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Article

Titanium and Zirconium Complexes of a Phosphorus-Containing *p-tert*-Butylcalix[5]arene Ligand: Importance of Metal and Conformation on Ligand/Metal Binding

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Binding of a calix[5]arene containing a single phosphorus ligand and three hydroxyl groups, calix[5]PNMe$_2$(OH)$_3$, **1**, toward titanium and zirconium is investigated to yield insight into the factors that determine the strength of the phosphorus/metal interaction within the constraint of the calix[5]arene. Treatment of **1** with tetrakis(dimethylamino)-titanium yields three complexes, **4a**, **4b**, and **4c**, each of which shows the loss of 3 mol of dimethylamine in the reaction with the titanium bound to three oxygens. Treatment of **1** with tetrakis(diethylamino)zirconium proceeds similarly, although only two products, **5a** and **5b**, were isolated. X-ray structures of the products were obtained. Complexes **4a** and **5a** show similar geometries, with the calix[5]arene in an approximate cone conformation and the phosphorus lone pair directed toward the metal. The P···M distances are, however, markedly different: 3.69 Å in **4a** and 3.18 Å in **5a**, the former indicative of no interaction and the latter a weak one. Complexes **4b** and **5b** each are dimers, featuring a planar four-membered M–O–M–O ring; however, the titanium is five-coordinate in **4b** with no phosphorus/metal bond, while the zirconium in **5b** is six-coordinate with a P–Zr distance of 2.95 Å. Complex **4c** is monomeric with the calix[5]arene in an approximate 1,2-alternate conformation with a P···Ti distance of 2.90 Å. The two most significant aspects controlling the phosphorus/metal contact are the metal, with the larger zirconium showing stronger interaction, and the calix[5]arene conformation, with the cone conformation showing the weaker interaction.

Because of their ease of synthesis, most calixarene research has focused on the even-numbered members of the family, particularly the calix[4]arenes, and to a lesser extent, the calix[6]- and calix[8]arenes.[1] Our work[2] has taken advantage of the constraint of the small cavity of the calix[4]arene to stabilize high-coordinate main-group element geometries and

study their transformations within the cavity. However, in most cases, the cavity is too small to study the interaction of two atoms within the framework. To that end, we reported[3] the control of a phosphorus/metal interaction within the cavity of a calix[5]arene[4] by changing the electronic requirements at the metal by ligand substitution. Specifically, replacing the excellent π-back-bonding amido ligand, NHBu^t, in **2** with the much weaker binding triflate, results in a significantly stronger phosphorus/tungsten interaction (Scheme 1). In addition, we recently reported insertion of silyl[5] and phosphorus[6] groups into *p-tert*-butylcalix[5]arene. We believe that this calix[5]arene cavity possesses the ideal balance between constraint and flexibility to study and control ligand/metal interactions. We herein report the reaction of **1** with

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Scheme 1. Preparation and P···W Interactions of Tungsen Complexes of **1**
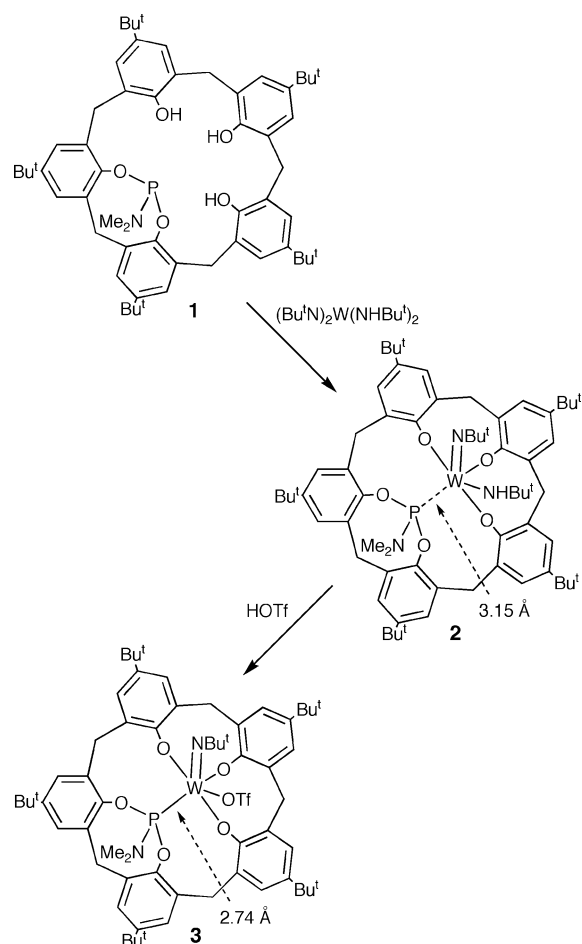
titanium and zirconium and demonstrate that calixarene conformation, as well as the specific metal, plays a crucial role in the phosphorus/metal interaction.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox or by using standard Schlenk techniques, unless otherwise indicated. Solvents were dried using standard procedures and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents tetrakis(dimethylamino)titanium and tetrakis(diethylamino)zirconium were obtained commercially and used without further purification. Ligand **1** was synthesized by the literature procedure.[3] All NMR spectra were recorded on a Bruker AVANCE DRX-400 multinuclear NMR spectrometer resonating at 400.137 (^{1}H) and 161.979 MHz (^{31}P). ^{1}H NMR resonances were measured relative to residual proton solvent peaks and referenced to Me$_4$Si. ^{31}P NMR resonances were measured relative to external 85% H$_3$PO$_4$. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from Complete Analysis Laboratories, Inc. (E + R Microanalytical Division), Parsippany, NJ. Elemental analyses calculated with solvent included were determined by NMR integrations.

Synthesis of Titanium Complexes. A stirred solution of **1** (2.09 g, 2.36 mmol) in toluene (40 mL) was treated dropwise with tetrakis(dimethylamino)titanium (0.535 g, 2.39 mmol). The reaction

mixture was stirred for 3 days after which the volatiles were pumped off leaving a red residue. The following procedure led to isolation of the products. (All crystallizations were performed at room temperature.) The residue was dissolved in hot toluene and allowed to sit at room temperature. Analytically pure **4a** crystallized from this solution. Concentration of the supernatant led to a small amount of precipitate. The precipitate was redissolved and further concentrated by boiling the solution. Crystals of **4b** came out at room temperature. Recrystallization led to analytically pure **4b**. The two supernatants were combined and concentrated again. This led to precipitation of crude **4c**, which was recrystallized twice from toluene. Although a satisfactory elemental analysis was obtained for **4b**, the ^{1}H NMR spectrum showed about a 20% unidentified impurity remaining in the final product. All three products are red and air-sensitive, and all yields are based on the final isolated compounds.

4a: 0.804 g (29%); mp: 128−130 °C (dec). Anal. Calcd for C$_{59}$H$_{77}$N$_2$O$_5$PTi·2C$_7$H$_8$: C, 75.76; H, 8.10. Found: C, 75.19; H, 8.29. ^{1}H NMR (CDCl$_3$, δ): 1.08 (s, 18H, t-Bu), 1.15 (s, 9H, t-Bu), 1.38 (s, 18H, t-Bu), 2.94 (d, 6H, PNMe$_2$, $^3J_{PH}$ = 10.4 Hz), 3.32 (d, 2H, CH$_2$, $^2J_{HH}$ = 15.0 Hz), 3.34 (d, 1H, CH$_2$, $^2J_{HH}$ = 12.3 Hz), 3.38 (d, 2H, CH$_2$, $^2J_{HH}$ = 13.6 Hz), 3.71 (s, 6H, TiNMe$_2$), 4.61 (dd, 1H, CH$_2$, $^2J_{HH}$ = 12.3 Hz, $^5J_{PH}$ = 2.7 Hz), 4.71 (overlapping d, 4H, CH$_2$, $^2J_{HH}$ = 13 Hz, approx), 6.98 (d, 2H, CH, $^4J_{HH}$ = 2.4 Hz), 7.01 (overlapping s, 4H, CH), 7.16 (s, 2H, CH), 7.24 (CH, overlapping with CDCl$_3$). ^{31}P NMR (CDCl$_3$, δ): 127.7.

4b: 0.344 g (15%); mp: >238 °C (dec). Anal. Calcd for (C$_{59}$H$_{77}$N$_2$O$_5$PTi)$_2$: C, 72.82; H, 7.98. Found: C, 72.95; H, 8.28. ^{1}H NMR (CDCl$_3$, δ): 0.78 (d, 12H, PNMe$_2$, $^3J_{PH}$ = 10.0 Hz), 1.17 (s, 18H, t-Bu), 1.18 (s, 36H, t-Bu), 1.25 (s, 36H, t-Bu), 3.03 (s, 12H, TiNMe$_2$), 3.42, 3.45, 3.50 (overlapping, 10H, CH$_2$), 4.40 (d, 4H, $^2J_{HH}$ = 16.6 Hz), 5.07 (d, 4H, $^2J_{HH}$ = 12.4 Hz), 5.36 (dd, 2H, CH$_2$, $^2J_{HH}$ = 15.7 Hz, $^5J_{PH}$ = 7.5 Hz), 6.86 (d, 4H, CH, $^4J_{HH}$ = 2.1 Hz), 6.89 (d, 4H, CH, $^4J_{HH}$ = 2.2 Hz), 6.98 (d, 4H, CH, $^4J_{HH}$ = 2.1 Hz), 7.04 (s, 4H, CH), 7.11 (d, 4H, CH, $^4J_{HH}$ = 2.3 Hz). ^{31}P NMR (CDCl$_3$, δ): 136.4.

4c: 0.575 g (24%); mp: >295 °C (dec). Anal. Calcd for C$_{59}$H$_{77}$N$_2$O$_5$PTi·0.5C$_7$H$_8$: C, 73.66; H, 8.01. Found: C, 73.69; H, 7.68. ^{1}H NMR (CDCl$_3$, δ): 1.16 (s, 9H, t-Bu), 1.23 (s, 18H, t-Bu), 1.40 (s, 18H, t-Bu), 2.20 (s, 6H, TiNMe$_2$, $^4J_{PH}$ = 2.0 Hz), 2.44 (d, 6H, PNMe$_2$, $^3J_{PH}$ = 10.7 Hz), 3.29 (d, 2H, CH$_2$, $^2J_{HH}$ = 14.5 Hz), 3.31 (d, 2H, CH$_2$, $^2J_{HH}$ = 14.8 Hz), 3.46 (d, 1H, CH$_2$, $^2J_{HH}$ = 13.0 Hz), 4.34 (dd, 1H, CH$_2$, $^2J_{HH}$ = 12.9 Hz, $^5J_{PH}$ = 4.1 Hz), 4.49 (d, 2H, CH$_2$, $^2J_{HH}$ = 14.4 Hz), 4.57 (d, 2H, CH$_2$, $^2J_{HH}$ = 14.7 Hz), 7.00 (s, 2H, CH), 7.14−7.19 (overlapping, 8H, CH). ^{31}P NMR (CDCl$_3$, δ): 128.6.

Synthesis of Zirconium Complexes. A stirred solution of **1** (2.20 g, 2.49 mmol) in toluene (40 mL) was treated dropwise with tetrakis(diethylamino)zirconium (0.954 g, 2.51 mmol). The mixture was stirred at room temperature for 3 days after which the volatiles were pumped off leaving a light-yellow residue. The residue was heated in toluene and filtered hot. The toluene filtrate was concentrated and left for several days to give **5a** as colorless crystals. Although spectra indicated a pure product, we were unable to obtain a reliable elemental analysis. The insoluble material from the filtration was recrystallized from chloroform/toluene to give analytically pure **5b** as colorless crystals. (Crystals of **5b** for X-ray crystallography were grown from chloroform.)

5a: 0.804 g (25%); mp: 150−152 °C (dec). Anal. Calcd for C$_{61}$H$_{81}$N$_2$O$_5$PZr·3C$_7$H$_8$: C, 74.56; H, 8.01. Found: C, 71.53; H, 8.03. ^{1}H NMR (CDCl$_3$, δ): 1.10 (s, 9H, t-Bu), 1.16 (s, 18H, t-Bu), 1.31 (s, 18H, t-Bu), 1.46 (t, 6H, ZrNCH$_2$*CH$_3$*, $^3J_{HH}$ = 7.1 Hz), 2.90 (d, 6H, PNMe$_2$, $^3J_{PH}$ = 10.4 Hz), 3.21 (d, 2H, CH$_2$, $^2J_{HH}$ = 13.9

Table 1. Crystal Data[a]

	4a	4b	4c
empirical formula	$C_{59}H_{77}N_2O_5PTi\cdot2C_7H_8$	$C_{118}H_{154}N_4O_{10}P_2Ti_2\cdot6C_7H_8$	$C_{59}H_{77}N_2O_5PTi\cdot C_7H_8$
fw	1157.36	2499.00	1065.23
cryst syst	hexagonal	triclinic	triclinic
space group	$P6_3/m$	$P\bar{1}$	$P\bar{1}$
a, Å	22.874(1)	16.781(1)	12.7577(11)
b, Å	22.874(1)	17.030(2)	13.080(2)
c, Å	23.625(3)	17.376(1)	20.4886(17)
α, deg	90	116.638(7)	72.614(10)
β, deg	90	118.220(4)	84.752(5)
γ, deg	120	92.656(7)	67.018(9)
V, Å^3	10705.0(15)	3694.4(5)	3002.4(6)
Z	6	1	2
ρ_{calcd}, g cm^{-3}	1.077	1.123	1.178
μ, mm^{-1}	0.189	0.187	0.219
extinctn coeff[b]	0.0030(6)	0.0004(3)	0.0014(4)
R1 [$I > 2\sigma(I)$][c]	0.104	0.103	0.106
wR2 [all data][c]	0.298	0.257	0.303

	5a	5b	
empirical formula	$C_{61}H_{81}N_2O_5PZr\cdot2C_7H_8$	$C_{122}H_{162}N_4O_{10}P_2Zr_2\cdot8CHCl_3$	
fw	1228.74	3043.88	
cryst syst	hexagonal	triclinic	
space group	$P6_3/m$	$P\bar{1}$	
a, Å	22.987(1)	14.605(3)	
b, Å	22.987(1)	16.059(2)	
c, Å	24.080(4)	17.379(3)	
α, deg	90	89.49(1)	
β, deg	90	72.51(2)	
γ, deg	120	72.72(1)	
V, Å^3	11019(2)	3697.7(11)	
Z	6	1	
ρ_{calcd}, g cm^{-3}	1.111	1.367	
μ, mm^{-1}	0.218	0.650	
extinctn coeff[b]	n/a	0.0003(6)	
R1 [$I > 2\sigma(I)$][c]	0.102	0.103	
wR2 [all data][c]	0.313	0.306	

[a] Graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å. [b] See ref 7. [c] R1 $= \sum||F_o| - |F_c||/\sum|F_o|$, wR2 $= \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + F_o^2]/3$.

Hz), 3.28 (d, 2H, CH_2, $^2J_{HH} = 13.2$ Hz), 3.57 (q, 4H, ZrNCH_2 CH_3, $^3J_{HH} = 7.1$ Hz), 3.52 (d, 1H, CH_2, $^2J_{HH} = 14.9$ Hz), 4.39 (d, 1H, CH_2, $^2J_{HH} = 14.9$ Hz), 4.50 (d, 2H, CH_2, $^2J_{HH} = 13.8$ Hz), 4.72 (d, 2H, CH_2, $^2J_{HH} = 13.1$ Hz), 6.99 (s, 2H, CH), 7.00 (d, 2H, CH, $^4J_{HH} = 2.3$ Hz), 7.13 (d, 2H, CH, $^4J_{HH} = 2.6$ Hz), 7.16 (4H, CH, overlapping). ^{31}P NMR (CDCl$_3$, δ): 118.0.

5b: 0.494 g (17%); mp: >370 °C (dec). Anal. Calcd for $(C_{61}H_{81}N_2O_5PZr)_2\cdot2C_7H_8$: C, 71.85; H, 7.89. Found: C, 72.21; H, 7.62. ^{1}H NMR (CDCl$_3$, δ): 0.08 (t, 12H, ZrNCH$_2$$CH_3$, $^3J_{HH} = 7.0$ Hz), 0.89 (d, 12H, PNMe$_2$, $^3J_{PH} = 8.6$ Hz), 1.15 (s, 18H, t-Bu), 1.19 (s, 36H, t-Bu), 1.27 (s, 36H, t-Bu), 3.23 (d, 2H, CH_2, $^2J_{HH} = 14.9$ Hz), 3.34 (d, 4H, CH_2, $^2J_{HH} = 14.9$ Hz), 3.38 (d, 4H, CH_2, $^2J_{HH} = 12.6$ Hz), 3.65 (br, 8H, ZrNCH_2CH$_3$), 4.00 (d, 2H, CH_2, $^2J_{HH} = 14.8$ Hz), 4.94 (d, 4H, CH_2, $^2J_{HH} = 14.8$ Hz), 5.25 (d, 4H, CH_2, $^2J_{HH} = 12.5$ Hz), 6.94 (d, 4H, CH, $^4J_{HH} = 2.3$ Hz), 6.99 (d, 4H, CH, $^4J_{HH} = 2.5$ Hz), 7.17 (s, 4H, CH), 7.18 (d, 4H, CH, $^4J_{HH} = 2.6$ Hz), 7.19 (d, 4H, CH, $^4J_{HH} = 2.2$ Hz). ^{31}P NMR (CDCl$_3$, δ): 121.4.

Single-Crystal X-ray Diffraction Studies. Three titanium crystal samples are orange colored, while the zirconium ones are colorless. All crystals were grown from toluene except for **5b**. Suitable X-ray quality crystals of **5b** could only be obtained from chloroform. All data were collected on a Siemens P4 diffractometer. The crystals were coated with mineral oil under a low-temperature nitrogen stream. Crystallographic data are summarized in Table 1. All structures were solved by direct methods and subsequent difference Fourier syntheses and refined by full-matrix least-squares methods
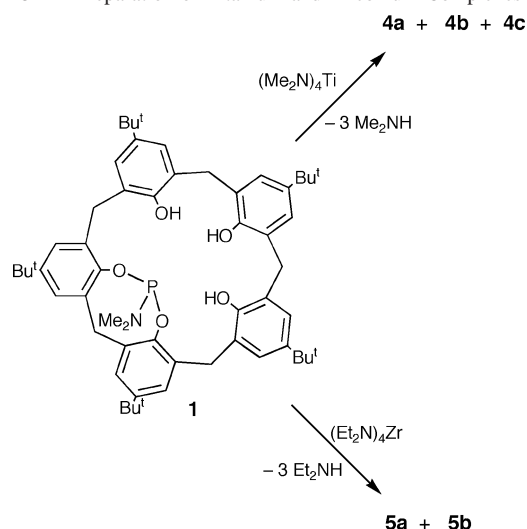
against F^2.[7] Solvate toluene molecules were found in each of the crystal lattices. Most solvent molecules, as well as some methyl groups of *tert*-butyls, are positionally disordered. These disordered atoms were refined with occupancy and distance restraints. All non-hydrogen atoms were refined anisotropically, while H atoms were constrained with a riding model. Further details regarding the crystal data and refinement, as well as full tables of bond lengths and angles for each structure reported in this paper, are presented in CIF format in the Supporting Information.

Results and Discussion

The three hydroxyl oxygens in **1** are ideally arranged to bind a single transition metal. However, choice of a suitable reagent is critical. For the Group 4 metals, we were unable to isolate any compounds with titanium(IV) and zirconium(IV) chlorides. Dialkylamino reagents were used instead.

Treatment of **1** with tetrakis(dimethylamino)titanium in a 1:1 molar ratio (Scheme 2) at ambient temperature led to a mixture of several products, **4a**, **4b**, and **4c**, which were isolated by fractional crystallization (see Experimental Section). Several key features in the ^{1}H NMR spectra of the products indicate a similarity among all three. First of all, the overall C_s symmetry of the free ligand is retained in the

(7) Sheldrick, G. M. *SHELXS97 and SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

Scheme 2. Preparation of Titanium and Zirconium Complexes of **1**

Figure 1. Molecular structure of **4a**. Thermal ellipsoids are shown at 50% probability. For clarity, carbon atoms of the calix[5]arene are shown at an arbitrary size and hydrogen atoms are omitted.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **4a** and **5a**

	4a	5a		4a	5a
M−O1	1.828(8)	2.005(10)	P−O3	1.638(5)	1.638(7)
M−O2	1.818(5)	1.984(7)	P−N2	1.673(10)	1.657(12)
M−N1	1.835(10)	1.976(14)	P⋯M	3.690	3.176(4)
O1−M−O2	102.1(2)	94.3(2)	O3−P−O3A	99.9(4)	103.0(5)
O1−M−N1	98.0(5)	95.6(5)	O3−P−N2	96.6(3)	98.1(4)
O2−M−N1	109.4(2)	112.8(2)	P−M−O1	179.7	176.3(3)
O2−M−O2A	130.2(3)	132.4(4)			

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **4b** and **5b**

	4b	5b		4b	5b
M−O1A	1.976(5)	2.181(8)	M⋯P		2.954(4)
M−O1	2.144(5)	2.260(8)	P−O3	1.654(6)	1.612(10)
M−O2	1.816(6)	2.010(9)	P−O4	1.638(6)	1.620(10)
M−O5	1.823(5)	2.005(11)	P−N2	1.648(7)	1.668(13)
M−N1	1.886(6)	2.041(11)			
O1A−M−O2	114.9(2)	104.6(3)	O2−M−P		77.2(3)
O1A−M−O5	115.4(2)	100.8(4)	O5−M−N1	98.8(3)	99.1(4)
O1A−M−O1	68.9(2)	66.5(4)	O5−M−P		75.7(3)
O1A−M−N1	92.8(2)	89.3(4)	N1−M−P		96.9(3)
O1A−M−P		173.2(3)	O3−P−O4	93.9(3)	105.1(5)
O1−M−O2	87.8(2)	88.7(3)	O3−P−N2	99.3(3)	106.8(6)
O1−M−O5	90.7(2)	86.2(3)	O4−P−N2	101.2(3)	96.0(6)
O1−M−N1	161.7(2)	155.9(4)	O3−P−M		94.1(4)
O1−M−P		107.2(2)	O4−P−M		114.8(3)
O2−M−O5	125.2(2)	149.5(4)	N2−P−M		136.7(4)
O2−M−N1	99.2(3)	97.7(4)	M−O1−MA	111.1(2)	113.5(4)

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for **4c**

Ti−O1	1.886(8)	Ti−P	2.897(4)
Ti−O2	1.871(8)	P−O3	1.642(8)
Ti−O5	1.853(7)	P−O4	1.635(8)
Ti−N1	1.848(10)	P−N2	1.664(10)
O1−Ti−O2	94.8(4)	O5−Ti−P	78.7(3)
O1−Ti−O5	100.7(3)	N1−Ti−P	98.9(3)
O1−Ti−N1	96.0(4)	O3−P−O4	98.3(4)
O1−Ti−P	164.8(3)	O3−P−N2	101.5(5)
O2−Ti−O5	141.4(4)	O3−P−Ti	116.1(3)
O2−Ti−N1	109.1(4)	O4−P−N2	98.5(5)
O2−Ti−P	77.4(3)	O4−P−Ti	120.0(3)
O5−Ti−N1	104.2(4)	N2−P−Ti	118.6(4)

compounds: three resonances are observed for the *tert*-butyl groups (in a 2:2:1 ratio). In addition, six doublets (due to $^2J_{HH}$ geminal coupling) are found for the methylene bridging groups (in a 2:2:2:2:1:1 ratio). Finally, two resonances assigned to dimethylamino groups are observed; one is the phosphorus-bound group, easily assigned by its characteristic doublet ($^3J_{PH}$ ca. 10 Hz), and the other, most likely dimethylamino bound to titanium. These integrate to a 1:1 ratio, signifying the loss of 3 mol of dimethylamine in the reaction, as expected.

Clues to the differences among the products are found upon closer examination of the spectra, specifically the chemical shifts of the dimethylamino groups. In **4a**, these appear at δ 2.94 (PNMe$_2$) and 3.71 (TiNMe$_2$). Both resonances appear upfield in the two other products: **4b**, δ 0.78 (PNMe$_2$) and 3.03 (TiNMe$_2$); **4c**, δ 2.44 (PNMe$_2$) and 2.20 (TiNMe$_2$). Such chemical shift differences are common in calixarene chemistry and usually indicate increased shielding due to protons positioned "above" an aromatic ring. One final observation is noted for **4c**: a small phosphorus coupling (2.0 Hz) is clearly observed in the Ti-bound dimethylamino resonance and absent in **4a** and **4b**, perhaps indicative of a stronger phosphorus/metal interaction compared to the other titanium complexes.

The reaction of **1** with tetrakis(diethylamino)zirconium proceeds similarly, except that only two complexes, **5a** and **5b**, could be isolated. Integration of the dialkylamino resonances supports the loss of 3 mol of diethylamine in the products. The PNMe$_2$ resonance in **5a** (δ 2.90) appears at almost the same chemical shift as in **4a,** while the methyl resonance of the diethylamino group appears at δ 1.46. In **5b**, these move upfield: δ 0.89 (PNMe$_2$) and 0.08 (CH$_3$ of ZrNEt$_2$).

X-ray structures of the products were obtained and illustrate some similarities, as well as several marked differences, among the titanium and zirconium products. Selected distances and angles are tabulated in Tables 2−4. While the structures obtained are not of the highest quality, key features are clear, and it is these that will be discussed.

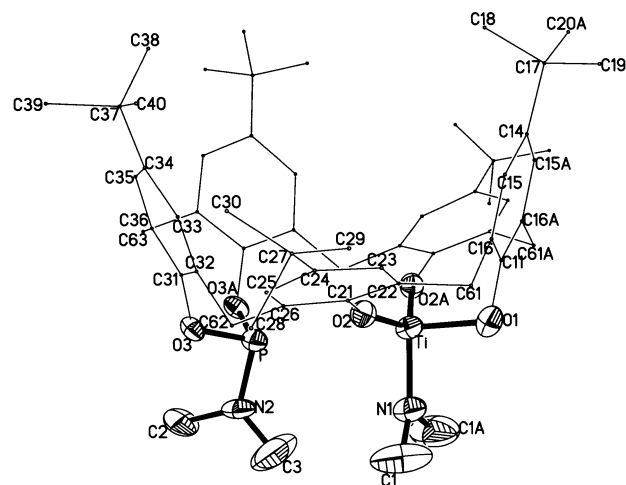The most similar titanium/zirconium structures are **4a** and **5a**, Figures 1 and 2, respectively (and Chart 1). Both are monomeric with the calix[5]arene backbone in an approximate cone conformation,[8] and the phosphorus lone pair is directed toward the metal atom. However, the P⋯Ti
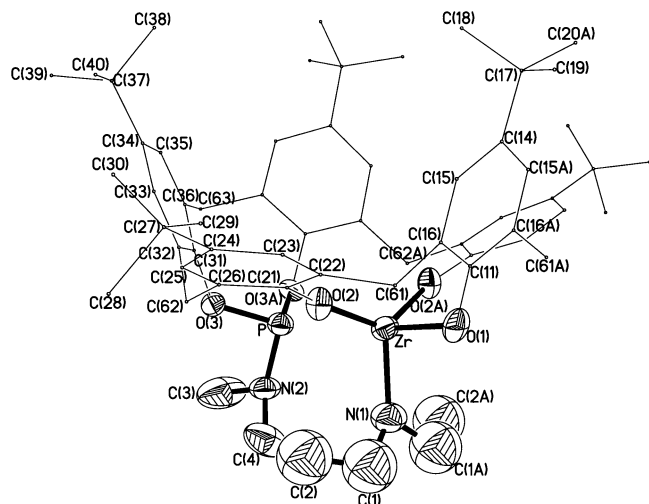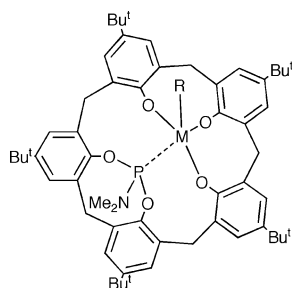
Figure 2. Molecular structure of **5a**. Thermal ellipsoids are shown at 50% probability. For clarity, carbon atoms of the calix[5]arene are shown at an arbitrary size and hydrogen atoms are omitted.
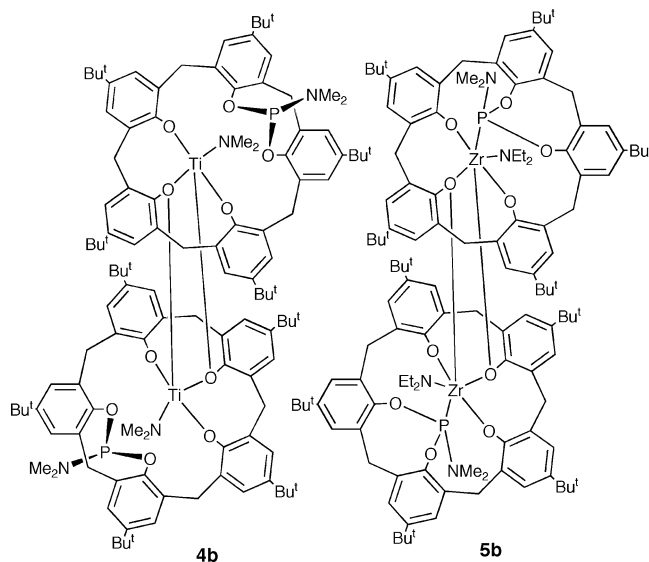
Chart 1

4a (M = Ti, R = NMe$_2$, P---M = 3.69 Å)
5a (M = Zr, R = NEt$_2$, P---M = 3.18 Å)
4c (M = Ti, R = NMe$_2$, P---M = 2.90 Å)

4b

5b

distance is 3.69 Å in **4a**, well outside the range of any conceivable interaction. In **5a**, the phosphorus atom is significantly closer to the metal (P⋯Zr distance of 3.18 Å),

Figure 3. Molecular structure of **4b**. Thermal ellipsoids are shown at 40% probability. For clarity, carbon atoms of the calix[5]arene are shown at an arbitrary size and hydrogen atoms are omitted.

Figure 4. Molecular structure of **5b**. Thermal ellipsoids are shown at 40% probability. For clarity, carbon atoms of the calix[5]arene are shown at an arbitrary size and hydrogen atoms are omitted.

suggesting a weak interaction. These values can be compared to typical P−Ti and P−Zr bond distances of 2.5−2.6 and 2.7−2.8 Å, respectively.[9] Complexes **4b** and **5b** are dimeric, featuring a planar four-membered M−O−M−O ring (Figures 3 and 4, respectively), a very common structure in titanium and zirconium chemistry.[10]

(8) For more accurate descriptions of calix[5]arene conformations, see (a) Thondorf, I.; Brenn, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2293. (b) Harada, T.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2231. (c) Stewart, D. R.; Krawiec, M.; Kashyap, R. P.; Watson, W. H.; Gutsche, C. D. *J. Am. Chem. Soc.* **1995**, *117*, 586.
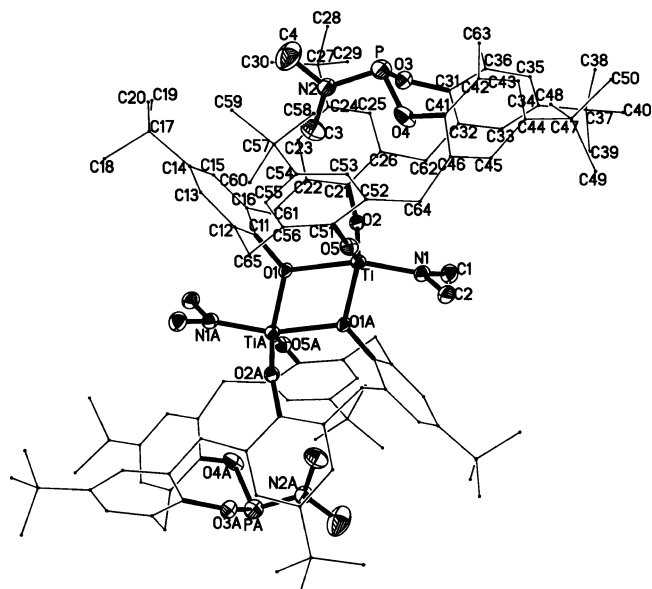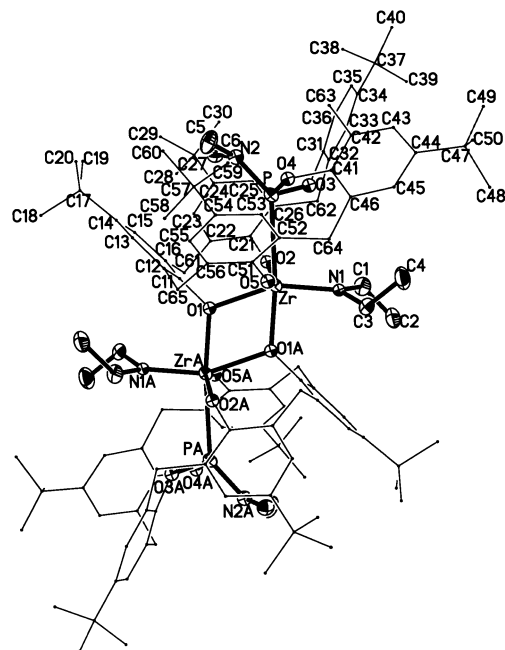
(9) See, for example, (a) Harvey, B. G.; Basta, R.; Arif, A. M.; Ernst, R. D. *Dalton Trans.* **2004**, 1221. (b) Ernst, R. D.; Freeman, J. W.; Stahl, L.; Wilson, D. R.; Arif, A. M.; Nuber, B.; Ziegler, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 5075. (c) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844.

(10) For recent examples, see Fric, H.; Schubert, U. *New J. Chem.* **2005**, *29*, 232, and references therein.
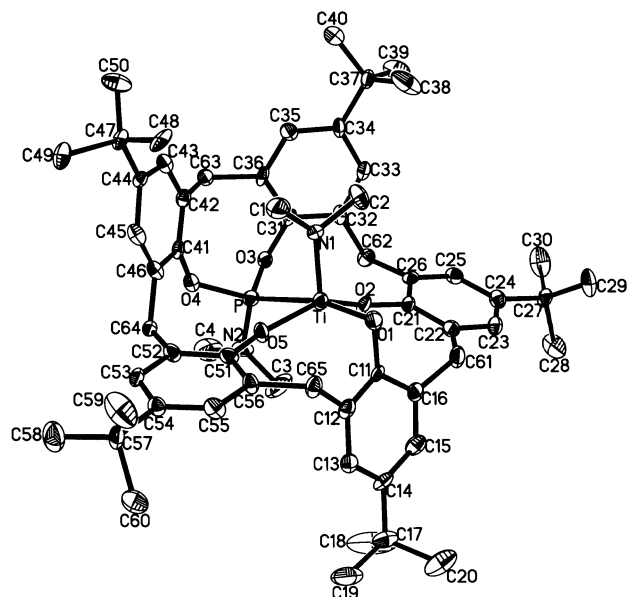
Figure 5. Molecular structure of **4c**. Thermal ellipsoids are shown at 30% probability. For clarity, hydrogen atoms are omitted.

Although the metal cores are similar in both complexes, the metal coordination numbers are not: titanium is five-coordinate with no phosphorus interaction, while zirconium is six-coordinate with a P···Zr distance of 2.95 Å. The calixarene backbone in **4b** is in an approximate 1,2-alternate conformation[11] with the phosphorus-bound oxygens on one "side" and the titanium-bound oxygens on the opposite; the phosphorus lone pair points away from the titanium. Perhaps the best way to describe the overall geometry of the zirconium analogue **5b** is that it is similar to **4b**, except that the phosphorus is inverted, allowing the lone pair to bind to the zirconium. Complex **4c** is again monomeric (Figure 5), but the calix[5]arene conformation is no longer in the cone conformation as in **4a**. The conformation can be approximated as 1,2-alternate. The most important observation in this complex is the P···Ti distance; it is 2.90 Å, 0.8 Å shorter than in **4a**. These structures are consistent with the ^{1}H NMR observations: overall C_s symmetry and, of the three titanium complexes, the only one that shows phosphorus coupling to the titanium-bound dimethylamino group corresponds to the structure with the shortest P···Ti distance. Upfield movement of the chemical shifts is also reasonable. In the cone conformation (**4a** and **5a**), the methyl protons of the dialkylamino groups cannot interact with the π systems of the aromatic rings, and these spectra show the most downfield chemical shifts for these resonances. In all of the other products, these protons can, at least to some extent, interact with the rings. For example, in **4c**, the C1···aromatic carbon (C41–C46) distances range from 3.5 to 3.7 Å. The C3···(C11–C16) range is significantly longer (4.9–5.3 Å). This long distance is the likely reason for the modest upfield shift of the PNMe$_2$ resonance ($\Delta\delta = -0.5$) compared to TiNMe$_2$ ($\Delta\delta = -1.5$). Similar arguments explain the other upfield resonances.

Table 5. Comparison of "Equatorial" Angles (deg) around the Metal in **4a**, **4c**, and **5a**[a]

	4a	**4c**	**5a**
O$_a$–M–O$_b$	130.1	141.4	132.4
O$_a$–M–N	109.5	109.1	112.7
O$_b$–M–N	109.5	104.2	112.7
sum	349.1	354.7	357.8

[a] O$_a$ and O$_b$ are O2 and O2A for **4a** and **5a**; they are O2 and O5 for **4c**. O$_c$ is O1 in all.

While the ^{1}H NMR chemical shifts give insight into the detailed structures, the ^{31}P NMR shifts do not. For example, **4a** and **4c** have almost identical chemical shifts (δ 127.7 and 128.6, respectively), even though the P···Ti distance is substantially shorter in the latter. This similarity could be due to the fact that the P···Ti distance in **4c** is still about 0.3 Å longer than a normal P–Ti bond. Both are shifted slightly *upfield* compared to the free ligand **1** (δ 130.6).[3] We observed a similar upfield shift in complex **3** (δ 125),[3] a compound with a long P–W bond (see below).

In an effort to ascertain the relative stabilities of the titanium and zirconium complexes, we attempted to inter-convert them thermally. Isolated samples of each complex were heated overnight in refluxing toluene, but no evidence of interconversion was found. A small amount of decomposition was observed in most cases, but otherwise, the spectra remained unchanged. Since there are many more low-energy conformations of calix[5]arenes compared to calix-[4]arenes,[8] it is likely that enthalpy differences among the products are not significant.

An examination of selected angles about the metal in the monomeric structures provides insight into the constraint imposed by the calixarene and the ability of the phosphorus to interact with the metal. Table 5 lists the angles at the metal involving nitrogen, O2, and O2A (or O5 for **4c**). The approach of the phosphorus should alter the angles at the metal from tetrahedral to trigonal bipyramidal. While this is the case to some extent (the sum of the "equatorial" angles in **4a** increases by 6° in **4c**), it is not that dramatic. Moreover, the sum of these angles in all three complexes is much closer to planar than tetrahedral. A closer examination of these angles shows the two O–M–N angles are close to tetrahedral in all three complexes. It is the O$_a$–M–O$_b$ angle that is different, 130–141°. The constraint of three adjacent phenolic calixarene groups bound to a single metal appears to impose this large angle. It is important to point out that it is the three adjacent groups that impart this constraint, rather than the overall calix[5]arene backbone, since the first calix-[4]arene titanium complex ever synthesized (**6**)[12] shows a relatively large value (127°) for the corresponding angle. In

(11) The four idealized conformations of calix[5]arenes are the same as calix[4]arenes: cone; partial cone; 1,2-alternate; 1,3-alternate.

(12) Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 8087.

the present case, this constraint should stabilize the addition of a fifth ligand to the metal coordination. The observation that this interaction is quite variable suggests that other factors are important.

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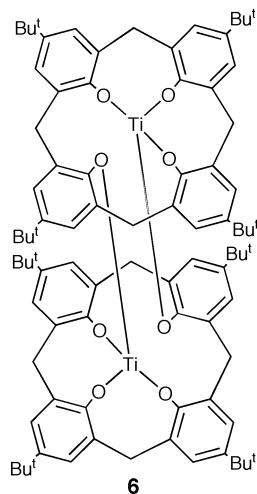
The P···M interaction in all complexes is weaker (or nonexistent) compared to normal bonds. The calix[5]arene backbone apparently restricts the approach of the phosphorus. This was previously observed[3] in the tungsten complex **3** that exhibits a P−W distance at the longer end of known

P−W bonds. The metal is also important, most clearly seen from a comparison of **4a** and **5a**. In the cone conformation, the phosphorus lone pair is ideally arranged to bind to the metal, yet only in the case of zirconium can the observed distance be described as an interaction, albeit weak. The larger zirconium, accompanied by larger M−O distances, is better able to accommodate the extra ligand within the calix-[5]arene. Comparison of **4a** and **4c** demonstrates the importance of calix[5]arene conformation, with the 1,2-alternate conformation yielding a complex with a markedly shorter P···Ti distance. Part of the reason for this decreased distance in **4c** may be the reduced steric repulsion of the dimethyl-amino groups in this conformation; however, this is not the only reason, since the tungsten complex **3** exhibits the cone conformation for the calix[5]arene, and it has the shorter P···W distance compared to **2** in which the calix[5]arene adopts an approximate 1,2-alternate conformation. We are currently investigating the binding of a calix[5]arene with two phosphorus ligands in order to compare the constraints in that ligand with **1**.