The common feature to isomers a, exo, and d, endo, is to have the propyl group *R* only in the vicinity of the nitrosyl ligand. On the other hand, it is likely that the six other isomers (Scheme XII) undergo steric hindrance between the propyl group and either the cyclopentadienyl ring or the triphenylgermyl moiety. The mechanism leading to this isomerization is not perfectly clear at the present time and does not seem to be just a rotation of the allylic ligand like that of cyclopentadienyl rings in ferrocene. Actually Faller et al.[22] have proposed an isomerization mechanism involving the decoordination of the η^3-allylic to an η^1-allylic ligand.

Conclusion

The reaction of anions $[(\eta^5\text{-}C_5H_5)(CO)(L)(M_{4B}Ph_3)M_T]^-$ with unsaturated iodides seems to be general, with some limitations however. Allyl iodides give the neutral σ-bonded square-pyramidal complexes in which the allyl and the group 4B metal ligands are trans to each other.

These complexes may undergo thermal reaction to η^2-allyl complexes via η^3-allyl ones. According to the nature of M_T and M_{4B} the η^1-, η^3-, or η^2-allylic complexes can be isolated. Nethertheless the reaction pathway seems to be the same in all cases, but the reaction can stop and give the η^3 intermediate.

σ complexes bearing ω-alkenyl ligands undergo thermal reaction to η^3-allylic ones, with isomerization of the chain. This structure is established unambiguously by an X-ray structure determination. Interestingly, among the possible isomers, the two having less steric hindrance are obtained.

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Registry No. 1, 89958-46-3; 2, 89958-47-4; 3, 89958-48-5; 4, 89975-08-6; 5, 89958-49-6; 6, 89958-50-9; 7, 89975-09-7; 8, 89958-51-0; 9, 89958-52-1; 10, 89958-53-2; a,*exo*-11, 89958-54-3; d,*endo*-11, 90025-74-4; a,*exo*-12, 89958-55-4; d,*endo*-12, 90129-08-1.

Supplementary Material Available: A table of vibrational thermal parameters (Table IX) and a listing of observed and calculated structure factors (Table X) (13 pages). Ordering information is given on any current masthead page.

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Preparation of Group 4A Complexes Containing Tri-*tert*-butylmethoxide (tritox), a Steric Cyclopentadienyl Equivalent

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Li(tritox), $((CH_3)_3C)_3COLi$, reacts stoichiometrically with MCl_4 (M = Zr, Ti) to form $(tritox)_2ZrCl_3{\cdot}Li(OEt_2)_2$ (**1**), $(tritox)_2MCl_2$ (M = Zr (**2**), Ti (**4**)), and $(tritox)TiCl_3$ (**5**). From $TiCl_3$ and Li(tritox) (1:2), a complex tentatively formulated as "$(tritox)_2TiCl$" (**3**) was obtained; **3** yielded the corresponding dichloride **4** upon treatment with CCl_4. Derivatization of the M(IV) chlorides with CH_3Li produced $(tritox)_2M(CH_3)_2$ (M = Zr (**6**), Ti (**7**)) and $(tritox)Ti(CH_3)_3$ (**8**). Controlled alcoholysis of $Zr(CH_2Ph)_4$, $Zr(CH_2C(CH_3)_3)_4$, and **6** with (tritox)H gave $(tritox)Zr(CH_2Ph)_3$ (**9**), $(tritox)Zr(CH_2C(CH_3)_3)_3$ (**10**), and $(tritox)_3ZrCH_3$ (**11**), respectively. An X-ray structure determination of **1** showed the tritox units equatorially disposed in this pseudo-tbp complex. Crystal data: monoclinic, $P2_1/c$, a = 12.946 (3) Å, b = 14.026 (3) Å, c = 26.257 (4) Å, β = 121.016 (12)°, Z = 4, and T = −75 °C. Standard refinement procedures yielded an R factor of 0.079 from 4346 data where $|F_o| \geq 3\sigma(|F_o|)$. The spatial resemblence of tritox to cyclopentadienyl (Cp) is discussed; the short Zr–O bonds (1.895 Å average) and near linear Zr–O–C ∠'s (169° average) of **1** also suggest that tritox may function as a five-electron donor, like Cp.

Introduction

An important challenge confronting the organometallic chemist concerns the synthesis of complexes that are coordinatively unsaturated, since this characteristic is necessary for observation of metal-centered reactivity.[1] One approach to this problem involves the use of both neutral and anionic ancillary ligands that sterically "saturate" a metal center that may remain coordinatively and electronically unsaturated. For example, by using bis(trimethylsilyl)amide, a number of workers have prepared low coordinate $M[N(Si(CH_3)_3)_2]_n$ complexes that span the periodic table.[2,3] In a similar fashion, sterically comparable phosphide ligands are currently being exploited.[4] Bulky neutral ligands, principally phosphines (PR_3, R = cyclohexyl, *tert*-butyl, etc.), have been used to prepare several

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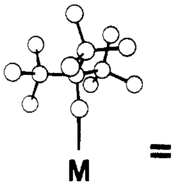
low coordinate group 6 and 8 complexes.[5] Both types of encumbering ligands suffer some drawbacks. Bulky phosphines at times may undergo substitution reactions by typical neutral substrates (i.e., CO, olefins, etc.), thus hampering their ability to function as ancillary ligands. Although amides and phosphides may not be easily displaced by neutral donors, they, unlike the phosphines, are best viewed as occupying a wedge of space and may pack together efficiently on a metal, thus impeding the path of small molecule substrates.

In an effort to combine the best properties of the aforementioned ligands, the application of the steric saturation theme to transition-metal alkoxide chemistry may be accomplished via the utilization of tri-*tert*-butylmethoxide[6] as an ancillary ligand. Recent notable advances in the chemistry of alkoxide-containing complexes lend credence to the application of this bulky ligand; the varied reactivity displayed by hexaalkoxydimolybdenum and -ditungsten complexes,[7] the acetylene metathesis capability of $(O\text{-}t\text{-}Bu)_3W{\equiv}C{-}R$ species,[8] and the development of potent Nb, Ta,[9] and W[10] olefin metathesis catalysts containing *tert*-butoxide and neopentoxide are convincing examples. Tri-*tert*-butyl methoxide (tritox) forms a steric cone[11] about a metal, similar to a bulky phosphine, yet is anionic and thus akin to bis(trimethylsilyl)amide. The cone angle of tritox (125°)[12] approaches that of cyclopentadienyl (Cp cone angle = 136°)[11,13] and models indicate that its methyl hydrogens overhang the oxygen in a manner sufficient to prevent the formation of alkoxide bridges that are prevalent for smaller RO^- ligands ($R = CH_3$, C_2H_5, etc.).[14] In view of the steric similarity to Cp (five-electron donor), the initial synthetic studies of tritox-containing complexes reported herein are modeled after known group 4 cyclopentadienyl species.[15]



= (tritox)M

$((CH_3)_3C)_3COM$

Synthetic Studies

The most straightforward route to alkoxy complexes is the displacement of halide by alkoxide.[16] The tritox reagent employed in these metathetical reactions is Li(tritox), prepared as a white crystalline solid in >90% yield via deprotonation of the parent alcohol (tritox)H[17] by *n*-butyllithium (eq 1).[18] Li(tritox) was shown to be far

$$\underset{\text{(tritox)H}}{((CH_3)_3C)_3COH} + n\text{-BuLi} \xrightarrow{\text{hexane}} \underset{\text{(tritox)Li}}{((CH_3)_3C)_3COLi} + C_4H_{10} \quad (1)$$

more versatile than either K(tritox) or BrMg(tritox), prepared via addition of $KCH_2C_6H_5$ or CH_3MgBr to (tritox)H, respectively, and was used exclusively.

Treatment of $ZrCl_4$ with 2 equiv of Li(tritox) in diethyl ether led to the isolation of white, crystalline $(tritox)_2ZrCl_3{\cdot}Li(OEt_2)_2$ (**1**) in high yield (80%) according to eq 2. The bound LiCl may be removed from the coordination sphere of **1** via addition of hexane, yielding the dichloride $(tritox)_2ZrCl_2$ (**2**) quantitatively (eq 3). Although easily isolable, **2** decomposes in benzene solution over a 24-h period at 25 °C[19] and must be stored as a solid under nitrogen at −20 °C. With the hope of obtaining a dimer analogous to the known diamagnetic $[Cp_2TiCl]_2$ complex,[20] $TiCl_3$ was treated with 2 equiv of Li(tritox) in diethyl ether (eq 4) over a 3.5-day period. Contrary to expectations, the

$$2Li(tritox) + ZrCl_4 \xrightarrow{Et_2O} \underset{\mathbf{1}}{(tritox)_2ZrCl_3{\cdot}Li(OEt_2)_2} + 2LiCl \quad (2)$$

$$\mathbf{1} \xrightarrow{\text{hexane}} \underset{\mathbf{2}}{(tritox)_2ZrCl_2} + LiCl + 2Et_2O \quad (3)$$

$$2Li(tritox) + TiCl_3 \xrightarrow{Et_2O} \underset{\mathbf{3}}{\text{“}(tritox)_2TiCl\text{”}} + 2LiCl \quad (4)$$

pale mint green precipitate **3** that was isolated from hexane solution exhibited a clean single-line EPR spectrum at $g = 1.952$ (2) accompanied by ^{47}Ti ($I = {}^5/_2$) and ^{49}Ti ($I = {}^7/_2$) satellites (a(Ti) = 13 G) and is thus tentatively formulated as “$(tritox)_2TiCl$” (**3**).[21] Surprisingly, no indication of

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trimethyl phosphite binding was observed by EPR, despite a 100-fold excess of the added ligand.[22] Reactivity complimentary to $[\text{Cp}_2\text{TiCl}]_2$ is displayed by "(tritox)$_2$TiCl" (**3**); **3** is cleanly transformed into the dichloride (tritox)$_2$TiCl$_2$ (**4**), via the addition of CCl$_4$ (eq 5). The pre-

$$\text{“(tritox)}_2\text{TiCl”} + \text{CCl}_4\text{(excess)} \xrightarrow{\text{hexane}} \underset{\mathbf{4}}{(\text{tritox})_2\text{TiCl}_2} \qquad (5)$$

$$2\text{Li(tritox)} + \text{TiCl}_4 \xrightarrow{\text{Et}_2\text{O}} \mathbf{4} + 2\text{LiCl} \qquad (6)$$

ferred route to the white, crystalline dichloride **4** is the metathesis reaction of TiCl$_4$ and Li(tritox) illustrated in eq 6 (51% yield). Although CH analysis of **3** indicates its purity is suspect, the transformation of **3** to the dichloride **4** was monitored by ^{1}H NMR and proceeded with minimal production (<5%) of observable impurities. When a crude sample of the Ti(III) chloride **3** was combined with an excess of CCl$_4$, **4** was isolated in ~60% yield. In total, these observations suggest that **3** may be monomeric and that the impurities present are inorganic; no (tritox)TiCl$_3$ (**5**) was detected upon CCl$_4$ addition to **3**.[23] The white crystalline monoalkoxy trichloride **5** was obtained in 57% yield upon addition of Li(tritox) to TiCl$_4$ in diethyl ether (eq 7). Attempts to generate the zirconium analogue of **5** via similar methathetical procedures proved futile.

$$\text{Li(tritox)} + \text{TiCl}_4 \xrightarrow{\text{Et}_2\text{O}} \underset{\mathbf{5}}{(\text{tritox})\text{TiCl}_3} + \text{LiCl} \qquad (7)$$

Derivatization of the dichlorides **2** and **4** was accomplished via the addition of 2 equiv of CH$_3$Li to form the corresponding white crystalline dimethyl complexes **6** and **7**, in 82 and 76% yield, respectively (eq 8). A similar

$$\underset{\substack{\mathbf{2},\ \text{M} = \text{Zr}\\ \mathbf{4},\ \text{M} = \text{Ti}}}{(\text{tritox})_2\text{MCl}_2} + 2\text{CH}_3\text{Li} \xrightarrow{\text{Et}_2\text{O}} \underset{\substack{\mathbf{6},\ \text{M} = \text{Zr}\\ \mathbf{7},\ \text{M} = \text{Ti}}}{(\text{tritox})_2\text{M(CH}_3)_2} + 2\text{LiCl} \qquad (8)$$

$$\underset{\mathbf{5}}{(\text{tritox})\text{TiCl}_3} + 3\text{CH}_3\text{Li} \xrightarrow{\text{Et}_2\text{O}} \underset{\mathbf{8}}{(\text{tritox})\text{Ti(CH}_3)_3} + 3\text{LiCl} \qquad (9)$$

treatment of **5** with 3 equiv of CH$_3$Li produced (tritox)Ti(CH$_3$)$_3$ (**8**), analogous to CpTi(CH$_3$)$_3$,[24] in moderate yield (60%) as depicted by eq 9. Both dimethyl complexes **6** and **7** exhibit far greater thermal stability than the corresponding dichlorides. The titanium species **7** shows less than 10% decomposition after 2 weeks at 100 °C in benzene solution; the zirconium dimethyl **6** is even more robust, displaying slight decomposition (~20%) after 100 °C thermolysis for about 3 weeks. Attempts to synthesize other zirconium dialkyls illustrated some general problems; while ^{1}H NMR evidence showed that (tritox)$_2$Zr(n-Bu)$_2$ is formed in high yield (>85%) from the addition of n-butyllithium to **2**, its extreme solubility prevented satisfactory purification. Hindered alkyllithiums (neopentyllithium and (CH$_3$)$_3$SiCH$_2$Li) react slowly with the dichloride **2**, thus allowing the competitive decomposition of **2** to interfere.

It has been shown that metathetical reactions leading to the preparation of bis(tritox) species proceed with no interference from the formation of mono- and tris(tritox) byproducts. Since metathetical approaches to the synthesis of (tritox)$_3$ZrCl and (tritox)ZrCl$_3$ had failed, the alcoholysis of pertinent zirconium alkyl complexes were considered as routes to the desired mono- and tris(tritox) alkyl species, given noted $\text{Zr}^{\delta+} - \text{C}^{\delta-}$ polarity of the zirconium–carbon bond.[25,26] Light yellow, crystalline (tritox)Zr(CH$_2$Ph)$_3$ (**9**) was prepared in excellent yield (82%) by refluxing a benzene solution containing Zr(CH$_2$Ph)$_4$[26] and a slight excess of the parent alcohol (eq 10). The

$$\underset{\text{X = H, D}}{(\text{tritox})\text{X}} + \text{Zr(CH}_2\text{Ph)}_4 \xrightarrow{\text{benzene}} \underset{\mathbf{9}}{(\text{tritox})\text{Zr(CH}_2\text{Ph)}_3} + \text{C}_6\text{H}_5\text{CH}_2\text{X} \qquad (10)$$

reaction of tetrabenzylzirconium and the deuterated alcohol (tritox)D was monitored by ^{1}H NMR, and the resulting toluene byproduct was shown to contain one deuterium incorporated at the methyl position. Synthesis of corresponding trineopentyl derivative (tritox)Zr(CH$_2$C(CH$_3$)$_3$)$_3$ (**10**) required prolonged heating (95 °C, 30 h) of Zr(CH$_2$C(CH$_3$)$_3$)$_4$[27] in virtually neat (tritox)H (eq 11).

$$(\text{tritox})\text{H} + \text{Zr(CH}_2\ \text{C(CH}_3)_3)_4 \xrightarrow[\substack{\text{benzene}\\ 95\ ^\circ\text{C}}]{\text{trace}} \underset{\mathbf{10}}{(\text{tritox})\text{Zr(CH}_2\text{C(CH}_3)_3)_3} + (\text{CH}_3)_4\text{C} \qquad (11)$$

Upon removal of the excess parent alcohol, **10** was isolated in 90–95% purity as a waxy colorless solid in near quantitative yield. Careful sublimation (55 °C, 10^{-1} torr) produced an analytically pure sample. Extensive heating (70 °C) of a slurry of (tritox)$_2$Zr(CH$_3$)$_2$ (**6**) and a 4–5-fold excess of (tritox)H in 1–2 mL of hexane for 15 days afforded, upon removal of excess alcohol and recrystallization from hexane, (tritox)$_3$ZrCH$_3$ (**11**) in 84% yield (eq 12). The lengthy reaction period is a testament to the steric inhibition of the alcoholysis pathway by the encumbering tritox ligands of **6**.

$$\underset{\text{excess}}{(\text{tritox})\text{H}} + \underset{\mathbf{6}}{(\text{tritox})_2\text{Zr(CH}_3)_2} \xrightarrow[\text{trace hexane}]{15\text{ days, }70\ ^\circ\text{C}} \underset{\mathbf{11}}{(\text{tritox})_3\text{ZrCH}_3} \qquad (12)$$

The complexes were characterized principally via ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (Table I), which proved valuable in establishing the purity of the unstable, yet crystalline (tritox)$_2$ZrCl$_2$ (**2**), (tritox)TiCl$_3$ (**5**), and (tritox)Ti(CH$_3$)$_3$ (**8**) complexes. From the spectral data, it is estimated that **2**, **5**, and **8** contain approximately <3% of tritox-containing or tritox-derived impurities. Infrared spectra of all compounds were obtained and used to further establish purity. Satisfactory C and H analyses were obtained on those species exhibiting sufficient thermal stability (see Experimental Section).

Molecular Structure of (tritox)$_2$ZrCl$_3$•Li(OEt$_2$)$_2$ (1)

The molecular structure of **1** is depicted in Figure 1 and the inner core of the complex in Figure 2. The overall coordination sphere is clearly pseudo trigonal bipyramidal; the equatorial plane is comprised of Cl1, O1, and O2 with Cl2 and Cl3 axially disposed about the zirconium. The

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Table I. ^{1}H and ^{13}C{^{1}H} NMR Data for $((CH_3)_3C')_3C''O$ Complexes (Benzene-d_6)

	^{1}H NMR,[a] δ			^{13}C{^{1}H} NMR,[b] δ				
compound	$((CH_3)_3C)_3C{-}O{-}$	other	assignmt	C	C′	C″	other	assignmt
(tritox)H	1.22 (s, 27 H)	1.10 (s, 1 H)	OH	32.6	45.0	85.1		
(tritox)Li	1.24 (s)			33.5	45.9			
(tritox)$_2$ZrCl$_2$ (2)	1.39 (s)			33.3	46.1	104.5		
(tritox)$_2$TiCl$_2$ (4)	1.50 (s)			33.6	47.6	117.2		
(tritox)TiCl$_3$ (5)	1.29 (s)			33.0	48.2			
(tritox)$_2$Zr(CH$_3$)$_2$ (6)	1.40 (s, 54 H)	0.69 (s, 6 H)	ZrCH$_3$	33.3	45.9	99.0	38.1	ZrCH$_3$
(tritox)$_2$Ti(CH$_3$)$_2$ (7)	1.54 (s, 54 H)	1.32 (s, 6 H)	TiCH$_3$	33.6	46.8	104.7	55.4	TiCH$_3$
(tritox)Ti(CH$_3$)$_3$ (8)	1.38 (s, 27 H)	1.33 (s, 9 H)	TiCH$_3$	33.2	46.8	107.2	61.7	TiCH$_3$
(tritox)Zr(CH$_2$C$_6$H$_6$)$_3$ (9)	1.40 (s, 27 H)	2.02 (s, 6 H)	ZrCH$_2^-$	33.3	46.1	102.8	65.7	ZrCH$_2$
		6.57–6.74 (m, 6 H)	C$_6$H$_5$				124.1	C$_6$H$_5$
							128.5	C$_6$H$_5$
		6.85–7.20 (m, 9 H)	C$_6$H$_5$				130.2	C$_6$H$_5$
							140.8	C$_6$H$_5$
(tritox)Zr(CH$_2$C(CH$_3$)$_3$)$_3$ (10)	1.41 (s, 27 H)	1.30 (s, 27 H)	CH$_2$C(*CH*$_3$)$_3$	33.3	46.2	93.2	35.0	CH$_2$C(*CH*$_3$)$_3$
		1.41 (s, 6 H)	*CH*$_2$C(CH$_3$)$_3$				35.4	*CH*$_2$C(CH$_3$)$_3$
(tritox)$_3$Zr(CH$_3$) (11)	1.48 (s, 81 H)	1.10 (s, 3 H)	ZrCH$_3$	34.4	45.6	100.2	33.4	ZrCH$_3$

[a] Referenced to C$_6$D$_5$H at δ 7.15. [b] Referenced to C$_6$D$_6$ at δ 128.0.

Table II. Selected Interatomic Distances (Å) for (tritox)$_2$ZrCl$_3$·Li(OEt$_2$)$_2$ (1)

Zr-Cl1	2.566 (5)	Cl2-Li	2.35 (2)
Zr-Cl2	2.556 (4)	O3-Li	1.95 (3)
Zr-Cl3	2.453 (3)	O4-Li	1.95 (2)
Zr-O1	1.900 (6)	C1-C11	1.63 (3)
Zr-O2	1.889 (8)	C1-C12	1.66 (3)
Zr-C1	3.305 (10)	C1-C13	1.62 (4)
Zr-C2	3.334 (12)	C2-C21	1.64 (2)
O1-C1	1.42 (2)	C2-C22	1.60 (3)
O2-C2	1.46 (3)	C2-C23	1.61 (2)
Cl1-Li	2.33 (2)		

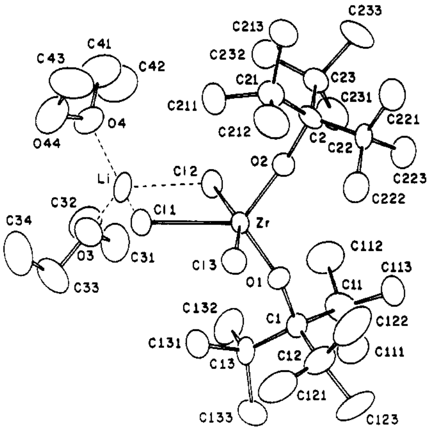

Figure 1. Molecular structure of (tritox)$_2$ZrCl$_3$·Li(OEt$_2$)$_2$ (1).

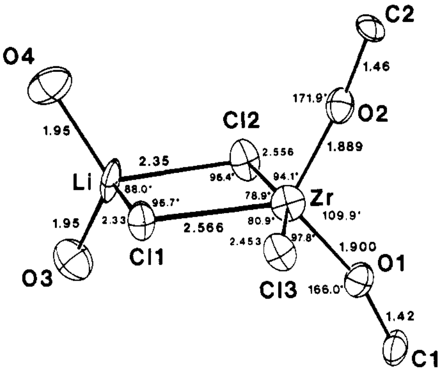

Figure 2. Inner coordination sphere of (tritox)$_2$ZrCl$_3$·Li(OEt$_2$)$_2$ (1).

Table III. Selected Bond Angles (deg) for (tritox)$_2$ZrCl$_3$·Li(OEt$_2$)$_2$ (1)

Cl1-Zr-Cl2	78.9 (2)	Cl1-Li-O4	107.9 (9)
Cl1-Zr-Cl3	80.9 (1)	Cl2-Li-O3	109.0 (7)
Cl1-Zr-O1	126.7 (3)	Cl2-Li-O4	115.9 (10)
Cl1-Zr-O2	123.1 (2)	O3-Li-O4	114.1 (11)
Cl2-Zr-Cl3	159.8 (1)	O1-C1-C11	106.9 (17)
Cl2-Zr-O1	94.1 (3)	O1-C1-C12	105.0 (17)
Cl2-Zr-O2	94.1 (2)	O1-C1-C13	105.2 (13)
Cl3-Zr-O1	97.8 (2)	O2-C2-C21	103.3 (16)
Cl3-Zr-O2	97.1 (2)	O2-C2-C22	105.7 (14)
O1-Zr-O2	109.9 (3)	O2-C2-C23	105.6 (19)
C1-Zr-C2	119.4 (3)	C11-C1-C12	114.6 (15)
Zr-O1-C1	166.0 (8)	C11-C1-C13	112.3 (19)
Zr-O2-C2	171.9 (6)	C12-C1-C13	111.9 (19)
Zr-Cl1-Li	96.7 (5)	C21-C2-C22	112.1 (17)
Zr-Cl2-Li	96.4 (5)	C21-C2-C23	114.7 (11)
Cl1-Li-Cl2	88.0 (8)	C22-C2-C23	114.1 (15)
Cl1-Li-O3	119.6 (8)		

slight deviation from tbp is due to the Li bound to one apical (Cl2) and one equatorial (Cl1) chlorine, which are equidistant from both the zirconium (2.56 Å average) and Li (2.34 Å average). The remaining chloride, Cl3, is slightly displaced away from the bulky tritox groups at a typical Zr–Cl distance (2.45 Å).[28] With the exception of a rather acute (88°) Cl1–Li–Cl2 angle, the geometry about the Li is near tetrahedral.

The molecular view clearly shows that the alkoxide oxygen atoms are buried within the surrounding methyl groups, thus reinforcing the forecasted nature of tritox. Substantial lengthening of the six central C–C bonds (1.63 Å average) concomitant with a flattening of the tri-*tert*-butylmethyl groups (O–C–C ∠'s, 105° average; C–C$_{1,2}$–C ∠'s, 113° average) attest to the dramatic distortion of these bulky ligands.[29] Note that the tritox ligands occupy the least-crowded equatorial sites in the pseudo-tbp arrangement. At first glance it is somewhat disconcerting that the O–Zr–O angle is 110°; however, upon closer inspection one finds the tri-*tert*-butylmethyl groups bent away from one another such that C1–Zr–C2 is 119° (Table III). The displacement of the tritox units about Zr is best described by this angle since these carbons are the true centers of each ligand's bulk. The 119° angle is in accord with a close packing of two ligands whose cone angle is measured to be 125°.[12] Sterically, it is reasonable to conclude that tritox approaches the bulk attributed to cyclopentadienyl.

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Table IV. Fractional Coordinates and Thermal Parameters[a] for (tritox)$_2$ZrCl$_3$·Li(OEt$_2$)$_2$ (1)

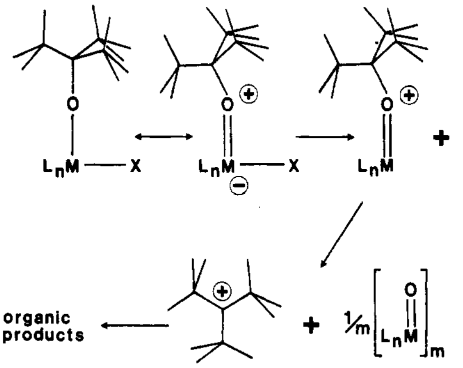
atom	x	y	z	B(eqv), Å^2
Zr	0.1376 (1)	−0.6664 (1)	−0.3450 (1)	2.6 (1)
Cl1	0.3044 (3)	−0.5721 (2)	−0.3479 (3)	2.4 (1)
Cl2	0.2747 (3)	−0.8011 (2)	−0.3408 (3)	2.4 (1)
Cl3	0.0609 (3)	−0.5044 (2)	−0.3504 (3)	2.5 (1)
O1	−0.0043 (7)	−0.7186 (6)	−0.4113 (7)	2.1 (3)
C1	−0.0981 (10)	−0.7469 (10)	−0.4686 (11)	2.1 (4)
C11	−0.1300 (16)	−0.8577 (12)	−0.4632 (14)	4.1 (6)
C111	−0.2029 (16)	−0.9100 (12)	−0.5231 (15)	4.5 (7)
C112	−0.0224 (17)	−0.9153 (12)	−0.4263 (16)	4.0 (6)
C113	−0.2072 (18)	−0.8639 (15)	−0.4321 (16)	5.1 (7)
C12	−0.2091 (15)	−0.6705 (14)	−0.4859 (15)	4.8 (7)
C121	−0.1855 (16)	−0.5706 (14)	−0.5017 (18)	5.7 (8)
C122	−0.2260 (18)	−0.6519 (18)	−0.4322 (18)	6.2 (9)
C123	−0.3317 (15)	−0.7041 (16)	−0.5373 (16)	5.0 (8)
C13	−0.0430 (12)	−0.7349 (12)	−0.5113 (13)	2.7 (4)
C131	0.0399 (15)	−0.6452 (14)	−0.4949 (14)	4.4 (7)
C132	0.0406 (15)	−0.8147 (15)	−0.5072 (16)	4.4 (6)
C133	−0.1383 (16)	−0.7273 (15)	−0.5786 (14)	4.5 (7)
O2	0.1478 (7)	−0.7026 (6)	−0.2733 (7)	2.1 (3)
C2	0.1681 (11)	−0.7209 (10)	−0.2141 (10)	1.8 (4)
C21	0.2566 (14)	−0.6332 (11)	−0.1743 (12)	3.4 (5)
C211	0.3526 (15)	−0.6124 (13)	−0.1919 (15)	4.4 (6)
C212	0.1952 (16)	−0.5376 (12)	−0.1841 (14)	4.2 (6)
C213	0.3218 (16)	−0.6510 (14)	−0.1071 (14)	4.5 (6)
C22	0.0387 (12)	−0.7145 (11)	−0.2207 (12)	2.7 (4)
C221	0.0408 (16)	−0.7027 (14)	−0.1623 (15)	4.4 (6)
C222	−0.0402 (13)	−0.6352 (13)	−0.2623 (15)	4.1 (6)
C223	−0.0427 (13)	−0.8055 (13)	−0.2517 (15)	3.9 (6)
C23	0.2291 (13)	−0.8252 (10)	−0.1957 (13)	3.0 (5)
C231	0.1711 (16)	−0.8966 (11)	−0.2466 (15)	3.7 (4)
C232	0.3656 (14)	−0.8282 (12)	−0.1794 (15)	4.0 (6)
C233	0.2267 (15)	−0.8703 (12)	−0.1428 (14)	4.3 (6)
O3	0.4253 (9)	−0.7364 (7)	−0.4149 (9)	3.5 (3)
C31	0.3815 (15)	−0.8270 (14)	−0.4429 (16)	4.3 (6)
C32	0.4741 (15)	−0.8892 (15)	−0.4453 (16)	5.0 (7)
C33	0.4225 (18)	−0.6705 (14)	−0.4558 (16)	5.3 (7)
C34	0.4935 (18)	−0.5822 (15)	−0.4198 (19)	5.6 (7)
O4	0.5752 (9)	−0.6950 (7)	−0.2718 (9)	3.5 (4)
C41	0.6416 (18)	−0.7754 (15)	−0.2328 (17)	5.9 (9)
C42	0.6155 (18)	−0.8626 (14)	−0.2626 (20)	5.8 (8)
C43	0.6351 (18)	−0.6059 (14)	−0.2526 (18)	5.8 (8)
C44	0.6322 (20)	−0.5664 (15)	−0.2010 (18)	6.5 (9)
Li	0.4194 (17)	−0.7036 (17)	−0.3449 (21)	1.9 (6)

[a] From the anisotropic thermal parameters in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$, the $B(\mathrm{eqv}) = 4.0[V^2 \det(\beta_{ij})]^{1/3}$.

Typical Cp(ring centroid)–M–Cp angles are ~136°;[13] lower values are common for Cp$_2$MX$_2$ complexes where X is halogen (126–128°)[30] and for Cp$_2$MX$_2$Y species (e.g., [(η^5-C$_5$H$_4$Me)$_2$ZrH]$_2$(μ-H)$_2$, Cp–M–Cp = 129°)[31] that are more closely related to 1.

Two interrelated structural features are of significance when the electronic saturation of the early metal in these new species is considered. The Zr–O bonds are exceptionally short (1.895 Å average), and the corresponding Zr–O–C angles are nearly linear (169° average), thus providing a clear manifestation of strong oxygen pπ–dπ donation. Similar combinations of short Zr–O bonds/linear Zr–O–C angles have been noted for [HB(3,5-(CH$_3$)$_2$pz)$_3$]Zr(O-t-Bu)(η^2-C(CH$_3$)NC(CH$_3$)$_3$) (1.924 Å, 174°),[32] Cp$_2$Zr(O-t-Bu)Ru(CO)$_2$Cp (1.910 Å, 169.6°),[33] Cp$_2$W=C(H)OZr(H)(η^5-C$_5$(CH$_3$)$_5$)$_2$ (1.970 Å, 166°),[34] and (Cp$_2$ZrCH$_3$)$_2$O (1.945 Å, 174.1°).[28] Mo and W alkoxide M–O–C angles are typically near 135°,[7,35] although some Mo siloxide species show Mo–O–Si angles greater than 170°, presumably due to oxygen π interactions with both Mo and Si.[36] The near linear Zr–O–C angles of 1 may be a consequence of the steric interaction of tritox with the metal center, but the extremely short Zr–O distances suggest that the alkoxides may serve as five-electron donors.[6] The unusual binding of LiCl to the (tritox)$_2$ZrCl$_2$ moiety is a testament to the electropositive character of the zirconium center. Donors such as Cl$^-$ have not been reported to bind to the analogous 16-electron Cp$_2$ZrCl$_2$ complex. Even allowing for five-electron donation by tritox, the resulting 16-electron (tritox)$_2$ZrCl$_2$ is considered a stronger Lewis acid than Cp$_2$ZrCl$_2$ (16-electron) by virtue of having a "harder" coordination environment. Considering the alkoxides as three-electron donors[6] merely evinces a stronger argument for the electronic unsaturation of (tritox)$_2$ZrCl$_2$.

Scheme I



Discussion

The metathetical procedures employed in synthesizing several of the tritox derivatives corresponding closely to those which yield analogous cyclopentadienyl complexes.[15,37] Presumably the parallel syntheses reflect the similar conical shape and steric bulk of both tritox and Cp, when attached to a metal. The ease of which bis(tritox) species are prepared manifests the contrasting spatial nature of tritox with respect to electronically similar, wedge-like ligands such as 2,6-di-*tert*-butylphenoxide[38] and bis(trimethylsilyl)amide.[3] Curiously, although tritox would appear to be an inviting target for displacement by alkyllithiums, in no preparation has this potentially disastrous side reaction been observed. Displacement of chloride is markedly favored over loss of alkoxide; this is in accord with the reactivity of tantalum alkoxy chlorides upon alkyllithium addition.[39] The stronger π-donating ability of –OR compared to chloride may render alkoxides less susceptible to substitution.

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Utilization of the alcoholysis reaction enabled the preparation of mono- and tris(tritox)zirconium species in cases where alkoxide addition to the appropriate metal chloride had failed. On the basis of eq 10, it is tempting to conclude that all the alcoholysis reactions (eq 10–12) proceed via prior coordination of (tritox)H followed by extrusion of alkane, since exclusive formation of DCH_2Ph was noted upon treatment of $Zr(CH_2Ph)_4$ with (tritox)D. Unfortunately, the fickle nature of the alcoholysis procedures that yield (tritox)$Zr(CH_2C(CH_3)_3)_3$ (**10**) and (tritox)$_3$$ZrCH_3$ (**11**) has frustrated efforts to engender supportive data. An attractive alternative, albeit in conflict with eq 10, would entail addition of (tritox)H across a transient alkylidene species generated via α abstraction. The rather harsh conditions required to form **10** and **11** substantiate this possibility.

The observed instability of (tritox)$_2$$ZrCl_2$ (**2**) and the contrasting robust nature of (tritox)$_2$$Zr(CH_3)_2$ (**6**) manifest both the potential problems associated with (tritox)M decompositions as well as an apparent solution. A plausible mode of decomposition for a (tritox)M species is depicted in Scheme I. Provided M is an oxophilic metal, facile cleavage of the C–O bond of the tritox generates the tri-*tert*-butylcarbonium ion, which rearranges according to known pathways.[40] As Scheme I illustrates, heterolytic dissociation of X^- can promote this process. The greater stability of (tritox)$_2$$TiCl_2$ (**4**) and (tritox)$TiCl_3$ (**5**) with respect to **2** may be attributed to the greater Lewis acidity of the latter, due to greater $d\pi$–$p\pi$ overlap of the second-row metal–oxygen bond. When X is an alkyl, the ease of dissociation is significantly decreased; consequently, this decomposition mode becomes unfavorable. In addition, the strong σ donation of an alkyl may counteract the oxygen π donation. The thermal stabilities of all the alkyl species (**6**, **7**, and **9**–**11**) except (tritox)$Ti(CH_3)_3$ (**8**) are in accord with this proposal. Considering the propensity of low coordinate polymethyl titanium species to undergo rapid decomposition at low temperatures,[15] the observations that **8** discolors in benzene solution over a 2–4-h period and in the solid state (25 °C) are not surprising. In preparing new tritox-derived compounds, the avoidance of heterolytically labile X groups may be required to ensure that the alkoxide functions as a stable ancillary ligand.

Contrary to chemistry observed for bis(trimethylsilyl)amide[3] and 2,6-di-*tert*-butylphenoxide complexes,[41] no clear cyclometalation reactions were evidenced in the thermolyses of the tritox alkyl species. Assuming the near linear Zr–O–C angles of **1** (169° average) are an appropriate model for all (tritox)M species and that substantial bending of this angle is difficult due to strong $p\pi$–$d\pi$ interactions, the effective bulk of the tritox unit is kept far from the metal center. In order to bring an external C–H bond proximate to the metal whereby a cyclometalation can occur, partial breakage of the strong π bond must occur. Given the lack of notable metalation reactions, concomitant with short Zr–O distances of **1** (1.895 Å average), it is tempting to conclude that tritox functions as an effective five-electron donor, via donation from both $p\pi$ oxygen orbitals.[6] Investigations into the reactivity of these new metal alkoxides are currently being undertaken. We and others[42] are also exploring the versatility of the tritox ligand with other metals.

Experimental Section

General Considerations. All manipulations were performed by using either glovebox or high vacuum line techniques. All solvents were purified by initial distillation from purple sodium/benzophenone followed by vacuum transfer from same. Small amounts of tetraglyme (2–5 mL/1200 mL) were added to hexanes in order to solubilize the Na/benzophenone. Benzene-d_6 was dried over activated 4-Å molecular sieves. Argon was passed over MnO on vermiculite and activated 4-Å molecular sieves. Zirconium tetrachloride (Alfa) was sublimed at 190 °C (10^{-4} torr) prior to use. Both $TiCl_3$ and $TiCl_4$ (Alfa) were used without further purification. Tetrabenzylzirconium[26] and tetraneopentylzirconium[27] were prepared from literature procedures, as was tri-*tert*-butylmethanol, (tritox)H.[17]

^1H NMR spectra were obtained by using Varian EM-390, Varian CFT-20, and Bruker WM300 spectrometers. ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer. EPR spectra were run on a Varian E-12 spectrometer. Infrared spectra were obtained by using a Perkin-Elmer 357 spectrophotometer. Analyses were performed by Analytische Laboratories, Germany.

Reactions such as the thermolyses of the (tritox)$_2$$M(CH_3)_2$ species **6** and **7** and the reaction of (tritox)D and $Zr(CH_2Ph)_4$ (eq 10) were conducted in sealed NMR tubes and monitored by ^1H NMR spectroscopy. For example, (tritox)D (13 mg, 0.065 mmol) and $Zr(CH_2Ph)_4$ (30 mg, 0.066 mmol) were placed in an NMR tube sealed to a ground glass joint and needle valve adapter. At 77 K, benzene-d_6 (0.4 mL) was distilled into the tube, which was then sealed with a torch. The conversion to (tritox)$Zr(CH_2Ph)_3$ (**9**) was then monitored and the byproduct toluene produced was >90% $H_2DCC_6H_5$.

Procedures. 1. Li(tritox). To a solution of 20.1 g of (tritox)H (0.100 mol) in 150 mL of hexane at −78 °C was added 70 mL of *n*-butyllithium (1.55 M in hexane, 0.108 mol) via syringe. The solution was allowed to warm to 25 °C. During a 5-h period white, crystalline Li(tritox) precipitated. The slurry was then concentrated, cooled to −78 °C, and filtered to yield 18.7 g of Li(tritox) (91%). Titration of Li(tritox) indicated that the conversion to the alkoxide was complete (98.9%).

2. (tritox)$_2$$ZrCl_3$·Li($Et_2O$)$_2$, 1. To a flask containing $ZrCl_4$ (500 mg, 2.15 mmol) and (tritox)Li (890 mg, 4.31 mmol) at −78 °C was added diethyl ether (40 mL) via distillation. The reaction was stirred at −78 °C for 3 h and allowed to warm to 25 °C over an 8-h period. The solution was concentrated to 30 mL and filtered twice with medium frits and once with a fine frit. Slow evaporation of the remaining diethyl ether at −20 °C yielded 1.21 g of **1** (75%). Loss of diethyl ether from solid **1** at room temperature was noted.

3. (tritox)$_2$$ZrCl_2$, 2. To a flask containing $ZrCl_4$ (2.00 g, 8.58 mmol) and Li(tritox) (3.60 g, 17.5 mmol) was distilled 100 mL of diethyl ether at −78 °C. After slow warming to 25 °C and 7 h of stirring, the Et_2O was removed and 50 mL of hexane was added at −78 °C. Filtration and crystallization gave 2.95 g of thermally sensitive white crystals (61% yield).

4. "(tritox)$_2$TiCl", 3. To a flask containing 350 mg of $TiCl_3$ (2.27 mmol) and 935 mg of Li(tritox) (4.54 mmol) was distilled 50 mL of Et_2O at −78 °C. During the 3 days of stirring at room temperature the reaction mixture changed from a colorless solution with purple/black particulate to a yellow-green solution with a grayish white precipitate. The diethyl ether was removed and 15 mL of hexane added. This mixture was stirred and the hexane removed under vacuum. This was repeated, and 30 mL of hexane was added after which the solution was filtered. Removal of hexane yielded an olive green oil to which 10 mL of hexane was added and removed by vacuum. Hexane (15 mL) was added and the solution cooled to −78 °C as the hexane was removed. The resulting mint green precipitate was filtered from the oily solution while cold and washed with 10 mL of cold hexane (660 mg, 60% based on "(tritox)$_2$TiCl"). Reprecipitation of this material (**3**) from cold hexane gave 300 mg of material (27%) which manifested a broad absorption (no diamagnetic material observed) at δ 1.42 (benzene-d_6) with $\nu_{1/2} \approx 153$ Hz. Addition of CCl_4 to the NMR tube resulted in the clean formation of (tritox)$_2$$TiCl_2$ (**4**) (the only H-containing impurity noted was ~5% Et_2O). Anal. Calcd for $C_{26}H_{54}TiO_2Cl$: C, 64.78; H, 11.29; Cl, 7.35. Found (sample no.

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1): C, 57.79; H, 10.32. Found (no. 2): C, 54.79; H, 9.47; Cl, 18.57. No 4 was detected by IR (<5%). Anal. Calcd for $(\text{tritox})_2\text{TiCl}_4\cdot\text{Li}_3(\text{OEt}_2)_2$: C, 54.88; H, 9.85; Cl, 18.72.

5. $(\text{tritox})_2\text{TiCl}_2$, 4. (a) From 3. Crude oily "$(\text{tritox})_2\text{TiCl}$" (275 mg, "0.57 mmol") was treated with an excess of CCl_4 (1 mL) in 15 mL of hexane at 25 °C. Filtration and crystallization yielded 175 mg of 4 (60%).

(b) From $TiCl_4$. Degassed $TiCl_4$ (810 mg, 4.26 mmol) and 80 mL of Et_2O were transferred to a flask to which Li(tritox) (1.76 g, 8.54 mmol) was added at −78 °C over a 15-min period. During 6 h of stirring the original yellow solution became green and finally light brown. Removal of the ether, addition of 65 mL of hexane, filtration, and crystallization netted 950 mg of off-white, crystalline 4 after one wash with 10 mL of cold hexane. In similar fashion a second crop yielded 800 mg (1.75 g total, 79% yield). Anal. Calcd for $C_{26}H_{54}O_2TiCl_2$: C, 60.34; H, 10.52; Cl, 13.70. Found: C, 60.07; H, 10.38; Cl, 13.85.

6. $(\text{tritox})\text{TiCl}_3$, 5. Li(tritox) (1.15 g, 5.58 mmol) was slowly added over a 1-h period to a solution of $TiCl_4$ (1.06 g, 5.58 mmol) in 60 mL of hexane. After the addition the solution was warmed to 0 °C and stirred for 0.5 h, then briefly warmed to 25 °C, and filtered. The residual LiCl was washed with 10 mL of Et_2O, and the ether was then replaced with hexane. Cooling and removal of hexane gave 1.12 g of white crystalline thermally unstable 5 (57% yield).

7. $(\text{tritox})_2\text{Zr}(\text{CH}_3)_2$, 6. To a flask containing $(\text{tritox})_2\text{ZrCl}_2$ (2) (1.45 g, 2.59 mmol) and 30 mL of diethyl ether at −78 °C was added 3.45 mL (5.18 mmol) of CH_3Li (1.5 M in ether). After being stirred at −78 °C for 2 h, the reaction mixture was warmed to 25 °C and stirred for 8 h. Upon removal of Et_2O, addition of 30 mL of hexane and filtration, cooling, and concentration yielded 1.10 g of white crystalline 6 (82%). Anal. Calcd for $C_{28}H_{60}O_2Zr$: C, 64.67; H, 11.63. Found: C, 64.54, H, 11.46.

8. $(\text{tritox})_2\text{Ti}(\text{CH}_3)_2$, 7. To a solution of $(\text{tritox})_2\text{TiCl}_2$ (4) (300 mg, 0.58 mmol) in 10 mL of Et_2O at −78 °C was added 0.64 ml (1.16 mmol) of CH_3Li (1.8 M in ether). The solution was stirred while being warmed to 25 °C for another 4 h. Replacement of Et_2O with hexane, filtration, cooling, and concentration gave 210 mg of white crystalline 7 (76% yield). Anal. Calcd for $C_{28}H_{60}O_2$: C, 70.55; H, 12.69. Found: C, 70.45; H, 12.52.

9. $(\text{tritox})\text{Ti}(\text{CH}_3)_3$, 8. To a solution of $(\text{tritox})\text{TiCl}_3$ (5) (1.00 g, 2.83 mmol) in 40 mL of Et_2O at −78 °C was added 5.66 mL of (8.49 mmol) of CH_3Li (1.5 M in ether). A bright yellow color appeared immediately and remained as the reaction mixture was slowly warmed to 25 °C and stirred for 4 h. Removal of Et_2O and filtration in hexane gave a viscous yellow filtrate from which 500 mg of white, crystalline, thermally sensitive 8 could be isolated (60% yield).

10. $(\text{tritox})\text{Zr}(\text{CH}_2\text{Ph})_3$, 9. $Zr(CH_2Ph)_4$ (700 mg, 1.538 mmol) and an excess of (tritox)H (350 mg, 1.75 mmol) were refluxed in 20 mL of benzene while shielded from light. After 7 h the benzene was replaced with hexane and the solution filtered. Crystallization yielded 710 mg of light yellow 9 (82%).

11. $(\text{tritox})\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$, 10. $Zr(CH_2C(CH_3)_3)_4$ (465 mg, 1.24 mmol) and (tritox)H (400 mg, 2.00 mmol) were "dissolved" in 2 mL of benzene and stirred at a carefully monitored 93–95 °C for 30 h. Removal of solvent left an off-colored oil that solidified under vacuum to give waxy, white 10, in near quantitative yield (~95% pure by ^{1}H NMR). Analytically pure clear waxy crystals (100 mg, 16% yield) were collected by sublimation (70 °C, 10^{-4} torr) prior to decomposition of the remaining solid. Anal. Calcd for $C_{28}H_{60}OZr$: C, 66.73; H, 12.00. Found: C, 66.51; H, 11.76.

12. $(\text{tritox})_3\text{ZrCH}_3$, 11. A slurry of $(\text{tritox})_2\text{Zr}(\text{CH}_3)_2$ (6) (740 mg, 1.42 mmol) and (tritox)H (1.50 g, 7.50 mmol) in ~1 mL of hexane was stirred for 15 days at 70 °C. Crystallization from hexane yielded 850 mg white crystalline 11 (84%). Anal. Calcd for $C_{40}H_{84}O_3Zr$: C, 68.21; H, 12.02. Found: C, 68.03; H, 11.87.

Single-Crystal X-ray Diffraction Analysis of 1. Slow evaporation of Et_2O solution of $(\text{tritox})_2\text{ZrCl}_3\cdot\text{Li}(\text{OEt}_2)_2$ (1) at −25 °C yielded a clear, colorless crystal (10 × 10 × 2 mm) from which a chip proved suitable for X-ray study. A single crystal of 1 with sides roughly 0.2 mm was sealed in a Lindemann capillary. Preliminary X-ray diffraction photographs displayed monoclinic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer measured 2θ values at −75 °C, were $a = 12.946$ (3) Å, $b = 14.026$ (3) Å, $c = 26.257$ (4) Å, and $\beta = 121.016$ (12)°. The cell volume is 4086.1 Å^3 with a calculated density of 1.169 g/cm^3. The space group was uniquely determined to be $P2_1/c$ and the asymmetric unit consisted of $C_{34}H_{74}O_4Cl_3ZrLi$. All unique diffraction maxima $(h,k,\pm l)$ with $2\theta \leq 55°$ were measured on a four-circle computer-controlled diffractometer with a variable speed, 1° ω scan using graphite-monochromated Mo Kα radiation (0.71069 Å). The agreement factor between symmetry equivalent reflections was 0.025. After correction for Lorentz, polarization, and background effects, 4346 (83%) of the 5205 reflections were judged observed ($|F_o| \geq 3\sigma(F_o)$).[43] Structure solution using the heavy-atom technique proceeded routinely.[44] The Zr was positioned from the Patterson synthesis, and the non-hydrogen light atoms were revealed in successive difference Fourier syntheses. Block-diagonal least-squares refinements (minimization of $\sum w(|F_o| - |F_c|)^2$, where w is based on counting statistics modified by an ignorance factor of $\rho = 0.03$) with 43 anisotropic non-hydrogen atoms and all hydrogens included at calculated positions have converged to a current residual (R) of 0.079 and a weighted residual (R_w) of 0.096 for the observed reflections.[45]

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Registry No. 1, 89958-99-6; 2, 89958-87-2; 3, 89958-88-3; 4, 89958-89-4; 5, 89958-90-7; 6, 89958-91-8; 7, 89958-92-9; 8, 89958-93-0; 9, 89958-94-1; 10, 89958-95-2; 11, 89958-96-3; Li(tritox), 89958-97-4; (tritox)H, 41902-42-5; $ZrCl_4$, 10026-11-6; $TiCl_3$, 7705-07-9; CCl_4, 56-23-5; $TiCl_4$, 7550-45-0; CH_3Li, 917-54-4; $Zr(CH_2Ph)_4$, 24356-01-2; $Zr(CH_2C(CH_3)_3)_4$, 38010-72-9.

Supplementary Material Available: Tables of bond distances, bond angles, observed and calculated structure factors, fractional coordinates and thermal parameters (39 pages). Ordering information is given on any current masthead page.

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(43) All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were as follows: REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, a system of computer programs for the automatic solutions of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

(44) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* 1968, *A24*, 321.

(45) $R = \sum||F_o| - |F_c||/(\sum|F_o|)$; $R_w = \{\sum w|F_o| - |F_c|)^2/(\sum w|F_o|^2\}^{1/2}$.