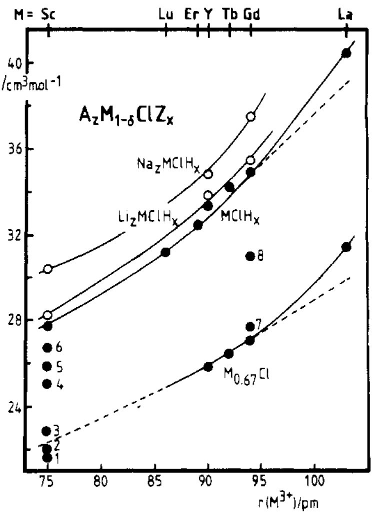

Figure 6. Molar volumes per chloride for $MClH_x$, $A^I{}_zMClH_x$ (A = Li, Na), and M_2Cl_3 = (=$M_{0.67}Cl$), etc. as a function of the ionic radius of M^{3+}: 1, $Sc_7Cl_{12}X_2$; 2, $Sc_5Cl_8X_2$; 3, $Sc_7Cl_{10}X_2$ (X = B, N, C); 4, Sc_4Cl_6N; 5, Sc_2Cl_2N; 6, Sc_2Cl_2C; 7, $Gd_5Cl_9C_2$; 8, Gd_3Cl_3C.

terstitials. Additionally, various scandium chlorides with carbon, nitrogen, etc. interstitials are included in this plot. The molar volumes of both the mono- and sesquichlorides lie on curves that have comparable appearances. Interestingly, the volumes of both $LaClH_x$ and La_2Cl_3 deviate equally from the broken lines in Figure 6. Generally, the monochloride–hydrides have much higher molar volumes than the sesquichlorides, $GdClH_{0.9}:{}^1/_3Gd_2Cl_3$ = 34.85:26.86 = 1.30:1. This large increase has to be attributed to the double-metal-layer structure of $GdClH_{0.9}$ and the volume necessary for hydrogen (and $^1/_3$Gd). Or, to put it the other way around, only because of the larger monohalide volume *can* hydrogen be inserted into the tetrahedral holes.

It is impressive to note that the sum of the molar volume increments that were derived by Biltz[42] some 50 years ago model the observed molar volumes of even these novel compounds. With his volume increments V_i (cm^3 mol^{-1}) of 20 for Cl^-, 11 for H^-, 2 for Sc^{3+}, 8 for La^{3+}, 6.5 for Gd^{3+}, and 5 for Lu^{3+}, one gets 39 ($\sum V_i$) vs. 40.4 (observed) for LaClH, 37.5 vs. 34.8 for GdClH, 36 vs. 31.2 for LuClH, and 33 vs. 28.0 for ScClH, all in cm^3 mol^{-1}. For Gd_2Cl_3, the sum of volume increments is 24 × 3 cm^3 mol^{-1} vs. 26.8 × 3 cm^3 mol^{-1} observed.

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Supplementary Material Available: A table of the observed and calculated structure factors for ScClH (1 page). Ordering information is given on any current masthead page.

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and University of Alabama, University, Alabama 34586

Siloxy–Zirconium Chemistry. 1. Reaction of Zr–C σ-Bonds with R_3SiOH and the Crystal Structure of (1,2-Dimethoxyethane)bis(triphenylsiloxy)dichlorozirconium(IV), $(DME)ZrCl_2(OSiPh_3)_2$

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Received May 23, 1986

Bis(cyclopentadienyl)dimethylzirconium reacts with R_3SiOH compounds to give $Cp_2Zr(OSiR_3)_2$. Tetrakis((trimethylsilyl)methyl)zirconium, $Zr[CH_2Si(CH_3)_3]_4$, reacts similarly, producing $Zr(OSiR_3)_4$. The disubstituted product $Zr(CH_2Si(CH_3)_3)_2(OSiR_3)_2$ could not be produced by this method, however. Synthetic strategies involving crown ether adducts of $ZrCl_4$ were used. Zirconium tetrachloride reacts with 12-c-4 to give the adduct (12-c-4)$ZrCl_4$. The compound is a poorly soluble, moderately air-stable solid. (12-c-4)$ZrCl_4$ reacts with $Na(OSiPh_3)$ in 1,2-dimethoxyethane (DME) to produce $(DME)ZrCl_2(OSiPh_3)_2$ and free 12-c-4. The compound crystallizes from C_6H_6 solution as the bis(benzene) solvate, $(DME)Zr(Cl)_2(OSiPh_3)_2\cdot 2C_6H_6$, in the monoclinic space group $C2/c$: a = 22.273 (8) Å, b = 10.233 (9) Å, c = 27.518 (9) Å, and β = 126.92 (4)° with Z = 4. This compound contains the first Zr–$OSiR_3$ bond to be structurally characterized. There is significant d_π–p_π interaction between the Zr and O atoms as evidenced by the short Zr–O bond distance of 1.91 (1) Å and the nearly linear Zr–O–Si bond angle of 171 (1)°.

Introduction

Over the years the Zr–carbon σ-bond has been studied intensely in compounds of the type $(\eta^5\text{-L})_2ZrR_2$, where η^5-L represents an η^5-bonded π-ligand such as $C_5H_5^-$, $C_5(CH_3)_5^-$, $C_9H_7^-$, or $C_{13}H_9^-$.[1] These species, while formally 16e complexes, are 8-coordinate and thus coordinatively saturated. This fact limits their usefulness as potential catalysts since the availability of sites on the metal is a necessary requisite for reaction. This problem can be obviated by removing the η^5 ligands from the metal's coordination sphere. Without these ligands, the number of stable Zr–alkyl complexes decreases dramatically, however.[2] We have undertaken a project

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[†] University of Texas at Dallas.

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to design and construct compounds of the type $L_xZrX_2R_2$ (**1**), where L_x represents a multidentate neutral ligand, X is an anionic inert ligand, and R is an alkyl group. Such a compound should possess the ability to obtain various degrees of coordinative unsaturation and should serve as a more suitable precursor to potential Zr-based catalysts. The initial approach has been to use crown ethers as the L_x ligand. Crown ethers possess multiple Lewis base sites, and the Zr can use as many as it needs in order to achieve a comfortable coordination environment. X has been chosen to be $^-OSiR_3$. The $Zr–OSiR_3$ bond should be fairly inert, thus fixing two coordintion sites and two valencies on the metal. In this report we describe our initial synthetic endeavors to prepare a zirconium compound containing a crown ether, siloxy ligands, and alkyl groups.

Experimental Section

General Procedures. All operations were carried out under a nitrogen atmosphere. 1,2-dimethoxyethane (DME) and diethyl ether were dried over the ketyl of Na/benzophenone and freshly distilled prior to use. Benzene, toluene, and heptane were dried over $LiAlH_4$ and freshly distilled prior to use. $Na(OSiPh_3)$ was prepared by a literature procedure.[3] Elemental analyses were by Galbraith Laboratories, Knoxville, TN. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX200 NMR spectrometer. Infrared spectra were recorded on a Nicolet 5DX FT-IR spectrometer. Bis(cyclopentadienyl)dimethylzirconium was prepared as previously described.[1b] Tetrakis((trimethylsilyl)methyl)zirconium(IV) was prepared by the method of Lappert.[2g]

Bis(η^5-cyclopentadienyl)bis(triphenylsiloxy)zirconium(IV). Dimethylzirconocene (1.0 g, 3.98 mmol) was dissolved in 100 mL of diethyl ether. Triphenylsilanol (2.19 g, 7.96 mmol) was added. The mixture was stirred for 18 h open to a bubbler. At the end of this time, the solvent was removed in vacuo. The white residue was extracted with 15 mL of toluene and cooled to −15 °C. The resulting white precipitate was collected on a frit and washed with 2 × 20 mL portions of heptane. The product was dried in vacuo: yield 1.15 g (60%); mp 292–296 °C. IR (Nujol mull); 1966 (w), 1898 (w), 1832 (w), 1111 (s), 1002 (s), 988 (s), 935 (vs), 802 (m), 709 (m), 703 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 7.73–7.17 (m, 30 H, SiC_6H_5), 5.91 (s, 10 H, C_5H_5). Anal. Calcd for $C_{46}H_{40}O_2Si_2Zr$: C, 71.54; H, 5.23; Si, 7.27; Zr, 11.81. Found: C, 71.12; H, 5.12; Si, 7.25; Zr, 11.15.

Bis(η^5-cyclopentadienyl)bis(triethylsiloxy)zirconium(IV). Dimethylzirconocene (1.5 g, 5.98 mmol) was dissolved in 50 mL of heptane. Triethylsilanol (1.7 mL, 11.96 mmol) was added to the solution. The reaction mixture was stirred until it stopped evolving gas. The solvent was removed in vacuo. The compound was obtained as an analytically pure oil in quantitative yield. IR (neat): 2950 (vs), 2911 (vs), 2878 (vs), 1234 (m), 1015 (s), 985 (s), 968 (s), 945 (s), 922 (s), 799 (s), 736 (s), 723 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 5.94 (s, 10 H, C_5H_5), 0.97 (t, 18 H, $SiCH_2CH_3$), 0.52 (q, 12 H, $SiCH_2$). $^{13}C\{^1H\}$ NMR: δ 112.68 (C_5H_5), 7.56 ($SiCH_2CH_3$), 7.10 ($SiCH_2CH_3$). Anal. Calcd for $C_{22}H_{40}O_2Si_2Zr$: C, 54.65; H, 8.28. Found: C, 54.00; H, 8.21.

(12-c-4)$ZrCl_4$. $ZrCl_4$ (2.6 g, 11 mmol) was slowly added to 40 mL of DME at 0 °C. 12-c-4 (1.76 mL, 11 mmol) was added dropwise to the solution. The mixture was warmed to room temperature and stirred for 6 h. The solvent was removed in vacuo, resulting in a pale beige solid. The solid was extracted with 40 mL of toluene. The mixture was filtered. The solid on the frit was washed with 2 × 10 mL portions of toluene and dried in vacuo: yield 3.78 g (84%); mp 219–223 °C dec. IR (Nujol mull): 1125 (m), 1048 (s), 1028 (m), 942 (s), 866 (m). Anal. Calcd for $C_8H_{16}Cl_4O_4Zr$: C, 23.49; H, 3.91; Cl, 34.72. Found: C, 24.51; H, 4.19; Cl, 34.03.

(1,2-Dimethoxyethane)bis(triphenylsiloxy)dichlorozirconium(IV) (9). (12-c-4)$ZrCl_4$ (2.0 g, 6.7 mmol) was mixed with $NaOSiPh_3$ (4.0 g, 13.4 mmol) in 40 mL of DME. The mixture was stirred for 45 min, after which the solvent was removed in vacuo. The resulting white solid was continuously extracted with 50 mL of toluene for 12 h. The toluene extract was concentrated to 30 mL and cooled slowly to −15 °C. The product precipitated as large well-formed needle crystals suitable for single-crystal X-ray diffraction analysis: yield 3.15 g (58.7%); mp 124–126 °C. ^1H NMR (C_6D_6): δ 7.67–7.13 (m, 30 H, Si*Ph*), 3.51 (s, 6 H, OCH_3), 3.36 (s, 4 H, OCH_2). $^{13}C\{^1H\}$ NMR: δ 135.98, 135.49, 129.60, 128.54, 128.00, 127.56 (Si-*Ph*, C_6D_6), 71.57 (CH_2O), 63.15 (CH_3O). Evaporation of the mother liquor revealed the presence of free 12-c-4 identified by its ^1H NMR spectrum: δ 3.46 (s).

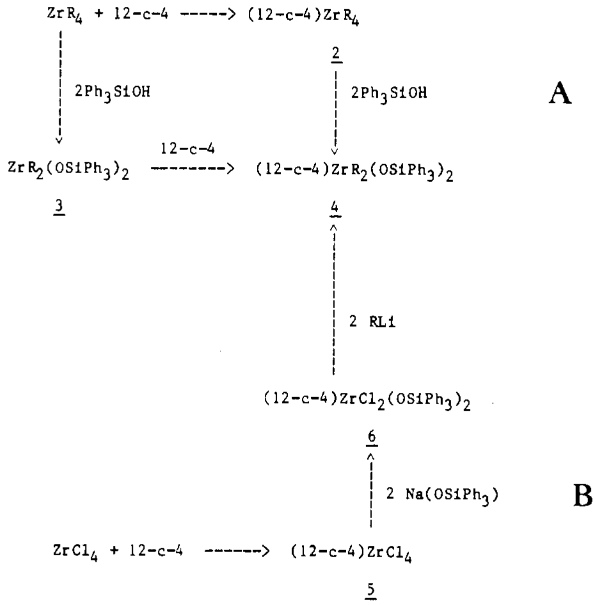

Figure 1. Possible synthetic routes to (crown ether)siloxyalkylzirconium compounds.

Reaction of $Zr[CH_2Si(CH_3)_3]_4$ with Ph_3SiOH. $Zr[CH_2Si(CH_3)_3]_4$ (4.4 g, 10 mmol) was added to 50 mL of toluene. Triphenylsilanol (5.5 g, 20 mmol) was added. An exothermic reaction began immediately, forming a white precipitate. The mixture was stirrred until it returned to room temperature. The white precipitate was collected on a frit, washed with C_6H_6 and $(C_2H_5)_2O$, and dried in vacuo; mp >350 °C. IR (Nujol mull): 930 (s, b) ($\nu_{Zr-OSiPh_3}$). Anal. Calcd for $C_{72}H_{60}O_4Si_4Zr$: C, 72.58; H, 5.03. Found: C, 70.46; H, 5.98. Removal of the solvent from the filtrate left a pyrophoric oil identified as $Zr[CH_2Si(CH_3)_3]_4$ by a comparison of its ^1H and ^{13}C NMR spectra to that of an authentic sample.

Crystal Structure. Crystals of $9{\cdot}2C_6H_6$ suitable for X-ray diffraction were grown by slow cooling of a saturated benzene solution. The crystals were mounted in thin-walled glass capillaries. Details of the data collection and structure solution have been described.[4] An empirical absorption correction was done according to Churchill and Hollander.[5]

Results and Discussion

There are several routes one can envision that might lead to the desired compound (Figure 1). Route A begins with the homoleptic ZrR_4 compound. Reaction with 12-c-4 should produce the crown ether adduct **2**. Two moles of Ph_3SiOH and **2** would

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(4) The crystal selected for data collection was sealed in a thin-walled glass capillary under an inert atmosphere. The sample was examined in a preliminary fashion on a CAD-4 diffractometer. Final lattice parameters were determined from the angular settings of 25 accurately centered reflections ($\theta > 10°$). Systematic absences allowed the space group to be *C*2/*c* or *Cc*. The centrosymmetric *C*2/*c* was demonstrated as the correct choice by the successful solution and refinement of the structure. The structure was solved by applications of the Patterson method followed by successive difference Fourier maps and partial least-squares refinement cycles. The SHELX system of computer programs was used. Data were collected out to a 2θ value of 42°, but the crystal did not diffract well from the start and observation of the standards showed that crystal decomposition occurred during data collection (this was corrected for). Out of 2319 reflections scanned, only 730 were considered observed ($I > 3\sigma(I)$). Because of the paucity of observed data, only the Zr, Cl, Si, and DME atoms were refined with anisotropic temperature factors. The benzene of crystallization was refined with isotropic thermal parameters. Hydrogen atoms were placed in calculated positions 1.00 Å from the bonded carbon atoms in cases where fixed geometry could be assumed. Further details of the method of data collection and the method of refinement can be found in: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(5) The transmission factors ranged from 0.87 to 0.95. An empirical absorption correction was applied as in: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957.

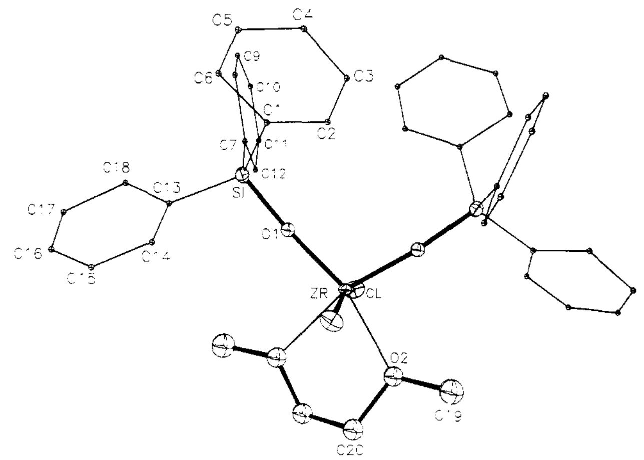

Figure 2. View of (DME)$ZrCl_2(OSiPh_3)_2$. Hydrogen atoms have been omitted for clarity.

lead to the desired compound **4**. It might be advantageous to replace the alkyl groups first, giving **3**, which would then undergo reaction with the crown ether. Route B begins with $ZrCl_4$. Reaction with 12-c-4 should produce the adduct **5**. **5** would undergo a substitution reaction with $NaOSiPh_3$ to give **6**, followed by alkylation producing **4**.

We chose to begin with route A because the reaction to make the Zr–$OSiPh_3$ linkage is much cleaner, producing RH as a byproduct as opposed to NaCl from B. Before the chemistry of Figure 1 was begun, the reaction of silanols with a model compound, $Cp_2Zr(CH_3)_2$, was examined to establish the conditions for silanol cleavage of Zr–C σ-bonds. $Cp_2Zr(CH_3)_2$ reacts with Et_3SiOH or Ph_3SiOH according to eq 1. The reaction occurs

$$Cp_2Zr(CH_3)_2 + 2R_3SiOH \rightarrow Cp_2Zr(OSiR_3)_2 \qquad (1)$$

$$R = Et, Ph$$

readily at room temperature in ether solution, producing the bis(siloxy)zirconocene species in good yield. When tetrakis((trimethylsilyl)methyl)zirconium, $Zr[CH_2Si(CH_3)_3]_4$, was reacted with triphenylsilanol in a 1:2 fashion only the tetrasubstituted compound **7** was obtained (eq 2). Unreacted $Zr[CH_2Si(CH_3)_3]_4$

$$2Zr[CH_2Si(CH_3)_3]_4 + 4Ph_3SiOH \rightarrow Zr(OSiPh_3)_4 + Zr[CH_2Si(CH_3)_3]_4 + 4Si(CH_3)_4 \qquad (2)$$

can be recovered from the reaction mixture. Similar reactions using sterically hindered alcohols afforded less highly substituted compounds.[6,7]

In the hope of slowing down the siloxylation reaction, the preparation of the crown adduct **2** was attempted. $Zr[CH_2Si(CH_3)_3]_4$ has been shown to be a good Lewis acid, reacting with bidentate phosphines such as 1,2-bis(dimethylphosphino)ethane, dmpe, to give the six-coordinate adduct dmpe$Zr[CH_2Si(CH_3)_3]_4$ (**8**).[8] 12-c-4 and $Zr[CH_2Si(CH_3)_3]_4$ failed to form the complex **2**. In retrospect this is not surprising given the crowded geometry about the Zr atom in **8**.[9] There appears to be insufficient room to accomodate a 12-c-4 ligand and four $CH_2Si(CH_3)_3$ groups around the zirconium.

Having exhausted the possibilities in route A, we turned to the chemistry of route B. Zirconium tetrachloride reacts with 12-c-4 to give the adduct **5** in good yield (eq 3). **5** is a moderately

$$12\text{-c-}4 + ZrCl_4 \rightarrow \underset{\textbf{5}}{(12\text{-c-}4)ZrCl_4} \qquad (3)$$

Table I. Summary of the Crystallographic Data for (DME)$ZrCl_2(OSiPh_3)_2 \cdot 2C_6H_6$

compd	$ZrCl_2Si_2O_4C_{40}H_{40} \cdot 2C_6H_6$
mol wt	958
space group	*C*2/*c*
cell constants	
a, Å	22.273 (8)
b, Å	10.233 (9)
c, Å	27.518 (9)
β, deg	126.92 (4)
cell vol, $Å^3$	5014
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.27
μ(calcd), cm^{-1}	4.05
radiation	Mo Kα
max cryst dimens, mm	0.4 × 0.13 × 0.25
scan width, deg	0.8 + 0.2 tan θ
std reflecns	40$\bar{4}$, 400, 020
decay of stds, %	23
reflecns measd	2319
2θ range	2–42
obsd reflecns	730
no. of parameters varied	147
GOF	4.1
R	0.087
R_w	0.074

Table II. Fractional Atomic Coordinates for (DME)$ZrCl_2(OSiPh_3)_2 \cdot 2C_6H_6$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq),[a] $Å^2$
Zr	0.0000	0.3237 (3)	0.7500	0.051
Cl	0.1345 (3)	0.2877 (6)	0.7993 (3)	0.094
Si	−0.0378 (4)	0.5475 (6)	0.6362 (3)	0.061
O(1)	−0.0151 (7)	0.438 (1)	0.6887 (5)	0.44
C(1)	−0.101 (1)	0.669 (2)	0.6345 (9)	0.053
C(2)	−0.103 (1)	0.693 (2)	0.6849 (9)	0.055
C(3)	−0.149 (1)	0.789 (2)	0.681 (1)	0.056
C(4)	−0.190 (2)	0.868 (3)	0.631 (1)	0.106
C(5)	−0.191 (2)	0.848 (3)	0.580 (1)	0.132
C(6)	−0.143 (1)	0.761 (3)	0.581 (1)	0.082
C(7)	0.049 (1)	0.616 (2)	0.655 (1)	0.059
C(8)	0.053 (2)	0.759 (3)	0.641 (1)	0.085
C(9)	0.121 (2)	0.805 (3)	0.656 (1)	0.107
C(10)	0.182 (2)	0.738 (3)	0.685 (1)	0.115
C(11)	0.185 (2)	0.610 (3)	0.702 (1)	0.087
C(12)	0.113 (1)	0.552 (3)	0.683 (1)	0.078
C(13)	−0.088 (1)	0.469 (2)	0.563 (1)	0.060
C(14)	−0.151 (2)	0.399 (3)	0.540 (1)	0.101
C(15)	−0.193 (2)	0.325 (3)	0.483 (1)	0.109
C(16)	−0.171 (1)	0.336 (3)	0.449 (1)	0.085
C(17)	−0.115 (2)	0.408 (3)	0.464 (1)	0.097
C(18)	−0.068 (1)	0.490 (3)	0.526 (1)	0.089
O(2)	0.014 (1)	0.144 (2)	0.808 (1)	0.111
C(19)	0.004 (3)	0.142 (3)	0.855 (2)	0.238
C(20)	−0.010 (2)	0.031 (3)	0.772 (1)	0.103
C(S1)	0.406 (2)	0.272 (3)	0.414 (2)	0.16
C(S2)	0.335 (2)	0.320 (4)	0.369 (2)	0.15
C(S3)	0.294 (2)	0.421 (4)	0.373 (2)	0.16
C(S4)	0.324 (2)	0.464 (3)	0.430 (2)	0.15
C(S5)	0.401 (3)	0.438 (5)	0.477 (2)	0.22
C(S6)	0.448 (2)	0.348 (5)	0.473 (2)	0.20

[a] Defined as $(U_{11} + U_{22} + U_{33})/3$.

air-stable solid that is poorly soluble in aromatic and ethereal solvents. It reacts with 2 mol of $Na(OSiPh_3)$ to give a crystalline compound readily soluble in warm benzene. The compound was identified as (DME)$ZrCl_2(OSiPh_3)_2$ (**9**). Free 12-c-4 can be isolated from the product mixture (eq 4). Expulsion of the crown

$$(12\text{-c-}4)ZrCl_4 + 2Na(OSiPh_3) \xrightarrow{\text{DME}} (\text{DME})ZrCl_2(OSiPh_3)_2 + 12\text{-c-}4 \qquad (4)$$

ether was unanticipated. An explanation involving steric arguments could be invoked; however, the solvent, DME, might be a better donor than 12-c-4, allowing formation of the six-coordinate complex. In order to study the environment about the Zr, a

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Table III. Selected Bond Distances (Å) and Angles (deg) for $(DME)ZrCl_2(OSiPh_3)_2{\cdot}2C_6H_6$

Zr–Cl	2.464 (7)	Zr–O(1)	1.91 (1)
Zr–O(2)	2.33 (2)	Si–O(1)	1.65 (2)
Si–C(1)	1.86 (3)	Si–C(7)	1.81 (3)
Si–C(13)	1.81 (2)	O(2)–C(19)	1.45 (7)
O(2)–C(20)	1.41 (4)	C(1)–C(2)	1.43 (4)
C(1)–C(6)	1.50 (3)	C(2)–C(3)	1.38 (4)
C(3)–C(4)	1.35 (3)	C(4)–C(5)	1.41 (6)
C(5)–C(6)	1.38 (5)	C(7)–C(8)	1.54 (4)
C(7)–C(12)	1.32 (4)	C(8)–C(9)	1.38 (5)
C(9)–C(10)	1.28 (5)	C(10)–C(11)	1.38 (4)
C(11)–C(12)	1.47 (4)	C(13)–C(14)	1.35 (4)
C(13)–C(18)	1.35 (5)	C(14)–C(15)	1.47 (4)
C(15)–C(16)	1.28 (6)	C(16)–C(17)	1.29 (5)
C(17)–C(18)	1.60 (4)	C(20)–C(20)	1.53 (9)

Cl–Zr–O(1)	95.1 (5)	Cl–Zr–O(2)	83.3 (6)
O(1)–Zr–O(2)	165.8 (8)	O(1)–Si–C(1)	108 (1)
O(1)–Si–C(7)	107.1 (9)	C(1)–Si–C(7)	114 (1)
O(1)–Si–C(13)	109.7 (9)	C(1)–Si–C(13)	109 (1)
C(7)–Si–C(13)	109 (1)	Zr–O(1)–Si	171 (1)
Zr–O(2)–C(19)	127 (2)	Zr–O(2)–C(20)	109 (2)
C(19)–O(2)–C(20)	114 (3)	Si–C(1)–C(2)	123 (1)
Si–C(1)–C(6)	118 (2)	C(2)–C(1)–C(6)	118 (2)
C(1)–C(2)–C(3)	120 (2)	C(2)–C(3)–C(4)	122 (3)
C(3)–C(4)–C(5)	121 (3)	C(4)–C(5)–C(6)	122 (3)
C(1)–C(6)–C(5)	117 (3)	Si–C(7)–C(8)	121 (2)
Si–C(7)–C(12)	125 (2)	C(8)–C(7)–C(12)	114 (3)
C(7)–C(8)–C(9)	118 (3)	C(8)–C(9)–C(10)	123 (3)
C(9)–C(10)–C(11)	123 (4)	C(10)–C(11)–C(12)	116 (3)
C(7)–C(12)–C(11)	125 (3)	Si–C(13)–C(14)	121 (3)
Si–C(13)–C(18)	121 (2)	C(14)–C(13)–C(18)	117 (3)
C(13)–C(14)–C(15)	125 (4)	C(14)–C(15)–C(16)	117 (3)
C(15)–C(16)–C(17)	123 (3)	C(16)–C(17)–C(18)	122 (4)
C(13)–C(18)–C(17)	115 (3)		

single-crystal X-ray structure determination was carried out on **9**.

The structure of the molecule is shown in Figure 2. Table I gives the pertinent crystallographic data for **9**. Fractional coordinates for the atoms are listed in Table II. Selected bond distances and angles are given in Table III. There is a distorted-octahedral geometry about the Zr characterized by the Cl–Zr–O(1) angle (95.1 (5)°) and the Cl–Zr–O(2) angle (83.3 (6)°). The molecule lies on a crystallographically required twofold axis, the halves being related by the transformation $[-x, y, {}^3/_2 - z]$. The bonding interaction between the Zr and the $OSiPh_3$ group is the first siloxy–Zr bond to be structurally characterized. The Zr–O(1) length is short, 1.91 (1) Å, implying some significant d_π–p_π bonding. This is also manifested in the Zr–O(1)–Si bond angle, which is nearly linear, 171 (1)°. These values compare well with zirconium alkoxide linkages in compounds where strong p_π–d_π donation has been claimed: $Cp_2Zr(O\text{-}t\text{-}Bu)Ru(CO)_2Cp$ (1.910 Å, 169.6°),[10] $(Cp_2ZrCH_3)_2O$ (1.945 Å, 174.1°),[1b] $[HB(3,5\text{-}(CH_3)_2pz)_3]Zr(O\text{-}t\text{-}Bu)(\eta^2\text{-}C(CH_3)NC(CH_3)_3)$ (1.924 Å, 174°),[11] $[(t\text{-}Bu)_3CO]ZrCl_3{\cdot}Li(OEt_2)_2$ (1.895 Å (av), 169° (av)).[7] The Zr–O(2) distance, 2.33 (1) Å, is normal and corresponds well with that found for other Zr–O coordinate bonds.[12] Methods to alkylate **9** are currently being explored and will be the subject of a future report.

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Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and atomic thermal parameters for **9** (4 pages); a table of observed and calculated structure factors for **9** (5 pages). Ordering information is given on any current masthead page.

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X-ray and Neutron Diffraction Study of the New Cationic Bis(hydrido)-Bridged Platinum–Iridium Complex $[(PEt_3)_2Pt(\mu\text{-}H)_2IrH_2(PEt_3)_2]^+[BPh_4]^-$

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The structure of $[(PEt_3)_2Pt(\mu\text{-}H)_2IrH_2(PEt_3)_2]^+[BPh_4]^-$ has been studied by X-ray and neutron diffraction techniques, at room temperature and 22 (1) K, respectively. At both temperatures, crystals of the title compound are monoclinic, with space group $P2_1/c$ and $Z = 4$. Unit cell parameters at 22 K are as follows: $a = 18.989$ (10) Å, $b = 15.314$ (3) Å, $c = 19.792$ (6) Å, $\beta = 118.73$ (3)°, and $V = 5047$ (4) Å^3. The coordination around the Ir atom is distorted octahedral, while that around Pt is distorted square planar. The neutron analysis shows that the Pt–Ir distance is 2.677 (1) Å and that the distances between the metals and bridging hydrido ligands differ by 0.15 Å (Ir–H = 1.879 (3) and 1.882 (3) Å; Pt–H = 1.726 (3) and 1.736 (3) Å). The two terminal Ir–H bonds are equivalent (1.586 (3) and 1.591 (3) Å) and comparable in length to those found in other neutron diffraction studies.

Introduction

Bimetallic hydrido-bridged complexes are receiving considerable attention because of their structural features and reactivity, particularly as related to homogeneous catalysis.[2-4]

Among the structural features of interest, mention may be made of (1) the relationship to the formal "donor–acceptor scheme", i.e.

$$L_mMH_2 + (\text{solvent})_2M'L'_n \rightarrow L_mM(\mu\text{-}H)_2M'L'_n + 2\,\text{solvent}$$

and (2) the influence of direct M–M′ interactions.[2]

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