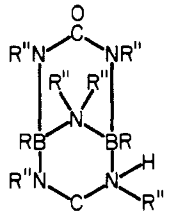
precipitate was collected and was identified as *N,N,N'*-trimethylurea (78% yield): $\delta(^1H)$ 4.4* (1 H, s) 2.89 (6 H, s), 2.79 (3 H, d, J = 4.7). Pentane was distilled off the filtrate under reduced pressure, and the remaining liquid was fractionally distilled under vacuum to yield $(CH_3)HNB(n\text{-}C_3H_7)_2$ and the unreacted excess of $(CH_3)_2NB(n\text{-}C_3H_7)_2$.

Results

The reaction of *N,N'*-dimethylurea (=DMU) with borazines according to eq 1 has previously been reported in a patent,[2] but no experimental details are available. It has now been observed that no reaction occurred when several borazines, $(\text{-RBNR'-})_3$ (R = C_2H_5, C_6H_5; R' = H, CH_3), were treated with the urea in heat-transfer media such as refluxing benzene, toluene, or xylene. However, heating of a neat mixture of the reactants to temperatures of 180–200 °C gave ready access to **1a** (R = C_2H_5, R' = H, R'' = CH_3) and **1b** (R = C_2H_5, R' = R'' = CH_3) originating from $(\text{-}C_2H_5BNR'\text{-})_3$ with R' = H and CH_3, respectively. When $(\text{-}C_6H_5BNCH_3\text{-})_3$ was heated with DMU to 200 °C, the mixture was not yet completely liquefied. Only at bath temperatures near 250 °C (boiling DMU) was a clear melt obtained and a reaction initiated. However, the resultant product consisted primarily of 1,3,5-triaza-2-boracyclohexane-4,6-dione (**2**) with R = C_6H_5 and R'' = CH_3. This result suggests that under the experimental conditions a condensation of DMU to *N,N',N''*-trimethylbiuret occurred first, and the latter reacted with the borazine to give the cited product. Compounds of type **2** have previously been obtained by transamination of bis(dimethylamino)organylboranes with biurets[7] and were also observed among the products of the condensation of dihaloorganylboranes with ureas.[3]

In the present work it was further found that bis(dimethylamino)organylboranes, $[(CH_3)_2N]_2BR$, react with DMU in a 1:1 molar ratio and with the release of only 1.5 equiv of dimethylamine to form diboron species. The process is independent of the ratio of the reactants. However, the products are most easily purified when an excess of the aminoborane is used. (No bis(ureido)boranes of the type $RB(NR'CONHR')_2$ could be obtained under the studied conditions, not even in the presence of a large excess of the urea). The resultant diboron species unexpectedly contained four-coordinate boron (as shown by ^{11}B NMR data), suggesting **4** as the structure of the species. This latter formulation is in complete consonance with all of the NMR data.



4a: R = R'' = CH_3
b: R = C_2H_5, R'' = CH_3
c: R = C_6H_5, R'' = CH_3

When a neat mixture of (dimethylamino)di-*n*-propylborane and DMU was refluxed (for 1–2 days) with an excess of the aminoborane as solvent, essentially quantitative conversion of DMU to *N,N,N'*-trimethylurea (=TMU) was observed in addition to the formation of (methylamino)di-*n*-propylborane. (Dimethylamino)diethylborane[11] did not react with DMU under analogous conditions (ca. 125 °C). However, with boiling xylene as solvent (ca. 140 °C) a reaction occurred that resulted again in an essentially quantitative conversion of DMU to TMU and of (dimethylamino)diethylborane to (methylamino)diethylborane within a period of 1 day. On refluxing of (the higher boiling) (dimethylamino)diphenylborane with DMU, a reaction occurred within a period of 15 h to again yield TMU and (methylamino)diphenylborane.

These observations illustrate that displacement of the dimethylamino groups of (dimethylamino)diorganylboranes by DMU in a transamination reaction does not occur readily. Rather, under the conditions used, DMU appears to decompose to methyl isocyanate and methylamine. Subsequently, methylamine exchanges with the dimethylamino group of the borane, and the generated dimethylamine interacts with the isocyanate to yield TMU. Indeed, an intermediate decomposition of *N,N'*-diorganylureas in the reaction with haloboranes has been noted earlier,[3] and displacement of dialkylamino groups of (dialkylamino)diorganylboranes by methylamine has been described as an exothermic reaction.[12]

In contrast, equimolar amounts of tris(dialkylamino)boranes, $B(NR'_2)_3$ (R' = CH_3, C_2H_5), and DMU have been reported to react in boiling xylene to give species of type **3** (with R = NR'_2 where R' = CH_3, C_2H_5).[4] Apparently, this latter reaction proceeds via the intermediate formation of the carbodiimide $CH_3N{=}C{=}NCH_3$ and the diboroxane (=diboryl oxide) $[(R'_2N)_2B]_2O$ (under release of 2 molar equiv of R'_2NH); the diboroxane then seems to react with a second DMU molecule in a transamination to yield a cyclic product of type **3**. In view of the observation that aminoboranes tended to react with DMU to form at least one $BNCH_3CONCH_3B$ unit, tris(dimethylamino)borane[13] was reacted with DMU in a 2:3 molar ratio in refluxing toluene (24 h). A glassy polymerlike material was obtained, the ^{11}B NMR spectrum of which showed at least four distinct resonance signals centered near 0 ppm (maxima at 2.4, –0.1, –1.0, and –1.4 ppm). The ^1H NMR spectrum of this product was inconclusive, and the 70-eV mass spectrum exhibited peaks up to m/z 572. This material was not further investigated.

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Synthesis and Characterization of the Organozirconium and Organohafnium Complexes $[(\eta^5\text{-}C_5Me_5)MCl]_3O(OH)_3Cl$ and $[(\eta^5\text{-}C_5Me_5)MCl]_3O(OH)_4$

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We recently reported a synthesis of the tetrahedral $(Cp^*Ti)_4O_6$ molecule ($Cp^* = \eta^5\text{-}C_5Me_5$) by base-assisted hydrolysis of Cp^*TiCl_3.[1] In an attempt to prepare similar Cp*Zr and Cp*Hf cage compounds, we have hydrolyzed Cp^*ZrCl_3 and Cp^*HfCl_3 in the presence of triethylamine. Unlike the titanium system, the zirconium and hafnium systems fail to yield cage compounds, generating instead trimeric species containing not only Cp* and oxo groups but also hydroxide and chloride ligands (see Scheme I). A preliminary account of the zirconium system has already appeared.[2] We provide here a full report of the synthesis, characterization, and solution stabilities of the four new complexes that have been prepared: $(Cp^*ZrCl)_3O(OH)_3Cl$ (**1**), $(Cp^*HfCl)_3O(OH)_3Cl$ (**2**), $(Cp^*ZrCl)_3O(OH)_4$ (**3**), and $(Cp^*HfCl)_3O(OH)_4$ (**4**).

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Experimental Section

Reagents, Solvents, and General Procedures. Pentamethylcyclopentadiene was prepared by a literature method.[3] Solutions of *tert*-butyllithium (Aldrich), 1.7 M in pentane, were used as received without further purification. Triethylamine (J. T. Baker) was distilled from sodium metal and stored over sodium metal pieces. Both $ZrCl_4$ and $HfCl_4$ (Cerac) were sublimed, at 170 and 190 °C, respectively, at 5 × 10^{-4} mmHg immediately prior to use. (Pentamethylcyclopentadienyl)zirconium and (pentamethylcyclopentadienyl)hafnium trichlorides were prepared by using a literature procedure[4] but heating the reaction solution to 70 °C for 8 h.

Pentane (Fisher), toluene (Fisher), and tetrahydrofuran (Mallinckrodt) were dried over sodium/potassium alloy, sodium metal, and sodium benzophenone ketyl, respectively, and were freshly distilled prior to use. Deuteriochloroform (Aldrich) was distilled from CaH_2 and stored under a nitrogen atmosphere over activated 4-Å molecular sieves. Molecular sieves were activated at 350 °C for 48 h and were stored in tightly sealed containers.

All reactions and reagents other than pentamethylcyclopentadiene were routinely handled under a dry nitrogen atmosphere in Schlenkware or in a drybox. The nitrogen was deoxygenated and dried by passing it throught a column of BASF oxygen-scavenging catalyst and then through a second column of activated 4-Å molecular sieves (Linde).

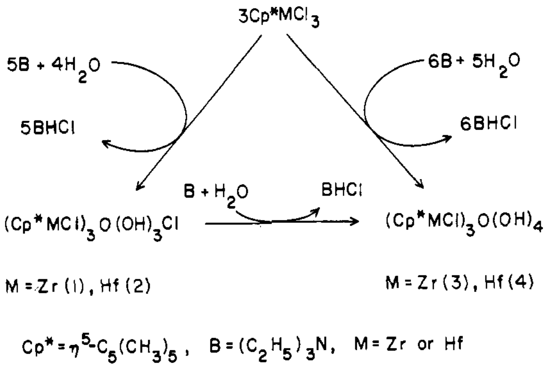
Analytical Procedures. Elemental analyses were performed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Infrared spectra were measured from mineral oil (Nujol) mulls prepared under a nitrogen atmosphere between KBr or CsI plates on a Perkin-Elmer 1330 spectrophotometer. The spectra were referenced to the 1028-cm^{-1} bands of a 0.05 mm thick polystyrene film.

Proton and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 and 75.5 MHz, respectively, on a General Electric QE-300 NMR spectrometer equipped with a deuterium lock. All ^1H NMR chemical shift values were internally referenced to tetramethylsilane. All $^{13}C\{^1H\}$ NMR chemical shift values were referenced to the central peak of the $CDCl_3$ triplet at 77.0 ppm.

Preparation of $[(\eta^5\text{-}C_5Me_2)ZrCl]_3O(OH)_3Cl{\cdot}C_7H_8$. (Pentamethylcyclopentadienyl)zirconium trichloride (1.00 g, 3.01 × 10^{-3} mol) was dissolved in 50 mL of tetrahydrofuran. Triethylamine (0.85 mL, 6.12 × 10^{-3} mol) and deionized water (0.54 mL, 3.01 × 10^{-3} mol) were added to 50 mL of tetrahydrofuran and transferred via cannula to the reaction flask. A white precipitate, $(CH_2CH_3)_3NHCl$, formed during the addition. The reaction solution was stirred for 4 h, filtered from the white precipitate, and allowed to sit at 22 °C overnight. The solution was again filtered from the small amount of $(CH_2CH_3)_3NHCl$ that had precipitated, and the tetrahydrofuran was removed under vacuum. The remaining solid was washed with 50 mL of pentane, and the washings were filtered into a second Schlenk flask. The pentane was removed under vacuum, the remaining white solids were washed with 20 mL of pentane, and the wash was discarded. The combined product was recrystallized by dissolving it in 40 mL of dry toluene, filtering the solution, and reducing the volume to 7 mL. Needle-shaped crystals of $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_3Cl{\cdot}C_7H_8$ (0.54 g, 5.51 × 10^{-4} mol, 55% yield) formed on cooling the solution to −20 °C for 10 h. Two recrystallizations were necessary to obtain analytically pure material. Anal. Calcd for $C_{37}H_{56}Zr_3Cl_4O_4$: C, 45.33; H, 5.76; Zr, 27.92; Cl, 14.46. Found: C, 45.52; H, 5.73; Zr, 27.97; Cl, 14.37. IR (Nujol; 900–500 cm^{-1}): 805 (w), 773 (m), 728 (s), 695 (w), 642 (s), 610 (m), 592 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 0.01 M, 17 °C): $\eta^5\text{-}C_5(CH_3)_5$, δ 2.07 (15 H), 2.00 (15 H), 1.97 (15 H); OH, δ 3.92 (d, 1 H), 3.52 (1 H), 2.78 (d, 1 H). ^1H NMR (C_6D_6, 0.01 M, 17 °C): $\eta^5\text{-}C_5(CH_3)_5$, δ 2.04 (15 H), 1.97 (15 H), 1.81 (15 H); OH, δ 4.38 (d, 1 H), 3.44 (1 H), 2.83 (d, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0.05 M, 17 °C): $\eta^5\text{-}C_5(CH_3)_5$, δ 125.93, 123.70, 123.24; $\eta^5\text{-}C_5(CH_3)_5$, δ 12.11, 11.85, 11.27; C_7H_8, δ 129.00, 128.20, 125.29. ^1H and $^{13}C\{^1H\}$ NMR data for **1** recrystallized from 1,2-$C_2H_4Cl_2$ are identical with that shown above.

Preparation of $[(\eta^5\text{-}C_5Me_5)HfCl]_3O(OH)_3Cl{\cdot}C_7H_8$. This compound was prepared by using the procedures and stoichiometries described above for its zirconium analogue, but in lower yield (35%). (Pentamethylcyclopentadienyl)hafnium trichloride (1.00 g, 2.38 × 10^{-3} mol) was dissolved in 50 mL of tetrahydrofuran. Triethylamine (0.66 mL, 4.76 × 10^{-3} mol) and deionized water (0.43 mL, 2.39 × 10^{-3} mol) were added to 50 mL of tetrahydrofuran and transferred via cannula to the reaction solution. Anal. Calcd for $C_{37}H_{56}Hf_3Cl_4O_4$: C, 35.78; H, 4.54; Hf, 43.11; Cl, 11.42. Found: C, 35.67; H, 4.61; Hf, 42.97; Cl, 11.34. IR (Nujol; 900–550 cm^{-1}): 812 (s), 800 (s), 760 (m, br), 730 (s), 695 (w), 655 (vs), 620 (m), 600 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 0.01 M, 17 °C): $\eta^5\text{-}C_5(CH_3)_5$, δ 2.12 (15 H), 2.05 (15 H), 2.02 (15 H); OH, δ 3.97 (d, 1 H), 3.33 (1 H), 2.86 (d, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0.05 M, 17 °C): $\eta^5\text{-}C_5(CH_3)_5$, δ 123.22, 121.44, 121.15; $\eta^5\text{-}C_5(CH_3)_5$, δ 11.79, 11.63, 11.04; C_7H_8, δ 129.01, 128.20, 125.29.

Scheme I



Preparation of $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4{\cdot}2THF$. (Pentamethylcyclopentadienyl)zirconium trichloride (1.00 g, 3.01 × 10^{-3} mol) was dissolved in 50 mL of tetrahydrofuran. Triethylamine (0.85 mL, 6.12 × 10^{-3} mol) and deionized water (0.11 mL, 6.11 × 10^{-3} mol) were added to 50 mL of tetrahydrofuran and transferred to the reaction solution via cannula. A white precipitate, $(CH_2CH_3)_3NHCl$, formed during the addition. The reaction solution was stirred for 3 h. The solution was then filtered from the white precipitate, and the solvent was removed under vacuum. The solid was washed with 50 mL and then 20 mL of pentane, and the washings were discarded. The product was recrystallized by dissolving it in 10 mL of tetrahydrofuran, filtering the solution, and reducing the volume to 5 mL. Clear, rectangular crystals formed on leaving the solution at 4 °C for 10 h. More crystals were obtained by reducing the remaining solvent volume to 2 mL and cooling to 4 °C for 10 h. The combined $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4{\cdot}2THF$ crystals were dried under vacuum (0.66 g, 6.52 × 10^{-4} mol, 65% yield). Crystals suitable for the single-crystal X-ray structure determination were obtained as described above except the flask was allowed to sit at 22 °C for 6–7 days. Anal. Calcd for $C_{38}H_{65}Zr_3Cl_3O_6$: C, 45.01; H, 6.46; Zr, 26.99; Cl, 10.49. Found: C, 44.89; H, 6.52; Zr, 27.01; Cl, 10.55. IR (Nujol; 1100–700 cm^{-1}): 1074 (m), 1056 (w), 1025 (w), 915 (w), 890 (w), 810 (w), 790 (w), 730 (s) cm^{-1}.

Preparation of $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4$. The solvate $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4{\cdot}2THF$ was recrystallized by dissolving 0.30 g in 20 mL of toluene, filtering the solution, and reducing the volume to 5 mL. Pentane (20 mL) was layered on top of the toluene solution and allowed to diffuse into the solution. A white powder, $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4$, precipitated from solution in several hours. Anal. Calcd for $C_{30}H_{48}Zr_3Cl_3O_5$: C, 41.43; H, 5.68. Found: C, 41.43; H, 5.65.

Preparation of $[(\eta^5\text{-}C_5Me_5)HfCl]_3O(OH)_4{\cdot}2THF$. This compound was prepared by using the procedures and stoichiometries described above for its zirconium' analogue. (Pentamethylcyclopentadienyl)hafnium trichloride (1.00 g, 2.38 × 10^{-3} mol) was dissolved in 50 mL of tetrahydrofuran. Triethylamine (0.66 mL, 4.76 × 10^{-3} mol) and deionized water (0.09 mL, 4.78 × 10^{-3} mol) were added to 50 mL of tetrahydrofuran and transferred via cannula to the reaction solution. Anal. Calcd for $C_{38}H_{65}Hf_3Cl_3O_6$: C, 35.78; H, 5.13; Hf, 41.97; Cl, 8.34. Found: C, 35.89; H, 5.15; Hf, 41.95; Cl, 8.39. IR (Nujol; 1100–700 cm^{-1}): 1075 (m), 1055 (s), 1030 (m), 919 (w), 895 (w), 845 (w), 816 (m), 760 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 0.01 M, 17 °C): $\eta^5\text{-}C_5(CH_3)_5$, δ 2.06 (30 H), 1.99 (15 H); OH, δ 3.72 (1 H), 3.21 (2 H), 3.14 (1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 0.05 M, 17 °C): $\eta^5\text{-}C_5(CH_5)_5$, δ 121.27, 120.59; $\eta^5\text{-}C_5(CH_5)_5$, δ 11.66, 11.11.

Preparation of $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4{\cdot}2THF$ from $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_3Cl{\cdot}C_7H_8$. The toluene solvate $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_3Cl{\cdot}C_7H_8$ (0.14 g, 1.43 × 10^{-4} mol) was dissolved in 25 mL of tetrahydrofuran. Triethylamine (20 μL, 1.43 × 10^{-4} mol) and deionized water (2.6 μL, 1.43 × 10^{-4} mol) were added to 25 mL of tetrahydrofuran and transferred via cannula to the reaction flask. The reaction solution was stirred at 22 °C for 1.5 h. The solution was filtered away from the white precipitate, $(CH_2CH_3)_3NHCl$, and the solvent was removed under vacuum. The remaining white solid was washed with 10 mL of pentane and the wash was discarded. The product was recrystallized by dissolving it in 3 mL of tetrahydrofuran, reducing the solvent volume to 1.5 mL,

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Table I. Atomic Coordinates for Non-Hydrogen Atoms and Hydroxyl Hydrogen Atoms in Crystalline $[(\eta^5\text{-}C_5Me_5)ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3\cdot 2OC_4H_8$[a]

Non-Hydrogen Atoms

atom type[b]	fractional coordinates			equiv isotropic thermal param,[c] B, Å^2
	10^4x	10^4y	10^4z	
		Metal Complex		
Zr$_1$	1879.4 (5)	3047.6 (3)	1517.0 (1)	2.61 (2)
Zr$_2$	1104.6 (5)	3081.7 (4)	845.9 (1)	2.99 (2)
Zr$_3$	−733.7 (5)	3630.8 (4)	1340.5 (1)	2.88 (2)
Cl$_1$	3190 (2)	4174 (1)	1613 (1)	4.6 (1)
Cl$_2$	607 (3)	1733 (1)	714 (1)	6.7 (1)
Cl$_3$	−794 (2)	5073 (1)	1350 (1)	5.2 (1)
O$_{12}$	2624 (4)	2812 (3)	1102 (1)	3.3 (1)
O$_{13}$	358 (4)	3552 (2)	1722 (1)	3.1 (1)
O$_{23}$	−635 (4)	3561 (3)	875 (1)	3.8 (1)
O$_{123}$	1181 (4)	3950 (2)	1194 (1)	2.8 (1)
O$_x$	412 (4)	2699 (2)	1266 (1)	2.8 (1)
C$_{11}$	1711 (6)	1726 (4)	1760 (1)	3.2 (2)
C$_{12}$	2689 (6)	1684 (4)	1578 (2)	3.7 (2)
C$_{13}$	3569 (6)	2196 (4)	1688 (2)	3.8 (2)
C$_{14}$	3120 (7)	2539 (4)	1941 (2)	4.3 (2)
C$_{15}$	1970 (7)	2256 (4)	1982 (1)	3.7 (2)
C$_{m11}$	630 (7)	1231 (4)	1742 (2)	4.8 (2)
C$_{m12}$	2810 (8)	1146 (4)	1327 (2)	5.2 (2)
C$_{m13}$	4799 (7)	2302 (5)	1569 (2)	6.1 (3)
C$_{m14}$	3818 (9)	3037 (5)	2149 (2)	6.7 (3)
C$_{m15}$	1225 (9)	2439 (5)	2245 (2)	5.8 (3)
C$_{21}$	1760 (7)	3025 (5)	314 (2)	4.9 (2)
C$_{22}$	2765 (7)	3228 (5)	474 (2)	4.5 (2)
C$_{23}$	2569 (7)	3956 (5)	596 (1)	4.5 (2)
C$_{24}$	1426 (7)	4206 (4)	513 (2)	4.5 (2)
C$_{25}$	936 (7)	3633 (5)	340 (1)	4.3 (2)
C$_{m21}$	1648 (9)	2313 (6)	116 (2)	7.0 (3)
C$_{m22}$	3875 (8)	2755 (7)	502 (2)	7.2 (3)
C$_{m23}$	3458 (8)	4435 (6)	767 (2)	7.0 (3)
C$_{m24}$	898 (10)	4994 (5)	577 (2)	6.9 (3)
C$_{m25}$	−227 (8)	3674 (6)	181 (2)	6.7 (3)
C$_{31}$	−2288 (6)	2586 (4)	1402 (2)	4.1 (2)
C$_{32}$	−2751 (6)	3097 (4)	1194 (2)	4.3 (2)
C$_{33}$	−2993 (6)	3803 (4)	1332 (2)	4.2 (2)
C$_{34}$	−2667 (6)	3739 (4)	1623 (2)	4.7 (2)
C$_{35}$	−2239 (6)	2977 (5)	1669 (2)	4.3 (2)
C$_{m31}$	−2009 (7)	1736 (4)	1341 (2)	6.0 (3)
C$_{m32}$	−3038 (8)	2878 (6)	892 (2)	6.2 (3)
C$_{m33}$	−3609 (8)	4491 (5)	1197 (2)	7.0 (3)
C$_{m34}$	−2848 (8)	4326 (6)	1856 (2)	7.7 (4)
C$_{m35}$	−1951 (8)	2638 (6)	1964 (2)	6.7 (3)
		Solvate Molecule 1		
O$_{s1}$	−2358 (8)	4763 (4)	516 (2)	10.1 (3)
C$_{s1}$	−3152 (11)	4684 (7)	273 (3)	11.9 (5)
C$_{s2}$	−3549 (15)	5482 (7)	186 (3)	12.5 (7)
C$_{s3}$	−2784 (17)	5982 (7)	348 (3)	13.6 (7)
C$_{s4}$	−2408 (15)	5566 (6)	596 (3)	11.9 (6)
		Solvate Molecule 2		
O$_{s2}$	456 (9)	4620 (4)	2158 (1)	11.9 (4)
C$_{s5}$	899 (20)	5373 (8)	2087 (3)	23.7 (12)
C$_{s6}$	876 (19)	5790 (7)	2326 (3)	23.8 (12)
C$_{s7}$	165 (35)	5435 (9)	2485 (5)	28.5 (15)
C$_{s8}$	103 (18)	4644 (7)	2404 (3)	17.6 (9)

Hydroxyl Hydrogen Atoms

atom type[b]	fractional coordinates			isotropic thermal param, B,[d] Å^2
	10^3x	10^3y	10^3z	
H$_{12}$	321 (7)	261 (4)	102 (2)	8 (2)
H$_{13}$	34 (5)	388 (3)	182 (1)	3 (1)
H$_{23}$	−90 (7)	379 (4)	76 (1)	6 (2)
H$_{123}$	159 (5)	426 (3)	119 (1)	3 (1)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 1–3. [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor. [d] For these hydrogen atoms, the isotropic thermal parameter given was actually refined.

and cooling it to 4 °C for 10 h. The remaining solution was removed from $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4\cdot 2THF$ (0.94 g, 9.28×10^{-5} mol, 65% yield), and the solid was dried under vacuum. The product was identified by infrared and ^1H NMR spectroscopy.

Preparation of $[(\eta^5\text{-}C_5Me_5)HfCl]_3O(OH)_4\cdot 2THF$ from $[(\eta^5\text{-}C_5Me_5)HfCl]_3O(OH)_3Cl\cdot C_7H_8$. The toluene solvate $[(\eta^5\text{-}C_5Me_5)HfCl]_3O(OH)_3Cl\cdot C_7H_8$ (0.30 g, 2.42×10^{-4} mol) was dissolved in 30 mL of tetrahydrofuran. Triethylamine (34 μL, 2.42×10^{-4} mol) and deionized water (4.5 μL, 2.42×10^{-4} mol) were added to 50 mL of tetrahydrofuran and transferred via cannula to the reaction flask. The reaction solution was stirred for 1.5 h at 22 °C. The crude product was purified by using the procedure just described for the analogous zirconium system to give $[(\eta^5\text{-}C_5Me_5)HfCl]_3O(OH)_4\cdot 2THF$ (0.22 g, 1.73×10^{-4} mol, 71.5%). The product was identified by infrared and ^1H NMR spectroscopy.

X-ray Crystallography Study of $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4\cdot 2THF$.[5] Single crystals of $C_{30}H_{49}O_5Cl_3Zr_3\cdot 2C_4H_8O$ were grown from tetrahydrofuran as described above. They were, at 20 ± 1 °C, orthorhombic, space group *Pbca*-D_{2h}^{15} (No. 61),[6] with $a = 11.320$ (3) Å, $b = 17.212$ (3) Å, $c = 46.253$ (8) Å, and $Z = 8$ (μ_a(Mo K$\bar{\alpha}$)[7] = 0.89 mm^{-1}; d(calcd) = 1.495 g cm^{-3}).

Diffracted intensity measurements (8246 reflections having 2θ(Mo K$\bar{\alpha}$) < 50.7°) were made in two concentric shells of 2θ on a Nicolet P$_1$ autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation ($\lambda = 0.71073$ Å) for a rectangular-parallelepiped-shaped specimen with dimensions of 0.52 × 0.60 × 0.67 mm. A detailed description of the data collection and reduction procedures and relevant equations employed during structure solution and refinement are given elsewhere;[5,8] the fixed scan rates for data collection in the present study were 8 and 3° min^{-1}.

The structure was solved by using the "heavy-atom technique", and the resulting structural parameters were refined to convergence (R_1(unweighted, based on F)[5,8] = 0.046 and R_2(weighted, based on F)[5,8] = 0.052 for 5036 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 50.7° and $I > 3\sigma(I)$) by using counterweighted[5] cascade block-diagonal least-squares techniques. These refinement cycles employed anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms of the methyl groups, which were refined as rigid rotors with idealized sp^3 hybridization and a C–H bond length of 0.96 Å. The four hydroxyl hydrogens were located from a difference Fourier synthesis and refined as independent isotropic atoms while methylene hydrogens of the THF solvent molecules were fixed as isotropic atoms at idealized positions.

Final atomic coordinates for all non-hydrogen atoms and the four hydroxyl hydrogen atoms are given in Table I. Anisotropic thermal parameters for non-hydrogen atoms, final atomic coordinates for methyl and methylene hydrogen atoms, detailed bond lengths and angles of the coordination groups, ligands, and solvent molecules, and hydrogen-bonding parameters are given with standard deviations in Tables II–VII.[5] Selected bond lengths and angles of interest are given in Table VIII.

Results and Discussion

Synthesis of complexes **1**–**4** from Cp*MCl$_3$ were optimized to 35–65% yield by following the stoichiometries given in Scheme I as guidelines but using a deficit of water for **1** and **2** and an excess of water for **3** and **4**. Conversions of compounds **1** and **2** to compounds **3** and **4** proceeded in greater than 65% yield using the stoichiometry indicated in Scheme I. All four compounds yielded satisfactory carbon, hydrogen, chlorine, and metal analyses.

X-ray structural analysis of crystalline (Cp*ZrCl)$_3$O(OH)$_4\cdot$2THF obtained from THF solution revealed the presence of a cluster that contains a nearly equilateral triangular core of three Zr atoms capped above and below by μ_3-O and μ_3-OH groups and symmetrically edge-bridged by three μ_2-OH groups that are coplanar with the three Zr atoms to within 0.07 Å (see Figure 1). The *pseudo*octahedral coordination sphere at each Zr center is completed by a terminal Cl ligand and η^5-C$_5$Me$_5$ ligand. Two chloride ligands and one η^5-C$_5$Me$_5$ ligand lie on one side of the (-Zr–O–)$_3$ ring while the remaining Cl and two η^5-C$_5$Me$_5$ ligands lie on the other side to give a molecule that approximates C_s-m symmetry: Zr$_2$, Cl$_2$, O$_x$, O$_{123}$, O$_{13}$, and Cp$_2$[9] are coplanar to within

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[5] See paragraph at the end of the paper regarding supplementary material.

[6] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1969; Vol. I, p 150.

[7] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 55–66.

[8] Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for Crystalline $[(\eta^5\text{-}C_5Me_5)ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3\cdot 2OC_4H_8$[a,b]

	Bond Lengths		
Zr_1–Cl_1	2.482 (2)	Zr_1–O_x	2.113 (4)
Zr_2–Cl_2	2.466 (2)	Zr_3–O_x	2.092 (4)
Zr_3–Cl_3	2.484 (2)	Zr_2–O_x	2.196 (4)
Zr_1–O_{12}	2.134 (4)	Zr_1–Cp_1[c]	2.249 (-)
Zr_2–O_{12}	2.140 (4)	Zr_2–Cp_2[c]	2.241 (-)
Zr_1–O_{13}	2.149 (4)	Zr_3–Cp_3[c]	2.255 (-)
Zr_3–O_{13}	2.159 (4)	O_{12}–H_{12}	0.84 (8)
Zr_2–O_{23}	2.140 (4)	O_{13}–H_{13}	0.73 (5)
Zr_3–O_{23}	2.158 (4)	O_{23}–H_{23}	0.73 (7)
Zr_1–O_{123}	2.296 (4)	O_{123}–H_{123}	0.71 (5)
Zr_3–O_{123}	2.336 (4)		
Zr_2–O_{123}	2.198 (4)		
	Bond Angles		
$Cp_1Zr_1Cl_1$[c]	104.9 (-)	$Zr_1O_{12}H_{12}$	142 (5)
$Cp_2Zr_2Cl_2$[c]	105.6 (-)	$Zr_2O_{12}H_{12}$	119 (5)
$Cp_3Zr_3Cl_3$[c]	105.6 (-)	$Zr_1O_{13}H_{13}$	128 (4)
$Zr_1O_xZr_2$	96.9 (2)	$Zr_3O_{13}H_{13}$	117 (4)
$Zr_1O_xZr_3$	100.3 (2)	$Zr_2O_{23}H_{23}$	123 (5)
$Zr_2O_xZr_3$	97.9 (2)	$Zr_3O_{23}H_{23}$	132 (5)
$Zr_1O_{123}Zr_2$	91.7 (1)	$Zr_1O_{123}H_{123}$	108 (4)
$Zr_1O_{123}Zr_3$	88.4 (1)	$Zr_2O_{123}H_{123}$	121 (4)
$Zr_2O_{123}Zr_3$	90.9 (1)	$Zr_3O_{123}H_{123}$	143 (5)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1 and Tables I–III. [c] The symbols Cp_1, Cp_2, and Cp_3 are used to represent the centers of gravity for the five-membered rings of the C_5Me_5 ligands bonded to Zr_1, Zr_2, and Zr_3, respectively.

0.03 Å and define a *pseudo* mirror plane. The two THF molecules are hydrogen-bonded to two of the μ_2-OH hydrogens. The Zr–Cl, Zr–C, Zr–(μ_2-OH), ring C–C, and ring-to-methyl C–C bond lengths are typical[10] and average[11] 2.477 Å (2, 8, 11, 3), 2.545 Å (7, 16, 45, 15), 2.147 Å (4, 9, 13, 6), 1.404 Å (11, 8, 20, 15), and 1.508 Å (11, 11, 26, 15), respectively. The Zr–O bonds to the μ_3-O and μ_3-OH ligands average[11] 2.134 Å (4, 42, 62, 3) and 2.277 Å (4, 52, 79, 3), respectively, and are at least 0.083 Å shorter when trans to a Cl ligand than when trans to a η^5-C_5Me_5 ligand (see Table I). A similar lengthening of Zr–(μ_2-OH) bonds trans to a cyclopentadienyl ligand is observed in $[(\eta^5\text{-}C_5H_5)Zr(\kappa^2\text{-}NO_3\text{-}O)_2(\mu_2\text{-}OH)]_2$.[12] The trans Cp[9]–Zr–O angles average 173.5° (-, 6, 8, 3).

The $M_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3$ (M = Zr and R = H) core of compound **3** (see Figure 1) has been previously observed in $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6$ (R = $CH(CH_3)_2$, $CH_2C(CH_3)_3$)[12] and in $U_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6$ (R = $C(CH_3)_3$).[13] An analogous but distorted zirconium–sulfur core is observed in $Zr_3(\mu_3\text{-}S)(\mu_3\text{-}SR)(\mu_2\text{-}SR)_3(SR)_6$ (R = $C(CH_3)_3$).[14]

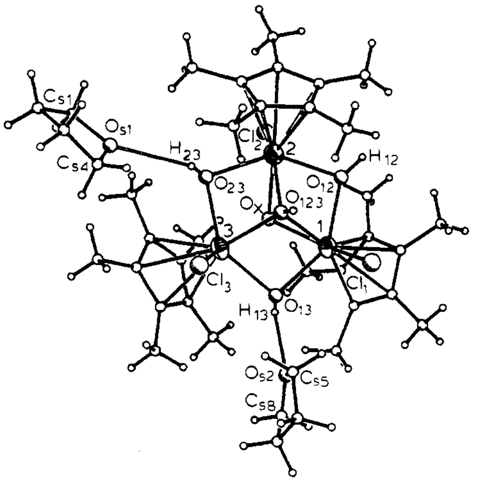
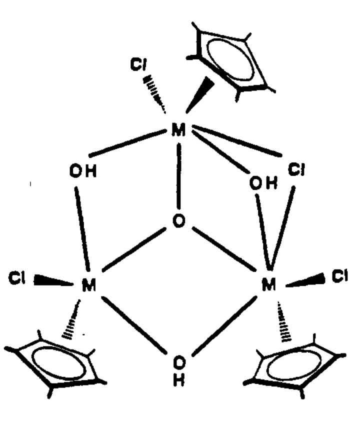


Figure 1. Perspective ORTEP drawing of the solid-state structure for the $[(\eta^5\text{-}C_5Me_5)ZrCl]_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3$ molecule as a THF solvate. The Zr atoms are labeled 1–3 and are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Chlorine and oxygen atoms are represented by large- and medium-sized shaded spheres while carbon and hydrogen atoms are represented by medium-sized and small open spheres, respectively. The μ_3-O and μ_3-OH ligands are labeled O_x and O_{123}, respectively. The μ_2-OH ligands are labeled O_{12}, O_{23}, and O_{13}; the hydrogen atoms bonded to O_{13} and O_{23} are hydrogen-bonded to THF oxygen atoms O_{s2} and O_{s1}, respectively.

The gross $(Cp^*M)_3(\mu_3\text{-}L)_2(\mu_2\text{-}L)_3L_3$ geometry observed for compound **3** is also adopted by the $[(Cp^*Ta)_3(\mu_3\text{-}O)_2(\mu_2\text{-}O)_3Cl(H_2O)]^+$ cation.[15]

Solution ^1H NMR spectra of compound **3** are complex and inconsistent with the simple C_s molecular structure derived from the crystal structure. This complication might arise from either structural degradation or aggregation by hydrogen bond formation. Compound **4**, however, displays simple ^1H and $^{13}C\{^1H\}$ solution NMR spectra, described in the Experimental Section, that are consistent with the C_s structure observed for compound **3** in its crystalline THF solvate (see Figure 1). Compounds **1** and **2** both display three types of Cp* and OH ligands in their $^{13}C\{^1H\}$ and ^1H solution NMR spectra (see Experimental Section) consistent with C_1-$(Cp^*MCl)_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)(\mu_2\text{-}OH)_3$ structures derived from the C_s structure observed for $(Cp^*TaCl)_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)(\mu_2\text{-}O)_3$[15] by shifting the μ_2-Cl ligand to the alternative bridging position:



Acknowledgment. We acknowledge the National Science Foundation for partial support of this work. L.M.B. was supported by the U.S. Department of Energy, Division of Materials Science, under Contract De-AC02-76ER01198.

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(9) The symbols Cp_1, Cp_2, and Cp_3 refer to the centers of gravity of the five-membered rings of the C_5Me_5 ligands bonded to Zr_1, Zr_2, and Zr_3, respectively.

(10) For comparisons, see the following references. (a) $(\eta^5\text{-}C_5Me_5)_2ZrCl(OH)$ and $(\eta^5\text{-}C_5Me_5)_2Zr(OH)_2$: Bortolin, R.; Patel, V.; Munday, I.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 456. (b) $[(\eta^5\text{-}C_5Me_5)_2ZrN_2]_2N_2$: Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351. (c) $[Zr_4(\mu_2\text{-}OH)_8(H_2O)_{16}]^{8+}$: Mak, T. C. W. *Can. J. Chem.* **1968**, *46*, 3491. (d) $[(CpZr)_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}C_6H_5CO_2)_3]^+$: Thewalt, U.; Döppert, K.; Lasser, W. *J. Organomet. Chem.* **1986**, *308*, 303. (e) $Zr_2(\mu_2\text{-}OH)_2(SO_4)_3(H_2O)_4$: McWhan, D. B.; Lundgren, G. *Inorg. Chem.* **1966**, *5*, 284. $[CpZr(NO_3)_2(\mu_2\text{-}OH)]_2$: Lasser, W.; Thewalt, U. *J. Organomet. Chem.* **1984**, *275*, 63.

(11) The first number in parentheses following an average value of a bond length, bond angle, or atom displacement is the root-mean-square estimated standard deviation of an individual value. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

(12) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 5967.

(13) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *95*, 207.

(14) Coucouvanis, D.; Hadjikyriacou, A.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1224.

(15) Jernakoff, P.; de Meric de Bellefon, C.; Geoffroy, G. L.; Reingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362.

Registry No. $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_3Cl$, 118318-67-5; $[(\eta^5\text{-}C_5Me_5)ZrCl_3]$, 75181-07-6; $[(\eta^5\text{-}C_5Me_5)HfCl]_3O(OH_3)Cl$, 118318-68-6; $[(\eta^5\text{-}C_5Me_5)HfCl_3]$, 75181-08-7; $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4$, 118318-69-7; $[(\eta^5\text{-}C_5Me_5)HfCl]_3O(OH)_4$, 118318-70-0; $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4 \cdot 2THF$, 118354-08-8.

Supplementary Material Available: A crystal structure analysis report, Table II (anisotropic thermal parameters), Table III (atomic coordinates for hydrogen atoms), Table IV (bond lengths and angles involving coordination groups), Table V (bond lengths and angles involving non-hydrogen atoms in C_5Me_5 ligands), Table VI (bond lengths and angles involving non-hydrogen atoms in THF molecules of crystallization), Table VII (hydrogen-bonding parameters), Figure 2 (ORTEP drawing showing labeling scheme for $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4$ molecules), and Figure 3 (ORTEP drawing of THF molecules of crystallization) (16 pages); structure factor tables for the X-ray structural study of $[(\eta^5\text{-}C_5Me_5)ZrCl]_3O(OH)_4 \cdot 2OC_4H_8$ (22 pages). Ordering information is given on any current masthead page.

Additions and Corrections

1988, Volume 27

Roger D. Willett,* Marcus R. Bond, W. G. Haije, O. P. M. Soonieus, and W. J. A. Maaskant: Crystal Structures of Three Phases of Tetramethylammonium Trichlorocuprate(II) (TMCuC).

Pages 614–620. The space group of the intermediate temperature phase was incorrectly reported as $P\bar{1}$ (Marsh, R. E. *Inorg. Chem.* **1988**, *27*, 2902–2903). We have refined the crystal structure in the correct space group, $C2/m$ (structure factors of equivalent reflections from the original half-sphere of data were averaged, $R_{\text{merge}} = 0.0553$; 1592 total reflections; 872 unique reflections, 650 with $|F| > 3\sigma(F)$). Final refinement of 83 least-squares parameters gave $R = 0.0694$ and $R_w = 0.0766$. Coordinates for all atoms are within three standard deviations of the symmetrized coordinates reported by Marsh. Bond lengths and angles are likewise within three standard deviations of the symmetrized reported values; hence, the chemical description of the structure is essentially unchanged. Two significant differences arise on refinement in the higher symmetry space group: (1) Disorder of the Jahn–Teller axis about Cu(1) is now constrained by symmetry to occupy both orientations equally, instead of the 54.0 (2)% probability for one orientation originally reported. (2) Thermal parameters for several carbon atoms increased significantly, implying the cation might be more disordered than previously thought.

Supplementary Material Available: Corrected listings of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom positions (3 pages); a corrected table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.—Marcus R. Bond

Dominique Luneau, Jean-Michel Savariault, and Jean-Pierre Tuchagues*: Synthesis, Structure, and Magnetic Properties of a Dodecamanganese(II) Complex Afforded by a Binucleating Acyclic N_2O_3 Schiff Base.

Page 3917. In the fourth paragraph of the magnetic susceptibility section, the second to last sentences should read as follows: Within the framework of this model, the experimental data are satisfactorily least-squares-fit with the parameters $J = -2.0$ cm^{-1}, $\Theta = 0.36$ K, and $g = 2.006$, which indicates that extended antiferromagnetic interactions are prevailing in this complex. However, as it does not seem totally appropriate to consider an infinite-chain hypothesis in the case of this spherical aggregate, the experimental magnetic susceptibility data were also least-squares-fit to the theoretical equation for an isotropic magnetic exchange interaction between two $S_1 = S_2 = {}^5/_2$ ions by employing the $H = -2JS_1S_2$ spin Hamiltonian.[22] The aim of this oversimplified approach was to ascertain the order of magnitude of the magnetic interactions operating in this aggregate. The lines in Figure 5 represent this fit, which affords the same Ginsberg standard error of estimate[8] (1.98×10^{-2}) as that obtained with a chain hypothesis. The parameters obtained from this fit are $J = -3.0$ cm^{-1} and $g = 1.91$; the $g = 1.91$ value is low compared to the $g = 2.01$ value measured from the X-band powder EPR spectra and to that obtained within the framework of the Heisenberg-chain hypothesis. However, these oversimplified approaches afford an estimate of the average value of the magnetic interactions operating in this aggregate. Reference 21 should read as follows: (a) Wagner, G. R.; Friedberg, S. A. *Phys. Lett.* **1964**, *9*, 11–13. (b) König, E.; Desai, V. P.; Kanellakopoulos, B.; Klenze, R. *Chem. Phys.* **1980**, *54*, 109.—Jean-Pierre Tuchagues