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Substitution or Nucleophilic Attack by Phosphines on $ZrCl_4(THF)_2$

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Phosphine adducts of early metal halides have been explored extensively by the research groups of Cotton, Schrock, Girolami, and others. Low-valent complexes exhibiting metal–metal bonding have received particular attention. Such species include clusters of the form $M_2X_6(PR_3)_4$ (M = Ti,[1] Zr,[2–5] Hf,[3,6] Ta, Nb,[7,8] X = Cl, Br, I), $M_2Cl_8(PR_3)_4$ (M = Nb,[9,10] Ta[11,12]), $Nb_3Cl_8(PMe_2Ph)_6$[13] and $[M_3Cl_{10}(PEt_3)_3]^-$ (M = Nb,[14] Ta[14,15]), $Nb_3Cl_7(PMe_2Ph)_6$,[15] $Nb_4Cl_{10}(PEt_3)_6$,[16] $Zr_6Cl_{12}(PMe_2Ph)_6$,[14] and $M_6Cl_{14}(PR_3)_4$.[17] High-oxidation phosphine complexes of the early metal halides have, in general, drawn less attention. Earlier studies have confirmed or suggested a variety of coordination geometries for such mononuclear species. For example, five,[18,19] six,[20–22] seven,[12] and eight[23,24] coordination has been confirmed for $TiCl_4(PMe_3)$,[19] $NbCl_4(PEt_3)_2$,[22] $NbCl_4(PMe_3)_3$,[12] and $NbCl_4(diars)_2$,[24] respectively. In this report we describe the reactions of $ZrCl_4(THF)_2$ with the phosphines PR_3 (R = Cy, Ph, Me). The products of these reactions demonstrate that either nucleophilic attack of the coordinated THF or straightforward substitution reactions can occur. The nature of the derived product depends on the electronic and steric properties of the phosphine ligands.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 in a Vacuum Atmospheres inert-atmosphere glovebox. The atmosphere quality is maintained by employing a constant-circulation 5 cf/min purifier containing the Chemical Dynamics Corp. catalyst R3-11. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze–thaw method at least three times prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 300 and 75 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were recorded using a Bruker AC-200 NMR spectrometer operating at 81 MHz and are reported relative to 85% H_3PO_4 as an external reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Microanalytical Laboratories, Woodside, NY. $ZrCl_4$, PCy_3, PPh_3, and PMe_3 were purchased from either the Aldrich Chemical Co. or the Strem Chemical Co. of $ZrCl_4(THF)_2$ was prepared by literature methods.[25]

Synthesis of $[ZrCl_4(OCH_2CH_2CH_2CH_2PR_3)]_2$ (R = Cy (1), Ph (2)) and $Cl_3Zr(\mu\text{-}Cl)_3ZrCl_2(PMe_3)_2$ (3). These species were prepared in a similar manner; thus, only one preparation is described. $ZrCl_4(THF)_2$ (50 mg, 0.133 mmol) and PCy_3 (37 mg, 0.133 mmol) were added to benzene. The solution was stirred overnight. On standing, crystals of **1** formed. It is noteworthy that the formation of **1** and **2** also occurs when THF is employed as the solvent. Data for **1** are as follows. Yield: 75%. Anal. Calcd for $C_{44}H_{82}Cl_8O_2P_2Zr_2$: C, 45.13; H, 7.06. Found: C, 45.00; H, 6.90. ^1H NMR (THF-d_8, δ, ppm): 4.36 (m, CH_2–O, 2 H), 2.55 (m, CH_2–P, 2 H), 2.10–1.20 (br m, CH_2, Cy, 37 H). $^{31}P\{^1H\}$ NMR (THF, δ, ppm): 32.89 (s). Data for **2** are as follows. Yield: 82%. Anal. Calcd for $C_{44}H_{46}Cl_8O_2P_2Zr_2$: C, 46.57; H, 4.09. Found: C, 46.20; H, 5.00. ^1H NMR (THF-d_8, δ, ppm): 8.05–7.70 (m, Ph, 15 H), 4.44 (m, CH_2–O, 2 H), 2.45 (m, CH_2–P, 2 H), 1.90–1.75 (m, CH_2, 4 H). $^{31}P\{^1H\}$ NMR (THF, δ, ppm): 24.76 (s). Data for **3** are as follows. Yield: 80%. Anal. Calcd for $C_6H_{18}Cl_8P_2Zr_2$: C, 11.66; H, 2.93. Found: C, 11.70; H, 3.00. ^1H NMR (THF-d_8, δ, ppm): 0.97 (br, s). $^{31}P\{^1H\}$ NMR (benzene, δ, ppm): 25.37 (s).

X-ray Data Collection and Reduction. Diffraction experiments were performed on a four-circle Rigaku AFC6 diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 20 machine-centered reflections. These data were used to determine the crystal systems. An automated Laue symmetry check routine was employed to show that the crystal symmetries were consistent with monoclinic crystal systems. Ultimately, 25 reflections ($20° < 2\theta < 35°$) were used to obtain the final lattice parameters and the orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space groups $P2_1/c$ and $P2_1/m$, respectively. The data were collected ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 150 reflections. The intensities of the standards showed no statistically significant change over the duration of the data collection. The data were processed using the TEXSAN program package operating on a Vax 3520 workstation. The reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. An empirical absorption correction was applied to the data.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[26] The metal atom positions were determined using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight, w, is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement all the non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases the hydrogen atom contributions were calculated but not refined. The final values of R and R_w are given in Table I. The maximum Δ/σ on any of the parameters in the final cycles of the refinement and the location of the largest peaks in the final difference Fourier map calculation are also given in Table I. The residual electron densities were of no chemical significance. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Thermal parameters (Table S1) and hydrogen atom parameters (Table S2) have been deposited as supplementary material.

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(1) Hermes, A. R.; Girolami, G. S. *Inorg. Chem.* **1990**, *29*, 313.
(2) Wengrovius, J. E.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844.
(3) Cotton, F. A.; Shang, M.; Wojtczak, W. A. *Inorg. Chem.* **1991**, *30*, 3670.
(4) Cotton, F. A.; Diebold, M. P.; Kibala, P. R. *Inorg. Chem.* **1988**, *27*, 799.
(5) Cotton, F. A.; Kibala, P. R. *Polyhedron* **1987**, *6*, 645.
(6) Morse, P. M.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1990**, *29*, 3200.
(7) Sattelberger, A. P.; Wilson, R. B.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 2392.
(8) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 4130.
(9) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 945.
(10) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 3592.
(11) Boyd, P. D. W.; Jones, T. C.; Nielsen, A. J.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1984**, 1086.
(12) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Polyhedron* **1985**, *4*, 1103.
(13) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 2833.
(14) Cotton, F. A.; Kibala, P. A.; Roth, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 298.
(15) Cotton, F. A.; Diebold, M. P.; Feng, X.; Roth, W. J. *Inorg. Chem.* **1988**, *27*, 3413.
(16) Cotton, F. A.; Shang, M. *J. Am. Chem. Soc.* **1988**, *110*, 7719.
(17) Imoto, H.; Hayakawa, S.; Morita, N.; Saito, T. *Inorg. Chem.* **1990**, *29*, 2007.
(18) Gordon, D.; Wallbridge, M. G. H. *Inorg. Chim. Acta* **1986**, *111*, 77.
(19) Nadasdi, T. T.; Stephan, D. W. Unpublished results.
(20) Jamieson, G.; Lindsell, W. E. *Inorg. Chim. Acta* **1978**, *28*, 113.
(21) Wilkins, J. D. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2095.
(22) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Acta Crystallogr.* **1990**, *C46*, 1624.
(23) Clark, R. J. H.; Errington, W.; Nyholm, R. S. *J. Chem. Soc. A* **1966**, 989.
(24) Clark, R. J. H.; Lewis, J.; Nyholm, R. S.; Pauling, P. J.; Robinson, G. B. *Nature* **1961**, *192*, 222.
(25) Manzer, L. E. *Inorg. Synth.* **1980**, *21*, 135.
(26) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 324. (b) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 390. (c) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

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Table I. Crystallographic Parameters

	molecule 1	molecule 3
formula	$C_{32}H_{55}Cl_4O_2PZr$	$C_3H_9Cl_4PZr$
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/m$ (No. 11)
a (Å)	10.691 (5)	10.109 (4)
b (Å)	18.503 (7)	11.260 (3)
c (Å)	19.008 (7)	10.711 (3)
β (deg)	90.62 (4)	115.21 (3)
V (Å^3)	3760 (3)	1103.0 (7)
Z	4	4
abs coeff μ (cm^{-1})	6.405	20.386
temp (°C)	24	24
R (%)	7.51	3.23
R_w (%)	7.61	3.73

Table II. Positional Parameters for 1 and 3

atom	x	y	z
		1	
Zr(1)	0.0414 (2)	0.0322 (1)	0.0838 (1)
Cl(1)	0.2451 (4)	0.0346 (3)	0.1433 (2)
Cl(2)	0.0077 (4)	−0.0868 (3)	0.1360 (2)
Cl(3)	0.0838 (5)	0.1524 (3)	0.0368 (3)
Cl(4)	−0.0844 (4)	0.0859 (3)	0.1752 (3)
P(1)	−0.4319 (4)	−0.1339 (3)	0.1888 (2)
O(1)	−0.1083 (9)	0.0186 (5)	0.0097 (5)
C(1)	−0.436 (2)	−0.077 (1)	0.112 (1)
C(2)	−0.322 (1)	−0.029 (1)	0.0999 (9)
C(3)	−0.335 (1)	0.009 (1)	0.030 (1)
C(4)	−0.222 (2)	0.059 (1)	0.0127 (9)
C(11)	−0.296 (1)	−0.192 (1)	0.186 (1)
C(12)	−0.283 (2)	−0.234 (1)	0.116 (1)
C(13)	−0.166 (2)	−0.279 (1)	0.116 (1)
C(14)	−0.156 (2)	−0.327 (1)	0.183 (1)
C(15)	−0.168 (2)	−0.287 (1)	0.248 (1)
C(16)	−0.287 (2)	−0.244 (1)	0.249 (1)
C(21)	−0.576 (2)	−0.189 (1)	0.184 (1)
C(22)	−0.634 (3)	−0.202 (2)	0.127 (1)
C(23)	−0.753 (2)	−0.242 (1)	0.125 (1)
C(24)	−0.804 (2)	−0.268 (1)	0.194 (2)
C(25)	−0.747 (3)	−0.247 (3)	0.252 (2)
C(26)	−0.628 (2)	−0.209 (1)	0.254 (1)
C(31)	−0.423 (2)	−0.081 (1)	0.2682 (9)
C(32)	−0.296 (2)	−0.049 (1)	0.285 (1)
C(33)	−0.294 (2)	−0.009 (1)	0.356 (1)
C(34)	−0.396 (3)	0.048 (1)	0.359 (2)
C(35)	−0.516 (3)	0.018 (2)	0.344 (2)
C(36)	−0.523 (2)	−0.023 (1)	0.272 (1)
C(41)	0.457 (3)	0.172 (2)	0.536 (1)
C(42)	0.578 (3)	0.190 (1)	0.540 (1)
C(43)	0.627 (2)	0.249 (2)	0.566 (1)
C(44)	0.538 (3)	0.305 (2)	0.586 (1)
C(45)	0.419 (2)	0.288 (1)	0.577 (1)
C(46)	0.372 (2)	0.226 (1)	0.555 (1)
O(2)	0.974 (2)	0.154 (1)	0.617 (1)
C(51)	0.886 (2)	0.064 (1)	0.533 (1)
C(52)	0.881 (2)	0.028 (2)	0.605 (1)
C(53)	0.933 (2)	0.079 (2)	0.659 (1)
C(54)	0.951 (2)	0.143 (1)	0.538 (1)
		3	
Zr(1)	0.17202 (7)	$^1/_4$	0.38980 (7)
Zr(2)	−0.16488 (8)	$^1/_4$	0.06786 (8)
Cl(1)	0.2968 (2)	0.0713 (1)	0.4977 (2)
Cl(2)	−0.0999 (2)	$^1/_4$	0.3370 (2)
Cl(3)	0.0547 (1)	0.1087 (1)	0.1708 (1)
Cl(4)	−0.1726 (3)	$^1/_4$	−0.1527 (3)
Cl(5)	−0.3265 (2)	0.0926 (2)	0.0447 (2)
P(1)	0.4029 (2)	$^1/_4$	0.3179 (3)
P(2)	0.1605 (2)	$^1/_4$	0.6407 (2)
C(1)	0.576 (1)	$^1/_4$	0.464 (1)
C(2)	0.4129 (7)	0.1232 (8)	0.2199 (8)
C(3)	0.336 (1)	$^1/_4$	0.785 (1)
C(4)	0.0688 (7)	0.1228 (6)	0.6712 (7)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for 1 and 3

	1		
	Distances		
Zr(1)–Cl(1)	2.444 (5)	Zr(1)–Cl(2)	2.445 (5)
Zr(1)–Cl(3)	2.441 (5)	Zr(1)–Cl(4)	2.421 (5)
Zr(1)–O(1)	2.14 (1)	P(1)–C(1)	1.79 (2)
P(1)–C(11)	1.81 (2)	P(1)–C(21)	1.85 (2)
P(1)–C(31)	1.81 (2)	O(1)–C(4)	1.43 (2)
	Angles		
Cl(1)–Zr(1)–Cl(2)	87.8 (2)	Cl(1)–Zr(1)–Cl(3)	89.1 (2)
Cl(1)–Zr(1)–Cl(4)	99.2 (2)	Cl(1)–Zr(1)–O(1)	164.9 (3)
Cl(1)′–Zr(1)–O(1)	95.1 (3)	Cl(2)–Zr(1)–Cl(3)	176.8 (2)
Cl(2)–Zr(1)–Cl(4)	89.6 (2)	Cl(2)–Zr(1)–O(1)	92.8 (3)
Cl(2)′–Zr(1)–O(1)	89.6 (3)	Cl(3)–Zr(1)–Cl(4)	89.8 (2)
Cl(3)′–Zr(1)–O(1)	90.4 (3)	Cl(3)–Zr(1)–O(1)	91.8 (3)
Cl(4)–Zr(1)–O(1)	95.9 (3)	Cl(4)′–Zr(1)–O(1)	165.7 (3)
O(1)–Zr(1)–O(1)	69.9 (4)	C(1)–P(1)–C(11)	109.4 (8)
C(1)–P(1)–C(21)	105.7 (9)	C(1)–P(1)–C(31)	111.1 (9)
C(11)–P(1)–C(21)	110.0 (1)	C(11)–P(1)–C(31)	108.4 (8)
C(21)–P(1)–C(31)	113.0 (1)	Zr(1)–O(1)–Zr(1)	110.1 (4)
Zr(1)–O(1)–C(4)	123.1 (9)	Zr(1)–O(1)–C(4)	123.6 (9)
	3		
	Distances		
Zr(1)–Cl(1)	2.395 (2)	Zr(2)–Cl(4)	2.330 (3)
Zr(2)–Cl(5)	2.351 (2)	Zr(1)–Cl(2)	2.559 (3)
Zr(1)–Cl(3)	2.659 (2)	P(1)–C(1)	1.782 (8)
P(1)–C(2)	1.800 (9)	Zr(1)–P(1)	2.751 (3)
Zr(1)–P(2)	2.739 (3)	P(2)–C(3)	1.786 (9)
Zr(2)–Cl(2)	2.670 (2)	P(2)–C(4)	1.809 (8)
Zr(2)–Cl(3)	2.567 (2)		
	Angles		
Cl(1)–Zr(1)–Cl(1)	114.34 (7)	Cl(1)–Zr(1)–Cl(2)	113.71 (5)
Cl(1)–Zr(1)–Cl(3)	82.43 (5)	Cl(1)–Zr(1)–Cl(3)′	150.91 (7)
Cl(1)–Zr(1)–P(1)	78.45 (6)	Cl(1)–Zr(1)–P(2)	76.13 (6)
Cl(1)–Zr(1)–Cl(2)	113.71 (5)	Cl(1)–Zr(1)–Cl(3)	150.91 (7)
Cl(1)–Zr(1)–Cl(3)′	82.43 (5)	Cl(1)–Zr(1)–P(1)	78.45 (6)
Cl(1)–Zr(1)–P(2)	76.13 (6)	Cl(2)–Zr(1)–Cl(3)′	76.81 (6)
Cl(2)–Zr(1)–P(1)	153.80 (7)	Cl(2)–Zr(1)–P(2)	74.12 (8)
Cl(3)–Zr(1)–Cl(3)′	73.50 (7)	Cl(3)–Zr(1)–P(1)	82.28 (6)
Cl(3)–Zr(1)–P(2)	132.55 (5)	P(1)–Zr(1)–P(2)	132.08 (7)
Cl(2)–Zr(2)–Cl(3)	76.49 (6)	Cl(2)–Zr(2)–Cl(4)	168.88 (9)
Cl(2)–Zr(2)–Cl(5)	87.37 (6)	Cl(3)–Zr(2)–Cl(3)′	76.61 (7)
Cl(3)–Zr(2)–Cl(4)	94.86 (8)	Cl(3)–Zr(2)–Cl(5)	90.74 (6)
Cl(3)–Zr(2)–Cl(5)′	161.36 (6)	Cl(4)–Zr(2)–Cl(5)	99.87 (7)
Cl(5)–Zr(2)–Cl(5)	97.9 (1)	Cl(2)–Zr(2)–Cl(5)	87.37 (6)
Zr(1)–Cl(2)–Zr(2)	89.19 (9)	Zr(1)–Cl(3)–Zr(2)	89.25 (6)
Zr(1)–P(1)–C(1)	112.8 (4)	Zr(1)–P(1)–C(2)	115.4 (3)
C(1)–P(1)–C(2)	103.5 (3)	C(2)–P(1)–C(2)′	104.9 (6)
C(4)–P(2)–C(4)′	104.6 (5)	Zr(1)–P(2)–C(3)	114.1 (4)
Zr(1)–P(2)–C(4)	114.6 (2)	C(3)–P(2)–C(4)	103.8 (3)

Results

The reaction of PCy_3 and PPh_3 with $ZrCl_4(THF)_2$ in benzene was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. As the reaction proceeds, the free phosphine is slowly consumed giving rise to new resonances at 32.89 and 24.76 ppm for the reactions of PCy_3 and PPh_3, respectively. On standing, each of these new products **1** and **2** crystallized from solution. In the case of the PCy_3 product **1**, ^1H and $^{13}C\{^1H\}$ NMR showed the expected cyclohexyl proton resonances as well as some additional downfield methylene resonances. In the case of **2**, phenyl resonances were observed. In addition, the observation of additional downfield methylene resonances similar to those in **1** suggested the incorporation of a fragmented THF moiety; however, the determination of the precise molecular architecture required a crystallographic study. The study of **1** (vide infra) confirmed the formulation as $[ZrCl_4(\mu\text{-}OCH_2CH_2CH_2CH_2PCy_3)]_2$ (Scheme I). In retrospect, formation of these phosphonium salts was suggested by the $^{31}P\{^1H\}$ NMR chemical shifts of **1** and **2**, which are indistinguishable from those of $[BuPR_3]^+$ (R = Cy, Ph).[27]

In the analogous reaction of PMe_3 the free phosphine resonance is replaced with the single resonance at 24.37 ppm. Also in a similar fashion to the above reactions, the product crystallizes

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(27) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *^{31}P Nuclear Magnetic Resonance*; Topics in Phosphorus Chemistry; Interscience Publishers: New York, 1967; Vol. 5.

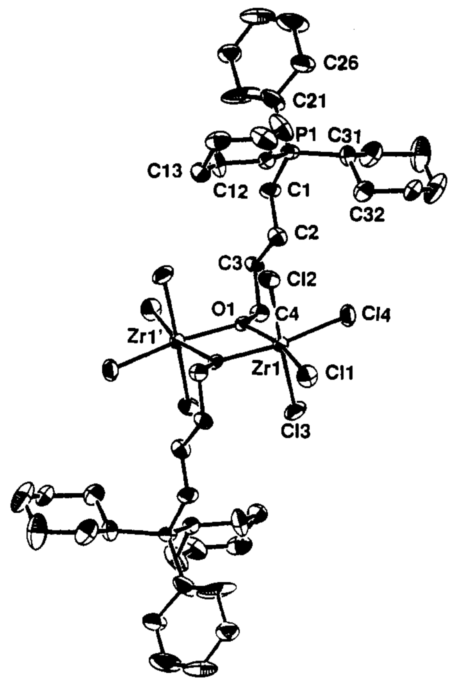
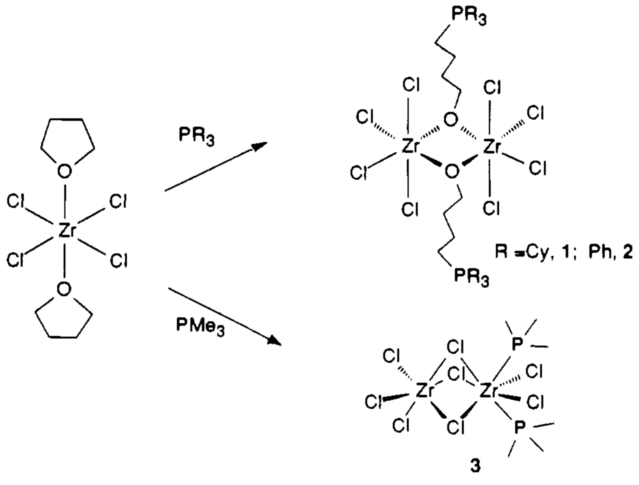


Figure 1. ORTEP drawing of molecule 1, showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme I



from solution. However, the ^{1}H NMR spectrum of **3** shows only methyl resonances. The structure of this product **3** was determined via a crystallographic study (vide infra). This confirmed the formulation of **3** as $Cl_3Zr(\mu\text{-}Cl)_3ZrCl_2(PMe_3)_2$ (Scheme I).

Structural Studies. X-ray structural studies of **1** and **3** confirmed the above formulations. Selected interatomic distances and angles are given in Table III, while ORTEP drawings of **1** and **3** are shown in Figures 1 and 2, respectively.

The Zr atoms in **1** adopt pseudooctahedral coordination spheres comprised of four chlorine atoms and two oxygen atoms. The oxygen atoms bridge the two Zr centers. A four-carbon fragment links the oxygen atoms to the PCy_3 moieties. Thus, this complex is a zwitterion with formal positive charges centered on the P atoms and negative charges at the metal centers. The Zr–Cl distances in **1** average 2.438 (5) Å. This is comparable to the Zr–Cl distances found in the dialkoxide-linked Zr(IV) species $Zr_2Cl_6(THF)_4(O_2C_6H_{10})$[28] and the terminal Zr–Cl bond lengths found in the Zr(III) dimer $Zr_2Cl_6(PR_3)_4$[2–4] and the Zr(IV) species $Zr_2Cl_6(THF)_4(O_2C_6H_{10})$[28] (2.412 (2)–2.460 (2) Å). The Zr–O distance of **1** was found to be 2.14 (1) Å, considerably longer in the terminally bound Zr–alkoxide bonds of $Zr_2Cl_6(THF)_4(O_2C_6H_{10})$[28] (1.870 (5) and 1.867 (5) Å). The Zr–O–Zr′ angle is 110.1 (4)°. The geometry about oxygen is essentially planar, suggesting π-bonding between the oxygen and the metal centers, an interaction which has been well documented in the past. The Zr_2O_2 core of **1** is also planar with Zr–O–Zr′ angles of 69.9 (4)°. This geometry dictates a Zr–Zr′ separation of 3.5 (1) Å. The alkyl groups adopt a symmetry transoid conformation with the phosphonium moieties on opposite sides of the Zr_2O_2 planes. Presumably this conformation minimizes steric congestion. The geometry of the pendant phosphonium moieties are otherwise as expected and require no further comment.

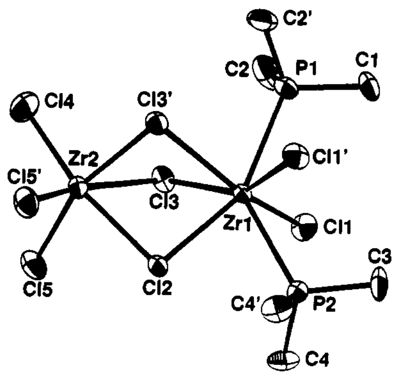
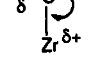


Figure 2. ORTEP drawing of molecule 3, showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The structural study of **3** revealed that the two Zr atoms are in inequivalent coordination environments. Two terminal chlorine atoms, three bridging chlorine atoms, and two phosphine ligands are bound to the seven-coordinate Zr1 center of **3**. The Zr2 center adopts a pseudooctahedral geometry with a coordination sphere comprised of three terminal and three bridging chlorine atoms. In **3**, the terminal Zr–Cl bond lengths average 2.359 (3) Å, which is slightly shorter than the terminal Zr–Cl distances found in $Zr_2Cl_6(PBu_3)_4$ (2.431 (2) Å).[2] In contrast, the bridging Zr–Cl distances in **3** average 2.609 (3) Å, which is longer than the bridging Zr–Cl distances in $Zr_2Cl_6(PBu_3)_4$ (2.544 (2) Å),[2] while the Zr–P bond distance in **3** is 2.751 (3) Å, slightly longer than the Zr–P distance of 2.835 (2) Å found in $Zr_2Cl_6(PBu_3)_4$. These differences between **3** and $Zr_2Cl_6(PBu_3)_4$ are consistent with the difference in the oxidation state of the Zr in the respective compounds and the presence of a M–M bond between the Zr(III) centers in $Zr_2Cl_6(PBu_3)_4$.[2] The effects of ligand basicity are reflected in a comparison of the bimetallic species **3** and its structural analogue $Zr_2Cl_8(PPh_3)_2$, which has been recently reported by Cotton et al.[29] In that case the Zr–P distances were found to be 2.855 (2) and 2.824 (2) Å, also significantly longer than the Zr–P distances in **3**, thus reflecting the greater Lewis basicity of PMe_3 compared to that of PPh_3.

Discussion

The mechanism of formation of **1** and **2** apparently involves nucleophilic attack of the THF coordinated to Zr by phosphine (**4**). Such ring opening reactions involving Lewis acidic metals



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have literature precedent. For example, Lewis acidic lanthanide[30–32] or transition metal[33–38] species have been shown to mediate both nucleophilic attack of THF and its polymerization.

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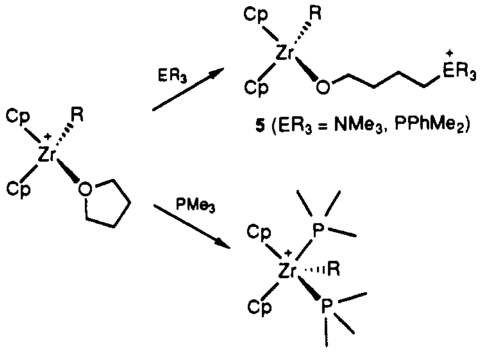
(28) Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955.

(29) Cotton, F. A.; Kibala, P. R. *Acta Crystallogr.* **1991**, *C47*, 270.

(30) Harwood, L. M.; Jackson, B.; Prout, K.; Witt, F. J. *Tetrahedron Lett.* **1990**, *31*, 1885.

More closely related are the recent results described by Jordan et al.[38] in which they show that the Zr cationic THF adduct $[Cp_2ZrR(THF)]^+$ is attacked by NMe_3 or $PPhMe_2$ to yield the THF ring Zr–alkoxide salt (**5**). It is also noteworthy that such nucleophilic attack is superseded by THF displacement when PMe_3 is employed as the nucleophile.



5 ($ER_3 = NMe_3$, $PPhMe_2$)

The similar reaction involving PMe_3 leads to the formation of **3**. How this dissymmetric species forms is not clear; however, Cotton et al.[29] have suggested that $ZrCl_4(PPh_3)_2$ is formed initially in the reaction of $ZrCl_4$ with PPh_3 and its subsequent reaction with $ZrCl_4$ affords the dimeric $Zr_2Cl_8(PPh_3)_2$. In a similar vein, we envision the formation of **3** from the reaction of $ZrCl_4(PMe_3)_2$ with $ZrCl_4(THF)_2$; however, attempts to spectroscopically observe such a precursor were unsuccessful.

The differing courses of the reactions of $ZrCl_4(THF)_2$ with these phosphines suggest that both steric and electronic factors alter the reaction pathway. Neither the sterically demanding phosphine PCy_3 nor the least basic of the phosphines employed PPh_3 react with $ZrCl_4(THF)_2$ to effect displacement of THF from the coordination sphere of the Zr. Rather, nucleophilic attack of the coordinated ether is seen. It is noteworthy that in the absence of coordinated THF coordination of PCy_3 and PPh_3 to Zr has been demonstrated. Merbach et al.[39] have recently shown that ligand-exchange processes for $ZrCl_4L_2$ species proceed through an associative route. In view of that result, it is not surprising that only the small, basic phosphine PMe_3 effects substitution upon reaction with $ZrCl_4(THF)_2$. Where ligand exchange does not proceed, the Lewis acidity of the Zr center activates the coordinated THF ring for nucleophilic attack. These results demonstrate an interesting reversal of nucleophilicity in that the poorer nucleophiles effect ring opening while the better nucleophiles do not. This same trend has been observed for related metallocene-mediated ring opening reactions.[31,38]

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Supplementary Material Available: Tables of thermal and hydrogen atom parameters and crystallographic details (8 pages). Ordering information is given on any current masthead page.

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(31) Evans, W. J.; Ilibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D. *Organometallics* **1990**, *9*, 2124.

(32) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *384*, C49.

(33) Tsuji, Y.; Kobayashi, M.; Okuda, F.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1253.

(34) DeShong, P.; Sidler, D. R. *J. Org. Chem.* **1988**, *53*, 4894.

(35) Woodhouse, M. E.; Lewis, F. D.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5586.

(36) Okuda, F.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1201.

(37) Oku, A.; Homoto, Y.; Harada, T. *Chem. Lett.* **1986**, 1495.

(38) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268.

(39) Turrin-Rossier, M.; Hugi-Cleary, D.; Frey, U.; Merbach, A. E. *Inorg. Chem.* **1990**, *29*, 1374.