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Reactions of Carbon Dioxide and Carbon Disulfide with η^2-Silanimine Complexes of Zirconium: Facile Deoxygenation and Desulfurization Reactions

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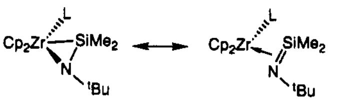
Reaction of the η^2-silanimine complexes $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(L)$ ($Cp \equiv \eta^5\text{-}C_5H_5$; L = PMe_3 (**1a**), CO (**1b**)) with carbon dioxide leads to a net oxygen atom insertion into the Zr–Si bond. The products are carbon monoxide and the dimeric oxazirconacycle $[cyclo\text{-}Cp_2Zr(OSiMe_2N^tBu)]_2$ (**2**). Compound **2** crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$) with a = 10.273(2) Å, b = 10.750(1) Å, c = 14.869(3) Å, and β = 97.82(2)°. Refinement of the structure resulted in the final agreement factors $R_1 = 0.026$, $R_2 = 0.040$, and goodness-of-fit = 1.481. Low-temperature ^1H and $^{13}C\{^1H\}$ NMR studies have allowed the *in situ* observation of $cyclo\text{-}Cp_2Zr[OC({=}O)SiMe_2N^tBu]$ (**3**), the initial intermediate formed by the insertion of the C=O multiple bond of CO_2 into the Zr—Si bond of **1a**. Decarbonylation of **3** at 25 °C and dimerization lead to the observed net oxygen insertion product **2**. Carbon disulfide reacts with **1** to yield the monomeric four-membered metallacycle $cyclo\text{-}Cp_2Zr(SSiMe_2N^tBu)$ (**5**). Carbonyl monosulfide leads to a mixture of the oxygen and sulfur atom insertion products **2** and **5**.

Introduction

For many years, transition metal complexes have been used to promote reactions between silanes and organic molecules containing carbon–oxygen unsaturation. In particular, the metal-catalyzed hydrosilylation of aldehydes and ketones has been extensively studied.[1] It is somewhat surprising, therefore, to discover that investigations of the metal-promoted reaction of carbon dioxide with hydrosilanes have been extremely limited.[2] Carbon dioxide represents an important C_1 raw material and displays a wealth of reactivity with transition metal complexes.[3] Numerous examples of CO_2 insertions, and to a lesser extent those involving the related heterocumulenes carbon disulfide and carbonyl monosulfide, into metal hydride[4] and alkyl[5] linkages are known. These reactions generally yield carboxylate derivatives L_nMO_2CR (R = H, alkyl, aryl) in which metal–oxygen and carbon–hydrogen (or carbon–carbon) bonds are formed.[4,5] In contrast, very few reports of reactions with metal silyls have surfaced over the years. In those cases studied, reactions of transition metal silyls with carbon dioxide have generally led to products best explained by initial metal–carbon and silicon–oxygen bond formation (i.e., $L_nMCO_2SiR_3$).[2]

Recently, we reported the synthesis and structure of the first examples of η^2-silanimine ($\eta^2\text{-}SiR_2{=}NR'$) complexes, $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(L)$ ($Cp \equiv \eta^5\text{-}C_5H_5$; L = PMe_3 (**1a**), CO (**1b**)) and described some of their reactivity with a variety of simple substrates.[6] Unsaturated organic molecules (e.g., alkenes, alkynes, aldehydes, ketones) were observed to insert into the Zr–Si bond to generate five-membered metallacycles (Scheme I). In particular, the reactivity of η^2-silanimine complexes **1a** and **1b** with organic carbonyl functionalities suggested that other species containing carbon–oxygen unsaturation, such as carbon dioxide, may also undergo similar insertion processes. We now report on the reactions of the η^2-silanimine



1a, L = PMe_3
1b, L = CO

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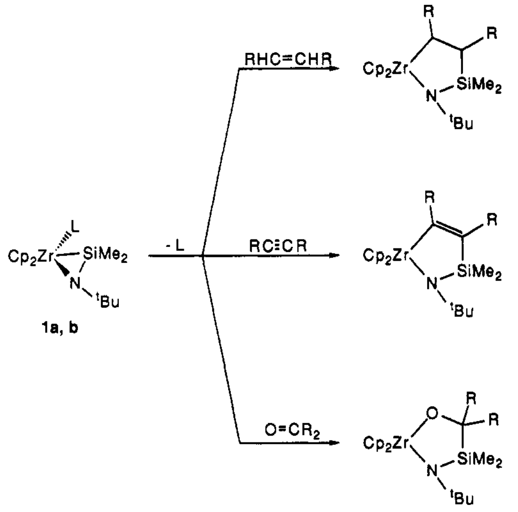
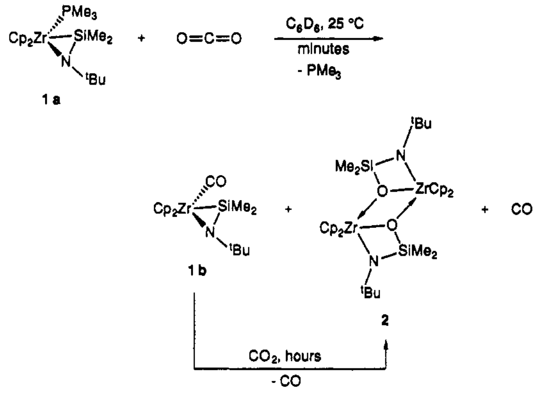
Scheme I



complexes $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(L)$ (1) with carbon dioxide, which result in a net one-atom insertion of oxygen into the metal–silicon bond. The crystal structure of the product is discussed, as well as low-temperature NMR studies providing details relating to the mechanism of its formation. In addition, reactions of 1 with the related heterocumulenes CS_2 and COS are also described.

Results and Discussion

Carbon dioxide (ca. 1 equiv) reacts very rapidly with a benzene-d_6 solution of $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(PMe_3)$ (**1a**) to yield after a few minutes a mixture of carbon monoxide and two zirconium products (eq 1). The minor product (ca. 30%) is the carbonyl adduct $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(CO)$ (**1b**), whereas the major product, the dimeric [*cyclo*-$Cp_2Zr(OSiMe_2N^tBu)]_2$ (**2**), is the result of net oxygen atom insertion into the Zr–Si bond. The dimeric nature of **2** was determined by the crystallographic study described below. The $^{13}C\{^1H\}$ NMR spectrum of the products from the reaction of **1a** and $^{13}CO_2$ confirms the presence of free ^{13}C-labeled carbon monoxide and **1b**-^{13}C but only displays resonances for the Cp (δ 114.1), ^tBu (δ 55.0, 35.0), and $SiMe_2$ (δ 4.1) groups of **2**. Thus as expected from the proposed formula, there is no incorporation of carbon from CO_2 into **2**. Carbonyl derivative **1b** also reacts with CO_2 to yield **2**, although much more slowly ($t_{1/2} \sim 4$ h), so that eventually reaction 1 quantitatively yields the oxametallacycle **2**. The slower reaction of **1b** is consistent with the lower lability of the carbonyl ligand compared to that of the phosphine ligand in **1a**.



(1)

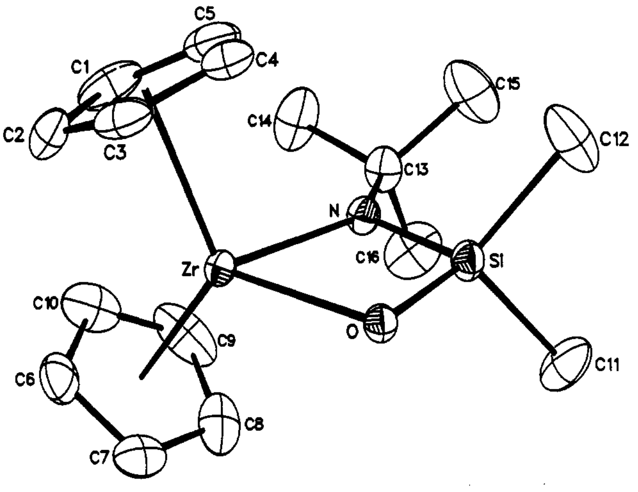


Figure 1. ORTEP drawing of the monomeric unit in [*cyclo*-$Cp_2Zr(OSiMe_2N^tBu)]_2$ (**2**), showing non-hydrogen atoms.

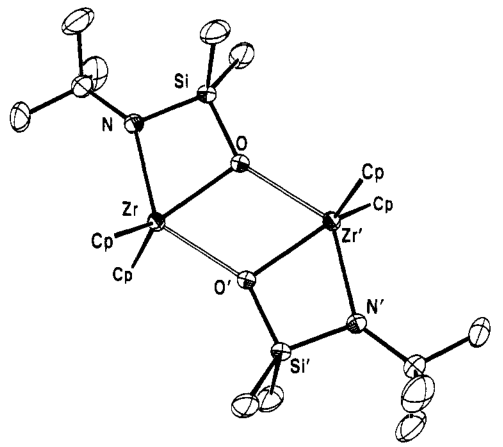


Figure 2. ORTEP drawing of [*cyclo*-$Cp_2Zr(OSiMe_2N^tBu)]_2$ (**2**), showing non-hydrogen atoms. $\eta^5\text{-}C_5H_5$ rings have been omitted for clarity.

Oxametallacycle **2** has been isolated as pale orange crystals in 74% yield from the preparative-scale reaction of **1a** with carbon dioxide. The ^1H NMR spectrum of **2** displays three singlets for the Cp (δ 6.05), ^tBu (δ 1.11) and $SiMe_2$ (δ 0.29) groups.

The structure of **2** has been conclusively established by a single-crystal X-ray diffraction study; an ORTEP drawing of the monomeric unit is shown in Figure 1, and the full dimeric structure is shown in Figure 2. Crystallographic data and selected bond distances and angles are given in Tables I–III. As shown in Figure 2, the centrosymmetric molecule is composed of two crystallographically equivalent *cyclo*-$Cp_2Zr(OSiMe_2N^tBu)$ units connected through Zr–O bridges. The Zr_2O_2 core displays short (2.170(1) Å) and long (2.302(1) Å) Zr–O bond lengths. The shorter Zr–O distance is found within the four-membered (i.e., ZrOSiN) oxametallacycle, while the long Zr–O bond is due to the Zr–O bridges between the monomeric units.

Several other oxazirconacycles have been reported to display dimeric structures analogous to **2**. The η^2-benzophenone complex of zirconocene, $[Cp_2Zr(\eta^2\text{-}O{=}CPh_2)]_2$, exhibits both short (2.109(2) and 2.112(2) Å) and long (2.287(2) and 2.304(2) Å) zirconium–oxygen bond distances.[7] Similar values are found for $[Cp_2Zr(\eta^2\text{-}$

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Table I. Summary of the Structure Determination for 2

formula	$C_{16}H_{25}NOSiZr$
fw	342.67
crystal dimens, mm	0.18 × 0.25 × 0.55
crystal class	monoclinic
space group	$P2_1/n$ (No. 14)
Z	4
cell constants	
a, Å	10.273(2)
b, Å	10.750(1)
c, Å	14.869(3)
β, deg	97.82(2)
V, Å^3	1626.9(9)
μ, cm^{-1}	7.27
D(calc), g/cm^3	1.399
F(000)	712
radiation (λ, Å)	Mo Kα (0.710 73)
θ range, deg	2.0–27.5
scan mode	ω–2θ
h,k,l collected	13,13,±19
no. of reflns measd	4131
no. of unique reflns	3716
no. of reflns used in refinement	3132 ($I > 3\sigma(I)$)
no. of params	181
data/param ratio	17.3
R_1	0.026
R_2	0.040
GOF	1.481

Table II. Bond Distances (Å) in 2[a]

Zr–O	2.170(1)	Zr–C5	2.615(3)
Zr–N	2.195(2)	Zr–C6	2.542(3)
Zr–Si	2.9170(7)	Zr–C7	2.571 (3)
Zr–O′	2.302(1)	Zr–C8	2.573(3)
Si–N	1.695(2)	Zr–C9	2.580(3)
Si–C11	1.873(3)	Zr–C10	2.580(3)
Si–C12	1.880(3)	C1–C2	1.422(5)
N–C13	1.487(3)	C1–C5	1.376(5)
Si–O	1.662(2)	C2–C3	1.378(4)
C13–C14	1.510(4)	C3–C4	1.364(4)
C13–C15	1.526(5)	C4–C5	1.369(5)
C13–C16	1.537(4)	C6–C7	1.375(4)
Zr–C1	2.553(3)	C6–C10	1.355(4)
Zr–C2	2.555(3)	C7–C8	1.377(4)
Zr–C3	2.593(3)	C8–C9	1.385(5)
Zr–C4	2.624(3)	C9–C10	1.359(6)

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

Table III. Selected Bond Angles (deg) in 2[a,b]

Cp1–Zr–Cp2	124.8	O–Si–C11	113.2(1)
Zr–O–Si	98.29(7)	O–Si–C12	111.9(1)
Zr–N–Si	96.31(8)	N–Si–C11	116.6(1)
O–Zr–N	69.53(6)	N–Si–C12	115.4(1)
O–Si–N	95.73(8)	C11–Si–C12	104.2(2)
O–Zr–O′	66.87(5)	Zr–N–C13	139.9(1)
O–Zr′–N′	136.26(6)	Si–N–C13	123.8(2)
Zr–O–Zr′	113.13(6)	N–C13–C14	113.9(2)
Si–Zr–O	34.31(4)	N–C13–C15	110.8(2)
Si–Zr–N	35.27(5)	N–C13–C16	110.3(2)
Zr–Si–O	47.40(5)	C14–C13–C15	108.4(3)
Zr–Si–N	48.42(6)	C14–C13–C16	106.9(2)
Zr–Si–C11	131.1(1)	C15–C13–C16	106.1(3)
Zr–Si–C12	124.5(1)		

[a] Cp1 and Cp2 refer to the centroids of the η^5-C_5H_5 rings. [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Reported Values of Zr–Si Bond Lengths

compound	D(Zr–Si), Å	ref
$Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(PMe_3)$	2.654(1)	*a*
$Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(CO)$	2.706(1)	*b*
$Cp_2Zr(H)(PMe_3)(SiHPh_2)$	2.707(5)	*c*
$Cp_2Zr(SiPh_3)(H)(PMe_3)$	2.721(2)	*d*
$(^tBuO)_3Zr[Si(SiMe_3)_3]$	2.753(4)	*e*
$[Cp_2Zr(\mu\text{-}H)(SiHPh_2)]_2$	2.7590(8)	*c*
$Cp_2Zr(SiPh_3)(Cl)$	2.813(2)	*f*
$Cp_2Zr(SiMe_3)(S_2CNEt_2)$	2.815(1)	*g*

[a] See ref 6a. [b] See ref 6b. [c] Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564. [d] Kreutzer, K. A.; Fisher, R. A.; Davis, W. M.; Spaltenstein, E.; Buchwald, S. L. *Organometallics* **1991**, *10*, 4031. [e] Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1989**, *28*, 1768. [f] Muir, K. W. *J. Chem. Soc. A* **1971**, 2663. [g] Tilley, T. D. *Organometallics* **1985**, *4*, 1452.

$O{=}CH_2)]_2$ (2.103(2) and 2.200(2) Å)[8] and [*cyclo*-$Cp_2Zr(OCH_2CH_2CHMe)]_2$ (2.190(3) and 2.234(7) Å).[9] In most cases the longer Zr–O bonds bridge the monomeric units; however, Hillhouse and co-workers have described the structure of an oxametallacyclobutene derivative of zirconocene, [*cyclo*-$Cp_2Zr(OC_6H_8)]_2$, in which the long Zr–O bond is found within the ZrC_2O ring.[10] One factor common to these dimeric structures is that the ring sizes of the oxametallacycles are small (three to five atoms). The influence of steric factors no doubt plays a large role in determining whether dimerization occurs. Crystallographic studies of zirconocene oxametallacycloheptene and oxametallacyclohexadiene complexes indicate these larger ring systems are monomeric in the solid state.[11] A monomeric oxazirconacyclobutene is also observed in the sterically hindered pentamethylcyclopentadienyl complex *cyclo*-$Cp^*{}_2Zr(OPhC{=}CPh)$ ($Cp^* \equiv \eta^5\text{-}C_5Me_5$).[12]

Other aspects of the structure of 2 appear typical for zirconocene compounds. The Cp1–Zr–Cp2 angle (Cp1 and Cp2 ≡ Cp ring centroids) of 124.8° is within the normal range observed for zirconocene complexes.[13] The Zr–N distance of 2.195(2) Å is only slightly longer than those found for 1a (2.167(3) Å)[6a] and 1b (2.162(4) Å).[6b] The Si–O and Si–N bond lengths (1.662(2) and 1.695(2) Å, respectively) fall within the range observed for these types of single bonds in a variety of silicon-containing compounds.[14]

One unusual feature of the structure of 2 is the short Zr–Si distance of 2.9170(7) Å across the four-membered ring. This nonbonded contact does not fall very far outside the observed range of Zr–Si single bond lengths (see Table IV). Although 2 does not contain a formal Zr–Si bond, the close contact imposed by the geometrical constraints of the four-membered ring may be the cause of the upfield shift of the Si atom (δ −45.11) in the $^{29}Si\{^1H\}$ NMR spectrum of 2. Contact of silicon with a transition metal has been shown to cause dramatic changes in the ^{29}Si chemical shift.[15]. A similar upfield ^{29}Si resonance (δ −57.89) is observed for the ring silicon in the four-membered ring of *cyclo*-$Cp_2Zr[CH(SiMe_3)SiMe_2N^tBu]$, which might also be expected to contain a short cross-ring Zr–Si distance.[6b] It should be noted, however, that Si atoms in small rings (three or four atoms) also generally display upfield ^{29}Si

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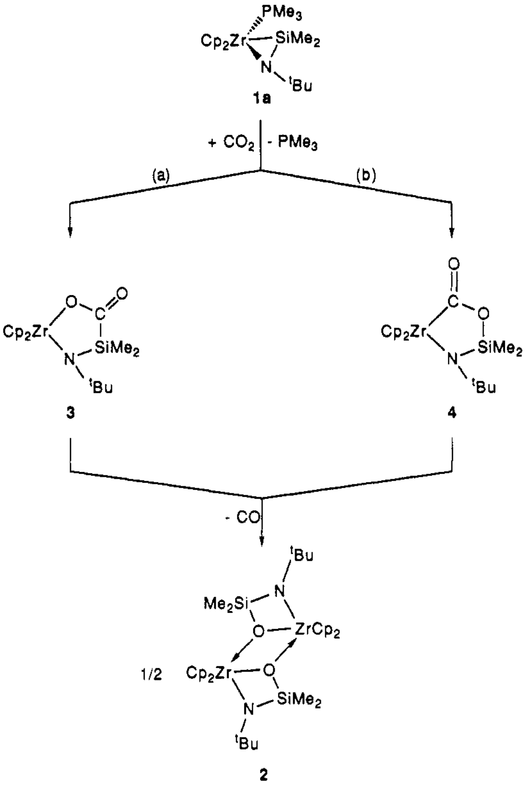
(14) Lukevics, E.; Pudova, O.; Sturkovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis-Horwood: Chichester, U.K., 1989.

chemical shifts[16] and that this effect could account for the observed chemical shifts in the zirconacycles.

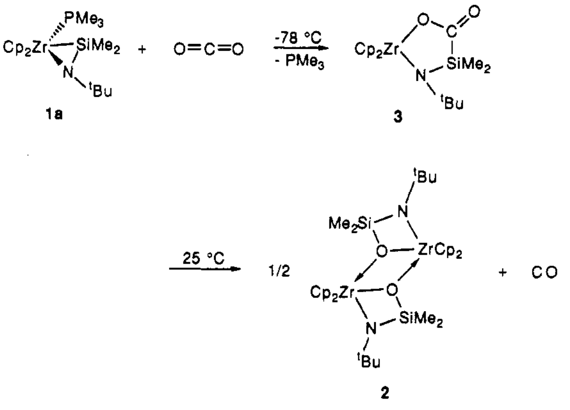
Cross-ring interactions with silicon have previously been postulated for several small-ring compounds. Short cross-ring Si–Si interactions have been demonstrated both by experiment and in theoretical calculations on cyclodisiloxanes[17] and M_2Si_2[18] and MSi_2O[17b,19] ring systems. Although theoretical work does not support the existence of a Si–Si bond in cyclodisiloxanes, the interesting idea of an "unsupported π-bond" (i.e., a π-bond without a supporting σ-bond) has been suggested.[17e] On the other hand, both experiment and theory support the idea of a Si–Si bond in several Pt_2Si_2 rings.[18b–d] Cross-ring Zr–Si distances even shorter than that in **2** have been observed in the molecular structures of *cyclo*-$Cp_2Zr(CH_2SiMe_2CH_2)$ (2.875(2) Å)[20] and {*cyclo*-$Zr(CHSiMe_2NSiMe_3)[N(SiMe_3)_2]$}$_2$ (ca. 2.78 Å),[21] but were not remarked upon by the authors.

Given the extreme oxophilicity of both zirconium and silicon, it is not surprising that the ultimate product of reaction 1 contains both Zr– and Si–O bonds. The nature of the oxygen-transfer process, however, is not completely obvious. The formation of carbon monoxide in reaction 1 suggests that **2** is formed by the decarbonylation of an intermediate CO_2 insertion product (Scheme II). Initial formation of the carbonyl adduct **1b** is simply explained by a rapid scavenging of CO by unreacted **1a**.[6] However, the insertion of a C=O double bond of carbon dioxide into the Zr—Si bond could proceed by two distinct paths: with formation of a Zr—O bond (intermediate **3**) or a Si—O bond (intermediate **4**.) This question has been directly addressed by a low-temperature NMR study of the reaction of **1a** with CO_2.

Scheme II



The ^1H NMR spectrum observed at −77 °C in toluene-d_8 of **1a** and ca. 2 equiv ^{13}C-labeled CO_2 exhibits resonances for unreacted **1a** and a single new species (ca. 35%). The new product displays resonances at δ 5.90 (s), 0.85 (s), and 0.52 (s), assigned to Cp, ^tBu, and $SiMe_2$ groups, respectively. More significantly, the $^{13}C\{^1H\}$ NMR spectrum shows an isotopically enriched peak at δ 187.1 (s), assigned to the carbonyl group of an insertion product. In addition, the peak clearly displays satellites due to coupling to the silicon of the $SiMe_2$ group ($^1J_{SiC}$ = 88.4 Hz), and the magnitude of this coupling unequivocally indicates the presence of a direct Si–C bond.[22] The ^1H and ^{13}C NMR data strongly support the structure for **3** shown in eq 2,



(2)

in which the five-membered metallacycle contains Si–C and Zr–O linkages. Metallacycle **3** appears to be fairly stable in solution at −78 °C, as no appreciable decomposition is observed after approximately 1 h. Warming to room temperature results in the complete decarbonylation of **3**-^{13}C within minutes to yield mainly **2** and free ^{13}CO. Only a small amount of **1b**-^{13}C (ca. 5%) was observed, indicating that nearly all of **1a** had been converted to **3**-^{13}C prior to decarbonylation. Thus, formation of **2** appears to proceed by an initial insertion of CO_2 to yield **3**, followed by a decarbonylation and dimerization (eq 2).

Although most metal alkyls and hydrides react with CO_2 to yield products containing new metal–oxygen

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(15) For examples, see: (a) Pannell, K. H.; Bassindale, A. R. *J. Organomet. Chem.* **1982**, *229*, 1. (b) Pannell, K. H.; Rozell, J. M.; Tsai, W.-M. *Organometallics* **1987**, *6*, 2085.

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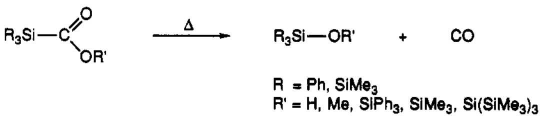
(20) Tikkanen, W. R.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646.

(21) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16.

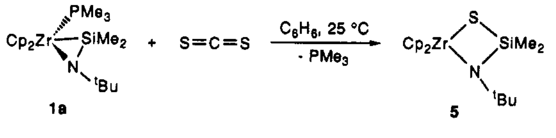
(22) Typical values of $^1J_{SiC}$ are 50–60 Hz for sp^3-hybridized carbon. Larger $^1J_{SiC}$ would be expected for sp^2-hybridized carbon. For example, a series of silyl-substituted acetylenes ($R_3SiC{\equiv}CX$) displayed $^1J_{SiC}$ = 70–90 Hz and $^2J_{SiC}$ = 12–18 Hz: Liepins, E.; Biegele, I.; Lukevics, E.; Bogoradovsky, E. T.; Zavgorodny, V. S. *J. Organomet. Chem.* **1990**, *393*, 11.

bonds,[4,5] previous work with late metal silyls indicates that CO_2 inserts with initial silicon–oxygen bond formation.[2] This has generally been attributed to the greater oxophilicity of silicon compared with the metals to the right of the transition series. However, a previous example of CO_2 insertion with formation of a Si–C bond has been described by Tilley and co-workers, who reported that scandium silyls $Cp_2Sc(SiR_3)(THF)$ (SiR_3 = $Si(SiMe_3)_3$, Si^tBuPh_2) react rapidly with CO_2 to generate the dimeric silanecarboxylate complexes $[Cp_2Sc(\mu\text{-}O_2CSiR_3)]_2$.[23] Small amounts of an additional product were also isolated from the reaction and, although not positively identified, is proposed to be the siloxide $[Cp_2ScOSi(SiMe_3)_3]_x$ generated by decarbonylation of $[Cp_2Sc(\mu\text{-}O_2CSi(SiMe_3)_3)]_2$. This proposal is certainly consistent with the present observations on the zirconium η^2-silanimine system. Presumably, the regiochemistry of CO_2 insertion for these scandium and zirconium systems reflects the extreme oxophilicity of these early transition metals, which is apparently effectively greater than that of silicon. Similar observations have been made for the reactions of early transition metal silicon compounds with ketones and aldehydes, which insert to yield metal–oxygen and silicon–carbon bonds.[6,24] The elimination of CO from intermediate **3** also finds an analog in the decarbonylations of silanecarboxylic acids and their esters (eq 3), which proceed at relatively low temperatures compared with reactions of typical organic acids and esters.[25]



(3)

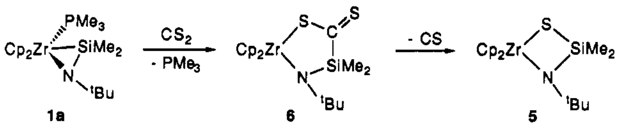
The η^2-silanimine complexes **1a** and **1b** also react readily with another heterocumulene, CS_2. A benzene-d_6 solution of **1a** and ca. 1.1 equiv of CS_2 changes color immediately upon mixing at 25 °C, becoming deep golden-brown. A small amount of unidentified solid is deposited. The ^1H NMR spectrum of the mixture shows the presence of a single major product (ca. 50% Zr product), along with a number of unidentified minor species. The reaction of **1b** with CS_2 also produces this major product (ca. 40%) under the same conditions, but the reaction requires 2 days for completion. The major product has been isolated by sublimation as an orange-yellow solid in 49% yield from the reaction of **1a** and CS_2 and has been identified as *cyclo*-$Cp_2Zr(SSiMe_2N^tBu)$ (**5**, eq 4) from spectroscopic data and elemental analysis.



(4)

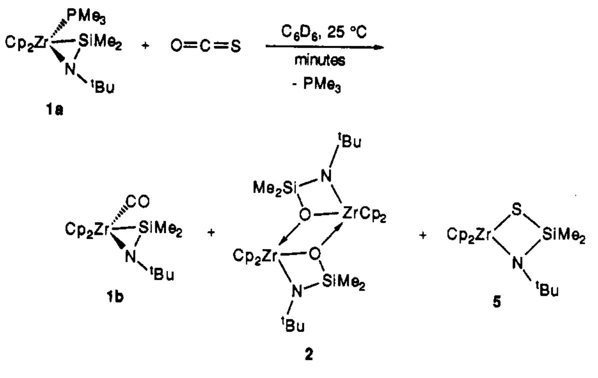
The ^1H NMR spectrum of **5** displays three singlets at δ 6.00, 1.07, and 0.45 due to Cp, ^tBu, and $SiMe_2$ groups, respectively. The $^{13}C\{^1H\}$ NMR spectrum also shows resonances for these three groups, and more importantly, no peak is observed which could be assigned to the thiocarbonyl carbon of an insertion product such as *cyclo*-$Cp_2Zr[SC(=S)SiMe_2N^tBu]$ or *cyclo*-$Cp_2Zr[C(=S)SSiMe_2N^tBu]$. The $^{29}Si\{^1H\}$ NMR spectrum of **5** exhibits a singlet at δ −42.3, very similar to the value observed for **2** (δ −45.1). Mass spectral and solution molecular weight determinations indicate the presence of only monomeric units for **5**. Thus, unlike the dimeric compound **2**, compound **5** is proposed to exist as a monomer in the solid state, no doubt as a result of the weaker Lewis basicity and larger size of sulfur, compared to oxygen.

Scheme III



The formation of **5** most likely proceeds by an initial insertion of a C=S bond of CS_2 to form the intermediate *cyclo*-$Cp_2Zr[SC(=S)SiMe_2N^tBu]$ (**6**, Scheme III), in analogy to the reaction of **1a** with CO_2. Attempts at observing intermediate **6** by low-temperature ^1H and $^{13}C\{^1H\}$ NMR, in analogy to the observation of **3** described above, were not successful. Elimination of carbon monosulfide from **6** would generate **5**. Carbon monosulfide is a highly reactive species,[26] and would be expected to either polymerize or react further with the zirconium species present. The large number (≥7) of minor products observed, as well as the formation of insoluble precipitate, suggests that these processes may well be occurring. Reaction 4 is unusual in that carbon disulfide is acting as a net sulfur-transfer agent. Normally, reaction of transition metal complexes with CS_2 leads to products in which the carbon atom of CS_2 has been incorporated, often as a thiocarbonyl ligand.[27]

The reaction of **1a** with carbonyl monosulfide, COS, leads to a mixture of the oxygen and sulfur atom insertion products, **2** and **5**. A benzene-d_6 solution of **1a** and ca. 1 equiv of COS reacts within minutes to yield **2**, **5**, and carbonyl adduct **1b** in an approximate 1:6:4.6 ratio (eq 5).



(5)

No evidence for the formation of a thiocarbonyl adduct, $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(CS)$, is found in this reaction or for the reaction of **1a** with CS_2. Carbonyl adduct **1b** eventually reacts with the excess COS, generating a final mixture of **2** and **5** in a 1:6 ratio. Because insertion of the C=X bond (X = O, S) into the Zr—Si linkage is most likely an irreversible process, the observed ratio seems to indicate a kinetic preference for C=S insertion.

Conclusions

Reactions of the heterocumulenes carbon dioxide, carbon disulfide, and carbonyl monosulfide with the η^2-

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[26] For example, see: Klabunde, K. J.; White, C. M.; Efner, H. F. *Inorg. Chem.* **1974**, *13*, 1778.

[27] Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801 and references cited therein.

silanimine complexes $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(L)$ (L = PMe_3 (**1a**), CO (**1b**)) have been found to result in net one-atom insertions of oxygen and sulfur into the Zr—Si bond. In the case of carbon dioxide, the reaction has been demonstrated to proceed by the initial insertion of the C=O double bond into the Zr—Si linkage, generating an intermediate containing metal–oxygen and silicon–carbon bonds. Decarbonylation of the initial product, *cyclo*-$Cp_2Zr[OC({=}O)SiMe_2N^tBu]$ (**3**), occurs readily below room temperature, yielding the dimeric oxazirconacycle [*cyclo*-$Cp_2Zr(OSiMe_2N^tBu)]_2$ (**2**). Analogous mechanisms are postulated for reactions involving carbon disulfide and carbonyl monosulfide. One difference is that reaction of **1** with carbon disulfide yields a monomeric metallacycle, *cyclo*-$Cp_2Zr(SSiMe_2N^tBu)$ (**5**). Dimerization probably does not occur in this case due to the larger size and decreased Lewis basicity of sulfur compared to oxygen.

Experimental Section

All manipulations were carried out under an inert atmosphere in a Vacuum Atmospheres drybox or by 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. ^{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 unless otherwise indicated. Chemical shifts are reported relative to tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer Model 1430 infrared spectrometer. Low-resolution mass spectroscopic analyses were carried out on a VG Instrument ZAB-E mass spectrometer at the University of Pennsylvania. Solution molecular weight determinations were carried out by isothermal distillation in benzene according to the literature method.[28] Elemental analyses were performed by Robertson Laboratory, Inc. (Madison, NJ).

All solvents were distilled from sodium benzophenone ketyl prior to use. Benzene-d_6 and toluene-d_8 were dried over Na/K alloy. Carbonyl monosulfide (Aldrich) and ^{13}C-labeled carbon dioxide (90% ^{13}C, ICON) were used as received. Carbon disulfide was dried over molecular sieves and degassed prior to use. Carbon dioxide was dried prior to use by passing it through a dry ice/acetone trap. The η^2-silanimine complexes $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(PMe_3)$ (**1a**) and $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(CO)$ (**1b**) were prepared as previously described.[6]

[*cyclo*-$Cp_2Zr(OSiMe_2N^tBu)]_2$ (2). Carbon dioxide (0.70 mmol) was condensed into a thick-walled glass pressure flask containing a frozen (−196 °C) solution of **1a** (0.255 g, 0.598 mmol) in 15 mL of benzene. The flask was warmed to room temperature, and the mixture was stirred for 3 h. Volatiles were removed in vacuo. The residue was recrystallized from toluene/petroleum ether, yielding 0.161 g of pale orange **2** (73% yield). Anal. Calcd for $C_{16}H_{25}NOSiZr$: C, 52.41; H, 6.87. Found: C, 52.43; H, 7.04. ^1H NMR: δ 6.05 (s, Cp), 1.11 (s, ^tBu), 0.29 (s, $SiMe_2$). $^{13}C\{^1H\}$ NMR: δ 114.1 (Cp), 55.0 ($NCMe_3$), 35.0 ($NCCH_3$), 4.1 ($SiMe_2$). $^{29}Si\{^1H\}$ NMR: δ −45.1 (s).

Observation of *cyclo*-$Cp_2Zr[OC^{13}({=}O)SiMe_2N^tBu]$ (3-^{13}C). An NMR tube was loaded with **1a** (15 mg, 35 μmol) and toluene-d_8 (0.5 mL) and placed under vacuum. ^{13}C-labeled carbon dioxide (64 μmol) was condensed into the tube at −196 °C and the tube sealed under vacuum. The tube was thawed in a dry ice/acetone bath (−78 °C), quickly shaken at this temperature, and immediately placed in the cooled NMR probe (−77 °C). ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained at 500 and 125 MHz, respectively. Characterization of **3**-^{13}C. ^1H NMR (toluene-d_8, −77 °C): δ 5.90 (s, Cp), 0.85 (s, ^tBu), 0.52 (s, $SiMe_2$). $^{13}C\{^1H\}$ NMR (toluene-d_8, −77 °C): δ 187.1 (s, $^1J_{SiC}$ = 88.4 Hz, $^{13}C{=}O$), 115.3 (br s, Cp), 57.6 (s, $NCMe_3$), 34.3 (s, $NCCH_3$), 3.4 (s, $SiMe_2$). The tube was removed from the probe several times between spectra and quickly shaken to increase the amount of **3**-^{13}C present (up to 67% Zr species at one point). After the tube was warmed to 25 °C for 5 min, the ^1H and $^{13}C\{^1H\}$ NMR spectra (at −77 °C) showed the presence of PMe_3, excess $^{13}CO_2$, ^{13}CO, **2**, and a small amount of **1b**-^{13}C (ca. <5% Zr species) and the loss of all signals due to **3**-^{13}C.

***cyclo*-$Cp_2Zr(SSiMe_2N^tBu)$ (5).** Carbon disulfide (0.523 mmol) was condensed into a thick-walled glass pressure flask containing a frozen (−196 °C) solution of **1a** (0.222 g, 0.520 mmol) in 20 mL of benzene. The flask was warmed to room temperature, the mixture immediately became dark brown, and the formation of a small amount of solid was observed. The solution was stirred for 20 min, and then volatiles were removed in vacuo. The residue was dissolved in toluene and the mixture was filtered, leaving ca. 29 mg of an unidentified insoluble light brown powder behind. Solvent was removed from the filtrate, and the crude product was sublimed (90 °C, 10^{-4} Torr) onto a water-cooled probe, yielding 0.097 g of bright orange-yellow **5** (49% yield). Anal. Calcd for $C_{16}H_{25}NSSiZr$: C, 50.21; H, 6.58. Found: C, 50.09; H, 6.61. ^1H NMR: δ 6.00 (s, Cp), 1.07 (s, ^tBu), 0.45 (s, $SiMe_2$). $^{13}C\{^1H\}$ NMR: δ 114.4 (s, Cp), 58.9 (s, $NCMe_3$), 35.3 (s, $NCCH_3$), 7.3 (s, $SiMe_2$, $^1J_{SiC}$ = 58.6 Hz). $^{29}Si\{^1H\}$ NMR: δ −42.3 (s). Mass spectrum (methane CI), *m/e*: 382 ($M^+ + 1$). Solution molecular weight (benzene): 349.

Reaction of $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(PMe_3)$ (1a) and COS. An NMR tube was loaded with a benzene-d_6 solution (0.5 mL) of **1a** (6 mg, 14 μmol) and placed under vacuum. Carbonyl monosulfide (15 μmol) was added by vacuum transfer, the tube sealed, and the reaction monitored by ^1H NMR. After 5 min at 25 °C, all starting material had been consumed and a mixture of **1b** (40%), **2** (9%), and **5** (51%) was present. The tube contained a mixture of only **2** and **5** (ca. 1:6) after 95 h at 25 °C.

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 I.

Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα 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 I. The raw intensities were corrected for Lorentz and polarization effects by using the program BEGIN from the SDP+ package.[29] 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.[29] The full-matrix least-squares refinement was based on *F*, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. 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 30–32. Agreement factors are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The goodness of fit is defined as GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o and N_p are the number of observations and parameters.

The coordinates of the zirconium and silicon atoms were obtained from a three-dimensional Patterson map. Analysis of

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(29) B. A. Frenz and Associates, Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland.

(30) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(31) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, *42*, 3175.

(32) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

subsequent difference Fourier maps led to location of the remaining heavy atoms. Refinement in $P2_1/n$ using anisotropic Gaussian amplitudes followed by difference Fourier synthesis resulted in the location of most of the Cp hydrogens and at least one hydrogen on each methyl group. All remaining hydrogen atoms were placed at idealized locations (D(C–H) = 0.95 Å) with use of the program HYDRO.[29] Final refinement included anisotropic Gaussian amplitudes for all non-hydrogen atoms and fixed positions and fixed isotropic parameters for the hydrogen atoms. Final agreement factors are listed in Table I. Complete listings of intermolecular bond distances and angles, final positional parameters, and Gaussian amplitudes for **2** are included in the supplementary material.

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Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, and intramolecular bond distances and angles for **2** (10 pages). Ordering information is given on any current masthead page.

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