually every aspect of their chemistry. For example, Wiberg has shown that the stable silanimine $^tBu_2Si{=}NSi(^tBu)_3$ readily reacts with donors such as THF to form an isolable adduct, $THF\cdot{}^tBu_2Si{=}NSi(^tBu)_3$.[15] This unusual compound, in which the silicon is four-coordinate and the nitrogen is two-coordinate, has no simple analog in organic chemistry, and nicely typifies the electrophilicity of silicon in unsaturated compounds.

Structural studies of transition metal complexes of disilenes[18] and silenes[19] also clearly indicate that the "silaolefin" is substantially rehybridized towards the metallacyclic limit; i.e. there is substantial π-back-bonding from the metal to the unsaturated silicon ligand. Furthermore, an extensive study of $Cp_2W(Me_2Si{=}SiMe_2)$ and $Cp_2W(Me_2Si{=}CH_2)$ by photoelectron spectroscopy confirms that the metal in these complexes is effectively tungsten(IV).[20] In other words, silaolefins are extremely effective electron acceptors, and certainly not net donors of electron density to a metal.

An alternative explanation for the low CO stretching frequency in **2** is that the electron donation into the CO π^* occurs directly from the silanimine ligand, rather than from the formally d^0 zirconium center. One possibility is donation from the amide lone pair of electrons. Because the lone pair orbital is not adjacent to the CO and is perpendicular to the valence orbitals on zirconium, overlap with the CO would require conjugation from nitrogen to a vacant π-symmetry Zr—Cp orbital and then to the out-of-plane π^* orbital on the carbonyl. The relatively high energy of the Zr—Cp antibonding orbitals would seem to disfavor this, and molecular orbital (MO) calculations do not support this possibility (*vide infra*).

Electron density could also be donated to the carbonyl from the adjacent silicon atom of the Si—N fragment. The idea of direct overlap between the CO π^* and adjacent ligand orbitals has been proposed to explain the structure[21] and CO stretching frequency[5] of the d^0 carbonyl complex, $Cp^{*}_{2}Zr(H)_2CO$, and in discussing the facile insertion of CO into metallocene alkyl bonds.[12] More recently, Stryker and Jordan and their co-workers reported cationic, d^0 zirconocene carbonyl complexes containing allyl[6c] and acyl[6d] ligands, and suggested the moderate backbonding observed is also the result of electron donation to the carbonyl directly from the adjacent ligand or metal–ligand σ-bond.

The viability of σ–π^* overlap between the silanimine and CO ligands in **2** was explored with MO calculations employing the ZINDO method and the atomic coordinates determined from the crystal structure.[22,23] Although no significant overlap between the nitrogen lone pair and either the zirconium or carbonyl is predicted by this calculation, examination of the HOMO (Fig. 2) clearly reveals a substantial interaction between the in-plane Zr—C—O π-system and a p-type orbital on the $SiMe_2$ fragment. The calculated bond order for the Si···C interaction is 0.59, barely below the 0.60 cutoff employed in the calculation to describe a "single bond". Interestingly, despite the relatively close proximity of the zirconium and silicon nuclei, the Zr—Si bond has a calculated bond order of only 0.34. In other words, there is substantially more overlap calculated in the σ–π^* interaction between the silicon and carbonyl than in the more traditional Zr—Si σ-bond!

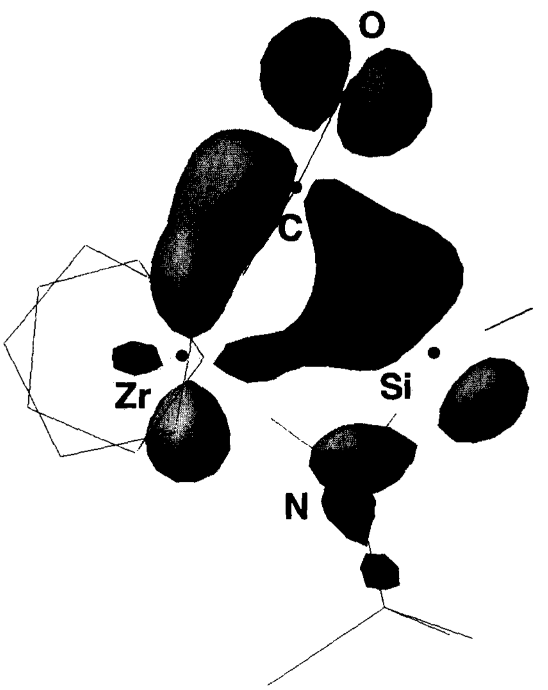
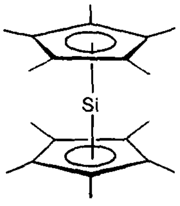
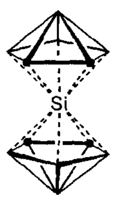


Fig. 2. Contour plot of the highest occupied molecular orbital (HOMO) of **2** showing overlap between a p-type orbital on silicon and the Zr—C—O π-system. All orbital lobes shown lie in the plane of the labeled atoms, except the p-orbital on nitrogen, which is perpendicular.

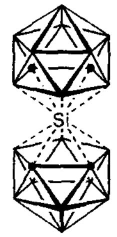
It was mentioned above that the Si···C distance in the structure of **2** [2.347(7) Å] is substantially longer than expected in a normal Si—C single bond (1.82–1.90 Å). However, a search of the Cambridge Structural Database reveals some interesting comparisons.[16] As expected, the vast majority of the >29,000 Si—C bond distances tabulated in the database fall very close to the single bond distance [mean d(Si—C) = 1.87±0.04 Å). Out of this tremendous sample, only 14 compounds exhibit Si—C distances >2.20 Å, and most of these can be dismissed as unreliable due to crystallographic disorder or poor data quality. However, the three compounds depicted below appear to exhibit reliable Si—C bond distances ranging from 2.22(1) to 2.541(7) Å:



$Si(C_5Me_5)_2$



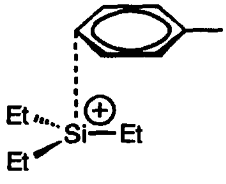
$Si((Me_3Si)_2C_2B_4H_4)_2$



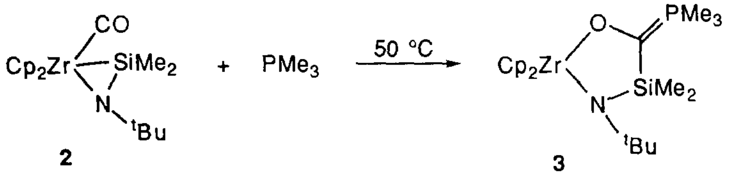
$Si(C_2B_9H_{11})_2$

These compounds are the silicon sandwich complex decamethylsilicocene[24] ($Cp^{*}_{2}Si$) prepared by Jutzi, and two of its carborane analogs, bis(η^5-dicarbollide)silicon[25] and $Si((Me_3Si)_2C_2B_4H_4)_2$.[26] In each case the silicon–carbon interactions are the result of multi-center bonding between orbitals on silicon and the delocalized π-system of the Cp or carborane ligand.

Recently, long silicon–carbon contacts have been the subject of some controversy in the debate regarding the existence of three-coordinate silyl cations.[27] Lambert and co-workers reported the structure of $[Et_3Si][B(C_6F_5)_4]$·toluene, and noted "distant coordination" to the toluene solvent;[27a] the distance between the silicon and nearest arene carbon is 2.18 Å. Reed and co-workers subsequently interpreted the structure in terms of a π-arene complex of silicon.[27b] Interestingly, neither



Et_3Si^{+}•toluene



(3)

group made the connection between the silyl cation–toluene complex and decamethylsilicocene, despite the fact that the toluene is apparently bonded to the silyl cation much more tightly than is the Cp* ring of Cp$^*_2$Si. That the Si-carbonyl carbon distance in **2** falls in the middle of the range of Si—C distances in these delocalized π-complexes strongly reinforces the conclusion of the MO calculation: there is significant *p–p* σ-overlap between the silicon and the carbonyl in **2**.

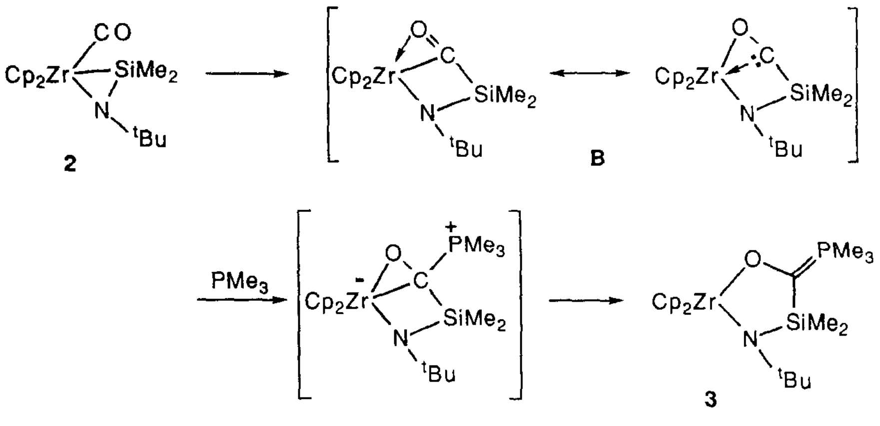
The phenomenon of intra-ligand σ–π* backbonding is conceptually identical in **2** and the original Bercaw d^0-carbonyl and the more recent Jordan and Stryker examples. However, as indicated by the CO stretching frequencies, the effect is relatively small in the latter three cases, but quite pronounced in **2**. This is undoubtedly due to several factors, the most significant of which is probably the large atomic radius of silicon [$r(\mathrm{Si}) = 1.17$ Å, $r(\mathrm{C}) = 0.77$ Å] and the resulting protrusion of the Si *p*-orbitals.

Although the molecular structure clearly establishes that **2** is not the product of full CO insertion into the Zr—Si bond (silaacyl **A**), evidence for such an insertion process is found in the reaction chemistry of **2**, as described in the following section.

Reaction of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**) *with trimethylphosphine*

Carbonyl adduct **2** might be reasonably expected to react with an excess of trimethylphosphine to generate carbon monoxide and phosphine adduct **1**, i.e. the reverse of eq. (1). However, after 20 h at 25°C, a benzene-d_6 solution of **2** and *ca* 10 equiv. PMe_3 shows no evidence for the formation of **1**. Thermolysis of **2** in neat PMe_3 at 50°C does result in a color change of the solution (from purple to yellow) over a period of hours. The product isolated after recrystallization was not **1**, however, but rather the five-membered metallacycle *cyclo*-$Cp_2Zr[OC({=}PMe_3)SiMe_2N^tBu]$ [**3**, eq. (3)]. Compound **3** has been isolated in 51% yield as an orange–yellow solid, and characterized by elemental analysis and multinuclear NMR spectroscopy.

The ^1H NMR spectrum of **3** consists of three singlets at δ 6.13, 1.34 and 0.30 for the Cp, ^{t}Bu and $SiMe_2$ groups, as well as a doublet at δ 0.75 ($J_{PH} = 12.4$ Hz) for the PMe_3 group. The $^{13}C\{^1H\}$ NMR spectrum contains a doublet at δ 50.8 for the metallacycle carbon bound to phosphorus. The large ^{31}P–^{13}C coupling constant of 73.2 Hz is similar to values found for a number of phosphorus ylides. Examples include $Me_3P{=}CH_2$ ($J_{PC} = 90.5$ Hz),



Scheme 1.

$Me_3P{=}CH(SiMe_3)$ ($J_{PC} = 88.2$ Hz), and $Me_3P{=}C(SiMe_3)_2$ ($J_{PC} = 63.3$ Hz).[28]

A singlet at δ 8.8 is observed in the $^{31}P\{^1H\}$ NMR spectrum of **3**. The $^{29}Si\{^1H\}$ NMR spectrum displays a doublet resonance at δ 12.6 with a large ^{31}P–^{29}Si coupling constant of 48.5 Hz. The magnitude of the coupling constant is larger than that found for the silyl-substituted phosphorus ylides $Me_3P{=}CH(Si^tBu_2H)$ ($J_{PSi} = 12$ Hz) and $Me_3P{=}CH(SiMe_2H)$ ($J_{PSi} = 16$ Hz).[29]

A possible mechanism to explain the formation of **3** is shown in Scheme 1, and relies on the initial insertion of the carbonyl ligand of **2** into the Zr—Si bond. The CO insertion generates silaacyl intermediate **B**, depicted in Scheme 1 as an η^2-silaacyl complex. The chemistry of η^2-acyl complexes of *f*-block and early transition metals tends to be dominated by electrophilicity at the acyl carbon, which has been explained by the presence of oxycarbene or oxycarbenium ion character.[30] Attack of trimethylphosphine at the acyl carbon in **B** generates **3**, presumably via a tetrahedral Lewis base adduct. Tilley and co-workers have described several analogous adducts, formed in the reactions of the tantalum silaacyl complex $Cp^*TaCl_3(\eta^2\text{-}COSiMe_3)$ with Lewis bases.[4,31] The stable adducts $Cp^*TaCl_3[\eta^2\text{-}OC(L)SiMe_3]$ (L = pyridine, PMe_3, PEt_3 or $P(OMe)_3$) were isolated, and the geometry confirmed by structural analysis of the pyridine adduct.[31a] Compound **3**, formally a zirconoxy ylide complex, is similar to the product of the reaction of $Cp_2Zr(CH_2PMe_2)_2$ and CO, reported by Karsch *et al.*[32] The product, *cyclo*-$Cp_2Zr[OC(CH_2PMe_2){=}PMe_2CH_2]$, most likely arises via initial CO insertion into the Zr—C bond of $Cp_2Zr(CH_2PMe_2)_2$, followed by an intramolecular attack of the phosphine on the resulting acyl carbon of $Cp_2Zr(\eta^2\text{-}COCH_2PMe_2)(CH_2PMe_2)$. The P—C ylide bond of *cyclo*-$Cp_2Zr[OC(CH_2PMe_2){=}PMe_2CH_2]$ is contained within the five-membered ring, however, while **3** contains an exocyclic P=C linkage. A number of related zirconoxycarbene complexes, in which the carbene is bound to a metal (e.g. Zr, W, Co) rather than phosphorus have also been described.[33]

Exchange of free PMe_3 with the coordinated phosphine in **3** occurs slowly at room temperature. Thus, the ^1H NMR spectrum of a benzene-d_6 solution of **3** and 5 equiv. PMe_3-d_9 shows *ca* 35% phosphine exchange after 7 days at 25°C. Thermolysis at 50°C leads to complete exchange in only 24 h. Dissociation of PMe_3 from **3** could regenerate silaacyl **B**, which would then be trapped by labeled phosphine. Tilley and co-workers have described a similar lability for the complexed Lewis bases in $Cp^*TaCl_3[\eta^2\text{-}OC(L)SiMe_3]$.[4d,31]

Thermolysis of **3** in benzene-d_6 regenerates **2**, indicating that eq. (3) is reversible. However, the conversion is not quantitative, as decomposition products are also observed by ^1H NMR. After 2 days at 50°C, conversion of **3** is ca. 70% complete. Carbonyl adduct **2** comprises *ca* 50% of the resulting zirconium products. Formation of **2** probably results from an initial dissociation of phosphine from **3**, which could regenerate silaacyl **B**. Deinsertion of CO from **B** would lead directly back to **2**.

Although the reaction of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**) with PMe_3 yields **3** instead of **1**, the majority of the reactions of **2** do indeed parallel that of **1**, and indicate that CO dissociation can indeed occur. For example, reaction of **1** or **2** with hydrogen generates the hydride complex $Cp_2Zr(H)(N^tBuSiMe_2H)$, which contains an agostic Si—H—Zr interaction.[34] Similarly, both **1** and **2** react with 2-butyne to produce the ring expansion product, *cyclo*-$Cp_2Zr(MeC{=}CMeSiMe_2N^tBu)$,[3] and with CO_2 to yield the four-membered ring *cyclo*-$Cp_2Zr(OSiMe_2N^tBu)$.[2] In all of the cases studied excepting PMe_3, reactions with **1** and **2** yield the same product, although **2** tends to react more slowly under the same conditions.

CONCLUSIONS

In most respects, the carbonyl silanimine complex $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**) can most consistently be formulated as a zirconium(IV) metallacycle, containing a Zr—Si—N three-membered ring and a linear, terminal carbonyl ligand. Although the geometry of the carbonyl is not particularly perturbed, the carbonyl stretching frequency is much lower than expected for a zirconium(IV) complex, and, indeed, lower than any other zirconocene carbonyl. MO calculations indicate that the origin of this anomalously low stretching band is donation of electron density into the CO π^* orbital directly from an orbital on the adjacent silicon center, i.e. σ–π^* back-bonding. The Si$\cdots$C carbonyl distance in **2** (2.347 Å) is much longer than a typical single bond (~1.87 Å), but falls in the range for delocalized organic π-ligands bonded to silicon. Although the bond between the silicon and carbonyl ligand is not fully formed in the ground state of **2**, thermolysis in the presence of PMe_3 yields the five-membered metallacycle *cyclo*-$Cp_2Zr[OC({=}PMe_3)SiMe_2N^tBu]$ (**3**), resulting from CO insertion into the Zr—Si bond and formation of a cyclic silaacyl, followed by attack of phosphine at the electrophilic acyl carbon.

EXPERIMENTAL

General considerations

All manipulations were carried out under an inert atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk and high vacuum line techniques. ^1H NMR spectra were obtained at 200-, 250-, and 500-MHz on Bruker AF-200, IBM AC-250 and IBM AM-500 FT NMR spectrometers, respectively. ^{13}C NMR spectra were obtained at 125-MHz on the AM-500 spectrometer, and $^{31}P\{^1H\}$ NMR spectra were recorded at 81-MHz on a Bruker WP-200 spectrometer. ^{29}Si NMR spectra were obtained at 40-MHz on the AM-200 spectrometer using a DEPT pulse sequence. All NMR spectra were recorded in benzene-d_6 as solvent. Chemical shifts are reported relative to tetramethylsilane for ^1H, ^{13}C and ^{29}Si NMR, and external 85% H_3PO_4 for ^{31}P NMR. Elemental analyses were performed by Desert Analytics (Tucson, Arizona) and Robertson Microlit, Inc. (Madison, New Jersey).

All solvents were dried over sodium benzophenone ketyl and degassed prior to use. Benzene-d_6 was dried over Na/K alloy. Carbon monoxide (Airco) and ^{13}C-labeled carbon monoxide (99% ^{13}C, Aldrich) were used as received. Trimethylphosphine[35] and $LiCH_2SiMe_3$[36] were prepared according to literature procedures. $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(PMe_3)$ (**1**) and $Cp_2Zr(I)(N^tBuSiMe_2H)$ (**3**) were prepared as previously described.[2,34]

Synthesis of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)$ (**2**)

Method 1. A toluene solution (10 cm^3) of **1** (0.300 g, 0.71 mmol) was stirred under 1 atm carbon monoxide for 1 h. Volatiles were removed *in vacuo* and the residue recrystallized from pentane, yielding 0.195 g of dark purple **2** (73% yield). Anal. found: C, 53.79; H, 6.63. Anal. calc. for $C_{17}H_{25}NOSiZr$: C, 53.96; H, 6.65. ^1H NMR: δ 5.30 (s, Cp), 1.05 (s, N^tBu), 0.26 (s, $SiMe_2$). $^{13}C\{^1H\}$ NMR: δ 290.7 (CO), 103.4 (Cp), 54.6 ($NCMe_3$), 34.5 ($NCCH_3$), 2.3 ($^1J_{SiC} = 55.5$ Hz, $SiCH_3$). $^{29}Si\{^1H\}$ NMR: δ −69.9 (s, $^2J_{SiC} = 24.1$ Hz). IR (benzene): 1797 cm^{-1} [$\nu_{(CO)}$].

Method 2. A mixture of $Cp_2Zr(I)(N^tBuSiMe_2H)$ (0.311 g, 0.650 mmol) and $LiCH_2SiMe_3$ (0.063 g, 0.670 mmol) was placed in a thick-walled glass pressure flask. Under vacuum, toluene (20 cm^3) was transferred into the flask at −196°C, and then carbon monoxide (7.3 mmol) was added. The frozen solution was warmed to room temperature and stirred for 1.7 h. The solution became progressively darker during this time period. Volatiles were removed *in vacuo* and the residue recrystallized from pentane, yielding 0.150 g of dark purple **2** (61% yield).

Formation of $Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(^{13}CO)$ (**2** ^{13}CO)

A NMR tube containing **1** (5 mg, 11.7 μmol) and 0.4 cm^3 benzene-d_6 was placed under vacuum and ^{13}CO (99% ^{13}C, *ca* 0.15 mmol) added. The tube was sealed, and after 10 min at room temperature, the ^1H NMR spectrum showed complete conversion to **2**—^{13}CO. The ^1H and $^{13}C\{^1H\}$ NMR spectra were identical to that found for unlabeled **2**, except for the increased intensity for the carbonyl resonance at δ 290.7 in the $^{13}C\{^1H\}$ NMR spectrum. $^{29}Si\{^1H\}$ NMR: δ −69.8 (d, $^2J_{SiC} = 24.1$ Hz). IR (benzene-d_6): 1756 cm^{-1} [ν(CO)].

Synthesis of cyclo-$Cp_2Zr[OC({=}PMe_3)SiMe_2N^tBu]$ (**3**)

A benzene solution (10 cm^3) of **1** (0.240 g, 0.562 mmol) was stirred under an atmosphere of carbon monoxide (3 atm) for 1 h. Volatiles were removed *in vacuo* and PMe_3 (10 cm^3) was added. The solution was heated at 50°C for 19 h. Volatiles were removed *in vacuo* and the residue recrystallized from petroleum ether, yielding 0.131 g of orange–yellow **3** (51% yield). Anal. found: C, 52.21; H, 7.66. Anal. calc. for $C_{20}H_{34}NOPSiZr$: C, 52.82; H, 7.54. ^1H NMR: δ 6.13 (s, Cp), 1.34 (s, ^tBu), 0.75 (d, $J_{PH} = 12.4$ Hz, PMe_3), 0.30 (s, $SiMe_2$). $^{13}C\{^1H\}$ NMR: δ 109.8 (s, Cp), 56.7 (d, $J_{PC} = 4.0$ Hz, $NCMe_3$), 50.8 (d, $J_{PC} = 73.2$ Hz, $OC{=}PMe_3$), 35.4 (s, $NCCH_3$), 13.0 (d, $J_{PC} = 55.8$ Hz, PMe_3), 6.8 (s, $SiMe_2$). $^{29}Si\{^1H\}$ NMR: δ 12.6 (d, $J_{PSi} = 48.5$ Hz). $^{31}P\{^1H\}$ NMR: δ 8.8 (s).

Reaction of cyclo-$Cp_2Zr[OC({=}PMe_3)SiMe_2N^tBu]$ (**3**) and PMe_3-d_9

A NMR tube was loaded with a benzene-d_6 solution (0.5 cm^3) of **3** (11 mg, 24 μmol) and PMe_3-d_9 (0.12 mmol) and sealed under vacuum. The reaction was monitored by ^1H NMR. After 7 days at 25°C in the dark, the ^1H NMR spectrum showed that *ca* 35% exchange had occurred. After 24 h at 50°C in the dark, exchange of the bound PMe_3 with PMe_3-d_9 was complete. Thermolysis also caused formation of **2** (*ca* 25% of Zr species).

Thermolysis of cyclo-$Cp_2Zr[OC({=}PMe_3)SiMe_2N^tBu]$ (**3**)

A NMR tube was loaded with a benzene-d_6 solution (0.5 cm^3) of **3** (40 mg, 88 μmol) and sealed under vacuum. The solution was heated at 50°C in the dark, and the reaction was monitored by ^1H NMR. After 2 days, conversion of **3** was *ca* 70% complete. Carbonyl **2** composed *ca* 50% of the Zr products. A large number of unidentified decomposition products were also formed.

Structure determination of **2**

Single crystals of **2** were grown from toluene/petroleum ether at -35°C under nitrogen. A crystal of suitable size was sealed under nitrogen in a 0.5 mm thin-walled Pyrex capillary and mounted on the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections with $2\theta > 25°$. Crystal data are summarized in Table 1.

Diffraction data were collected at 295 K on an Enraf–Nonius four-circle CAD-4 diffractometer employing Mo-K_α radiation filtered through a highly oriented graphite crystal monochromator. The intensities of three standard reflections measured at intervals of *ca* 80 reflections showed no systematic change during data collection. Data collection is summarized in Table 1. The raw intensities were corrected for Lorentz and polarization effects by using the program BEGIN from the SDP+ package.[37] An empirical absorption correction based on ψ-scans was applied.

All calculations were performed on a DEC Microvax 3100 computer with the SDP+ software package.[37] The full-matrix least-squares refinement was based on F, and the function minimized was $\Sigma w(|F_o|-|F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. Atomic scattering factors and complex anomalous dispersion corrections were taken from refs 38–40. Agreement factors are defined as $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$and $R_2 = [\Sigma w\,||F_o|-|F_c||^2/\Sigma w\,|F_o|^2]^{1/2}$. The goodness-of-fit is defined as $\mathrm{GOF} = [\Sigma w(|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}$, where N_o and N_p are the number of observations and parameters.

The coordinates of the zirconium were obtained from a three-dimensional Patterson map. Analysis of subsequent difference Fourier maps led to location of the remaining heavy atoms. All hydrogen atoms were placed at idealized locations [d(C—H) = 0.95 Å] with use of the program HYDRO.[37] Final refinement included anisotropic Gaussian amplitudes for all non-hydrogen atoms. Hydrogen atoms were included as constant contributions to the structure factors and were not refined. Final agreement factors are listed in Table 1. Final positional parameters, Gaussian amplitudes, and complete tables of bond distances and angles for **2** are included as supplementary material available from the author on request.

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