product in which alkyne insertion into each Ir–H bond has occurred. It is not clear how this relates (if at all) to the catalytic hydrogenation of alkynes by the rhodium analogue, $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$, although further studies are currently underway to investigate this possibility. It may also be that it is the initial tetrahydride species **4** which is analogous to the catalytically important species in the rhodium-catalyzed cycle and further studies are currently underway in attempts to characterize this tetrahydride species and to investigate its subsequent chemistry with unsaturated substrates.

In contrast, the reaction of **1** with H_2 produces a dihydride species which subsequently reacts with only 1 equiv of DMA. Spectroscopic evidence shows that the alkyne has inserted into only one of the Ir–H bonds. Although this insertion occurs at only one metal center, we can forsee how the second metal can become involved through π-coordination of the metalated olefin moiety to the second metal and subsequent hydrogen transfer to the olefin to form a dimetalated alkyl group which then reductively eliminates as the olefin. Attempts to induce the second hydrogen transfer and subsequent reductive elimination have not yet met with sucess in the complex studied. It is not clear whether this is due to the steric bulk of the phosphine and alkyne groups or whether it is a function of the low lability of the chloro or carbon monoxide ligands, failing to generate the required coordinative unsaturation. Attempts to react this single alkyne-inserted product (**6**) with H_2 under ambient conditions have also been unsuccessful. Further studies are underway in attempts to react **6** further and to determine the reasons for the apparent lack of reactivity under the conditions studied.

The reason that the neutral compound **3** reacts with only 1 equiv of alkyne whereas the cationic species **5** reacts with 2 equiv seems to be due to "incipient coordinative unsaturation" in the latter; the coordinative unsaturation required for alkyne coordination at each metal center in turn can be generated in **5** by movement of the halide ligand from the bridging position to a terminal site on the opposite metal. This transfer of the halide ligand back and forth between the metals, generating coordinative unsaturation, shows one way in which adjacent metal centers can cooperate in catalysis.

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Supplementary Material Available: Listing of observed and calculated structure factors, thermal parameters for the anisotropic atoms, and idealized hydrogen parameters (36 pages). Ordering information is given on any current masthead page.

Tantalum Organometallics Containing Bulky Oxy Donors: Utilization of Tri-*tert*-butylsiloxide and 9-Oxytriptycene

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Procedures entailing the preparation of alkyl- and chlorotantalum complexes containing 9-oxytriptycene (TpO) and $(t\text{-}Bu)_3SiO^-$ (silox) are described. Addition of 2 equiv of $TpOSiMe_3$ to $TaCl_5$ yielded $(TpO)_2TaCl_3$ (**2**); alcoholysis of $Np_3Ta{=}C(H)CMe_3$ (Np = neopentyl) with TpOH produced $(TpO)_2TaNp_3$ (**3**). An X-ray structure determination of **3** indicated that the axially disposed TpO units are nearly eclipsed in this pseudo-tbp complex. Crystal data: orthorhombic, $Pn2_1a$, $a = 16.024$ (2) Å, $b = 13.607$ (4) Å, $c = 21.377$ (1) Å, $Z = 4$, and $T = 25$ °C. From 2651 data were $|F_o| \geq 3\sigma(|F_o|)$, an R factor of 0.054 was obtained via standard refinement methods. Short Ta–O bonds (1.869 (16) Å average) concomitant with near linear Ta–O–C angles (170.3 (19) and 163.9 (16)°) suggest that strong π-bonding is evident. Treatment of $TaCl_5$ and R_3TaCl_2 (R = Me, CH_2Ph, Np) with stoichiometric amounts of Na(silox) gave $(silox)_2TaCl_3$ (**4**), $(silox)_2TaR_3$ (R = Me (**5**), CH_2Ph (**6**)), $(silox)_2NpTa{=}C(H)CMe_3$ (**11**), and $(silox)TaNp_3Cl$ (**9**), respectively. From Np_2TaCl_3 and 2Na(silox), $(silox)_2TaNp_2Cl$ (**10**) was obtained. Either **9** and Na(silox) or **10** and NpLi also afforded **11**. Thermolysis of **6** provided $(silox)_2Ta{=}C(H)Ph(CH_2Ph)$ (**7**), and the addition of $PhCH_2MgCl$ to **4** in Et_2O resulted in $(silox)_2TaCl_2(CH_2Ph)$ (**8**). $Np_3Ta{=}C(H)CMe_3$ reacted with (silox)H to form $(silox)Np_2Ta{=}C(H)CMe_3$ (**12**), but further silanolysis was not observed. Discussions pertaining to the effective size of the oxygen donor ligands, the stability of the complexes, and their relationship to analogous Cp species are presented.

Introduction

The generation of organotransition-metal complexes possessing a degree of coordinative unsaturation remains a critical problem in regard to the catalytic and stoichiometric transformations of small molecules.[1] In this regard, the approach of sterically saturating a metal center, which can remain electronically deficient, may be a plausible

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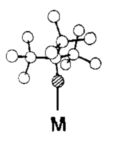
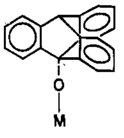
[1] Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980.

solution. Initial explorations in this laboratory have focused on the application of bulky alkoxide ligands as steric mimics of the ubiquitous cyclopentadienyl (Cp) moiety.[2] In view of the common two- or four-electron donor properties of alkoxides (vs. six for Cp^-), the reactivity of $(RO)_nML_m$ complexes analogous to known 18-electron Cp_nML_m species should manifest this desired degree of electronic unsaturation.

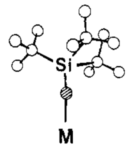
In accord with this basic premise, tri-*tert*-butyl methoxide (tritox)[3,4] was utilized in the preparation of a number of group 4 derivatives,[2] which were subsequently shown to activate dioxygen[5] in a fashion unlike that of corresponding Cp complexes.[6] In attempting to extend the chemistry of the tritox ligand to group 5, preparative efforts were thwarted by a facile C–O bond heterolysis of the $(t\text{-Bu})_3C\text{–}OM$ ((tritox)M; M = Nb, Ta) unit. Reasoning that the ease of tri-*tert*-butyl carbonium ion formation was, in part, responsible for a heterolytic degradation of the (tritox)M species, 9-hydroxytriptycene (TpOH)[7] was prepared; the inability of the bridgehead position to achieve planarity apparently inhibits this undesired decomposition pathway. Given the strength of silicon–oxygen bonds and their kinetic stability with respect to heterolytic Si–O cleavage, tri-*tert*-butyl siloxide ($(t\text{-Bu})_3SiO^-$, silox)[8] was thought to be an attractive alternative to tritox. As precedent suggested,[9] silox proved to be the most robust and versatile of the three ligands. Its steric bulk (cone angle[10] ≈ 125°) approaches that of tritox, whereas the flat phenyl rings of TpO render this alkoxide less encumbering than what was anticipated from cone angle measurements (~150°). This report describes the preparation and characterization of a series of tantalum complexes containing TpO and silox.



(tritox)M



(TpO)M



(silox)M

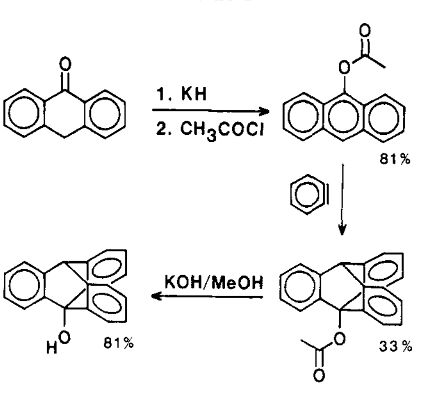
Synthetic Studies and Discussion

Tritox. All attempts to prepare tritox-derived Ta species via either metathetical or alcoholysis pathways proved unsuccessful. Treatment of TaX_5 (X = Cl, F) with (tritox)M′ (M′ = Li, K, MgBr)[2] in ether or hydrocarbon solvents resulted in products apparently derived from C–O heterolysis. Reasoning that alkyl substitution on Ta would render the metal center less oxophilic ("softer"), the displacement of halide from Cl_xTaR_{5-x} (x = 2, 3) species was investigated. However, both Np_3TaCl_2[11] and $Cl_2Ta(CH_2Ph)_3$[12] were unreactive below their decomposition temperatures. When Me_3TaCl_2[13] was treated with (tritox)Li at −78 °C, substantial quantities of (tritox)H were released, perhaps indicating that the tritox anion served to deprotonate the tantalum methyls. Only in the case of Np_2TaCl_3[11] was there any indication of desired product. ^1H NMR evidence was obtained for (tritox)Np_2TaCl_2 (1) as a fleeting intermediate, which rapidly degraded at the temperatures required to effect the alkoxylation (20 °C).

$$(\text{tritox})\text{Li} + \text{Np}_2\text{TaCl}_3 \xrightarrow[-\text{LiCl}]{\text{benzene}} \underset{1}{[(\text{tritox})\text{Np}_2\text{TaCl}_2]} \xrightarrow{20\ ^\circ\text{C}} \text{decomp} \quad (1)$$

Alcoholysis procedures also proved futile; $TaMe_5$[12] underwent rapid decomposition when subjected to an excess of (tritox)H at −78 °C (Et_2O), and $Np_3Ta{=}C(H)CMe_3$[11] remained unreactive up to its decomposition temperature (>120 °C, neat (tritox)H). Given the noted sensitivity of Me_5Ta, its presumed autocatalytic degradation[12] in the presence of excess (tritox)H was not surprising. The inability of $Np_3Ta{=}C(H)CMe_3$ to undergo alcoholysis was unexpected; Np_4Zr was smoothly converted to (tritox)$ZrNp_3$ under similar conditions.[2] This apparent discrepancy can be rationalized on the basis of the ~0.1-Å difference in covalent radii between Zr (1.45 Å) and Ta (1.34 Å); in contrast to Zr, access to the more sterically constrained tantalum center by (tritox)H is precluded.

Scheme I



TpO (9-Oxytriptycene). In order to circumvent the problem of heterolytic C–O bond cleavage attributable to tritox, the construction of analogues which could not achieve a planar tertiary carbonium ion seemed a logical solution. The triptycene framework meets this requirement; its bridgehead position is constrained by the three phenyl substituents such that tetrahedral geometry must be maintained. Furthermore, the cone angle of 9-oxytriptycene was measured to be 150°. Scheme I illustrates the preparation of the parent alcohol, obtained in 22% overall yield from anthrone (three steps).

Deprotonation reactions of TpOH brought to light both expected and unanticipated problems pertaining to the TpO moiety. Although the formation of TpO^- occurred smoothly (eq 2), the precipitated anion exhibits clathrate

$$\text{TpOH} + \text{RLi} \xrightarrow{25\ ^\circ\text{C}} [\text{TpOLi}\cdot(\text{solvent})_x]_n + \text{RH} \quad (2)$$

R = *n*-butyl; solvent = hexane, toluene; x = 3–4

R = Me; solvent = Et_2O; x = 1

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(3) (a) Syper, L. *Rocz. Chem.* **1973**, *47*, 433. (b) Bartlett, P. D.; Lefferts, E. B. *J. Am. Chem. Soc.* **1955**, *77*, 2804.

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(10) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. The cone angle measurements described in the text were made using Framework Molecular Models (Prentice-Hall, Inc.). In comparison with Tolman's measurements (space-filling models), these models appear to underestimate the bulk of a number of ligands such as Cp by as much as 10°.

(11) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

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(13) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

$$\mathrm{TpOLi{\cdot}Et_2O + Me_3SiCl \xrightarrow[-\mathrm{Et_2O}]{90\ ^\circ\mathrm{C},\ 48\ \mathrm{h}} TpOSiMe_3 + LiCl} \tag{3}$$

behavior, entrapping upwards of 3–4 equiv of hydrocarbon solvents, presumably in the spaces between the phenyl rings. Only treatment of TpOH with CH_3Li in diethyl ether resulted in a reproducible stoichiometry of the desired anion $TpOLi{\cdot}Et_2O$ (eq 2). Washing any Li salt with a different solvent simply caused solvent exchange in the lattice. Prolonged heating under vacuum had little effect. Whereas hydrocarbon solvated TpOLi displayed little solubility. $TpOLi{\cdot}Et_2O$ proved to be soluble in ether, benzene, and CH_2Cl_2. Unfortunately, all metathetical procedures utilizing this anion and R_3TaCl_2 (R = Np, CH_2Ph, Me) or Np_2TaCl_3 led to complex mixtures. Conversion of $TpOLi{\cdot}Et_2O$ to the trimethylsilyl derivative $TpOSiMe_3$ (eq 3) resulted in the only practical TpO^- equivalent.

The extreme solubility problems associated with TpO became evident upon preparing $(TpO)_2TaCl_3$ (**2**) from the addition of $TpOSiMe_3$ to $TaCl_5$ according to eq 4.

$$\mathrm{2TpOSiMe_3 + TaCl_5 \xrightarrow{benzene} \underset{\mathbf{2}}{(TpO)_2TaCl_3} + 2Me_3SiCl} \tag{4}$$

Spectral (^1H NMR) evidence for **2** could only be obtained in Me_2SO-d_6. Ridding **2** of small amounts of occluded C_6H_6 could not be accomplished. In order to prepare a more easily characterized complex, **2** was treated with several different alkyl anion equivalents. Only the additon of NpLi to **2** yielded identifiable products (eq 5). White,

$$\mathrm{\underset{\mathbf{2}}{(TpO)_2TaCl_3} + 3NpLi \xrightarrow[25\ ^\circ C]{benzene} \underset{\mathbf{3}}{(TpO)_2TaNp_3} + Np_3Ta{=}C(H)CMe_3 + \ldots} \tag{5}$$

crystalline $(TpO)_2TaNp_3$ (**3**) could be easily isolated from the more soluble $Np_3Ta{=}C(H)CMe_3$.[11] The preferred route to **3** is a high yield (79%) alcoholysis of $Np_3Ta{=}C(H)CMe_3$ with TpOH (eq 6). The facility of this reaction

$$\mathrm{Np_3Ta{=}C(H)CMe_3 + 2TpOH \xrightarrow[25\ ^\circ C]{benzene} \underset{\mathbf{3}}{(TpO)_2TaNp_3} + NpH} \tag{6}$$

provided the first indication that the TpO ligand behaved as though it were much smaller than its measured cone angle (150°). Surprisingly, **3** proved to be remarkably inert, undergoing slow decomposition to unidentifiable products at elevated temperatures (120 °C, 48 h). When **3** was subjected to O_2, LiNp, or H_2, no substrate reactivity was discerned prior to thermolytic decomposition. Water slowly effected the cleavage of TpO from **3** (120 °C, $t_{1/2} \approx 12$ h) and the complex was notably resistant to acid hydrolysis (12 M HCl, 25 °C, $t_{1/2} \approx {}^1/_2$ h).[14] X-ray structural analysis of **3** provided a rationale which adequately explained the robust nature of this trialkyl (see below).

Silox. Contrary to the observed instability of (tritox)TaX species, silox-containing tantalum complexes proved to be almost indestructable. In addition, the solubility properties of these complexes were far superior to those derived from TpO. Although direct treatment of group 5 halides with (silox)H have been reported,[9] metathetical reactions of Na(silox), prepared from NaH and the parent silanol as indicated in eq 7 (79%), were shown

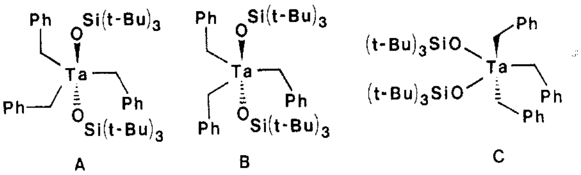

Figure 1.

$$\mathrm{(silox)H + NaH \xrightarrow[25\ ^\circ C,\ 12\ h]{THF} (silox)Na + H_2} \tag{7}$$

to be the most convenient. Additon of 2 equiv of Na(silox) to $TaCl_5$ afforded $(silox)_2TaCl_3$ (**4**) as a colorless, crystalline solid (80%, eq 8). Derivatization of **4** with MeLi yielded

$$\mathrm{2Na(silox) + TaCl_5 \xrightarrow[25\ ^\circ C,\ 12h]{toluene} \underset{\mathbf{4}}{(silox)_2TaCl_3} + 2NaCl} \tag{8}$$

$$\mathrm{\mathbf{4} + 3MeLi \xrightarrow[25\ ^\circ C,\ 2\ h]{Et_2O} \underset{\mathbf{5}}{(silox)_2TaMe_3} + 3LiCl} \tag{9}$$

$(silox)_2TaMe_3$ (**5**) according to eq 9 (66% yield). Alternatively, the trimethyl (**5**) may be prepared from Me_3TaCl_2[13] (60%) (eq 10); $(silox)_2Ta(CH_2Ph)_3$ (**6**) is sim-

$$\mathrm{R_3TaCl_2 + 2Na(silox) \xrightarrow[25\ ^\circ C,\ 24\ h]{benzene} (silox)_2TaR_3 + 2NaCl} \tag{10}$$

$$\mathbf{5},\ \mathrm{R = Me}$$
$$\mathbf{6},\ \mathrm{R = CH_2Ph}$$

ilarly synthesized from $Cl_2Ta(CH_2Ph)_3$[12] (70%). The ^1H NMR spectrum of **6** indicated the presence of three conformational isomers (5:1.1:1). Only the resonances pertaining to the major isomer could be assigned with confidence (see Table I). The minor benzylic singlets suggest that structures requiring diastereotropic methylenes may be ruled out. Figure 1 illustrates possible conformers (A, B, and C) consistent with the data. Conformer A is the most likely candidate for the major isomer since both ^1H and ^{13}C NMR manifest only one type of benzyl. Solubility problems prevented further analysis of the minor isomers by ^{13}C NMR. In an effort to establish whether the isomers interconverted, a variable-temperature NMR experiment was attempted. However, upon heating the sample, quantitative formation of $(silox)_2Ta{=}CHPh(CH_2Ph)$ (**7**) occurred concomitant with the formation of one equivalent of toluene (eq 11). This red oil (**7**) could also be prepared

$$\mathrm{\underset{\mathbf{6}}{(silox)_2Ta(CH_2Ph)_3} \xrightarrow[120\ ^\circ C]{benzene,\ \Delta} \underset{\mathbf{7}}{(silox)_2Ta{=}CHPh(CH_2Ph)} + MePh} \tag{11}$$

in an impure fashion from **4** and 3 equiv of $PhCH_2MgBr$ in THF, but in Et_2O, only the monobenzylated material $(silox)_2TaCl_2(CH_2Ph)$ (**8**) could be obtained in moderate yield (37%, eq 12). Neopentyltantalum precursors,

$$\mathrm{\underset{\mathbf{4}}{(silox)_2TaCl_3} + PhCH_2MgCl \xrightarrow[-MgCl_2]{Et_2O} \underset{\mathbf{8}}{(silox)_2TaCl_2(CH_2Ph)}} \tag{12}$$

$$\text{25 °C, 20 h}$$

$Np_{5-x}TaCl_x$ (x = 2, 3),[11] were converted to mono and bis-silox derivatives according to eq 13 (31%) and 14 (90%).

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[14] For pronounced W–C bond stability to H_2O, see: Feinstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305.

$$\mathrm{Np_3TaCl_2 + Na(silox) \xrightarrow[100\ ^\circ C,\ 18\ h]{toluene} \underset{\textbf{9}}{(silox)TaNp_3Cl} + NaCl} \quad (13)$$

$$\mathrm{Np_2TaCl_3 + 2Na(silox) \xrightarrow[25\ ^\circ C,\ 20\ h]{benzene} \underset{\textbf{10}}{(silox)_2TaNp_2Cl} + 2NaCl} \quad (14)$$

Both (silox)TaNp$_3$Cl (**9**) and (silox)$_2$TaNp$_2$Cl (**10**) serve as precursors to the neopentylidene (silox)$_2$NpTa=C(H)CMe$_3$ (**11**) via the addition of Na(silox) and NpLi (>95%, ^{1}H NMR), respectively (eq 15). The complex is

$$\left.\begin{array}{l}\mathbf{9} + \mathrm{Na(silox)} \xrightarrow[\mathrm{benzene,\ 130\ ^\circ C}]{\mathrm{-NaCl,\ NpH}} \\ \mathbf{10} + \mathrm{NpLi} \xrightarrow[\mathrm{-LiCl,\ NpH}]{\mathrm{benzene}}\end{array}\right\} \underset{\textbf{11}}{\mathrm{(silox)_2NpTa{=}C(H)CMe_3}} \quad (15)$$

routinely prepared directly from Np$_3$TaCl$_2$ and two Na(silox) (33% yield). In many of the reactions above, the low to moderate yields reflect the problems associated with crystallizing these extremely soluble materials and not difficulties inherent to the transformations themselves.

Treatment of Np$_3$Ta=C(H)CMe$_3$ with (silox)H in toluene resulted in the formation of (silox)Np$_2$Ta=C(H)CMe$_3$ (**12**) after heating (75 °C) for 48 h (eq 16). As

$$\mathrm{Np_3Ta{=}C(H)CMe_3 + \underset{Y\,=\,H,\,D}{(silox)Y} \xrightarrow[48\ h]{75\ ^\circ C} \underset{\textbf{12}}{(silox)Np_2Ta{=}C(H)CMe_3} + NpY} \quad (16)$$

indicated, when (silox)D was used, **12** contained no deuterium; Gc–mass spectral analysis of the volatiles showed that NpD had indeed formed (>90%, d_1). This silanolysis is thereby construed as occurring via direct protonolysis (deuterolysis) of a Ta–Np bond rather than by addition across the neopentylidene, followed by an α-abstraction.

NMR Spectral Data. Pertinent ^{1}H and ^{13}C NMR spectral data for compounds **4**-**12** are listed in Table I. As expected, the CH coupling constants of the crowded alkylidene alkyl complexes reflect the interactions of Cα protons with the Ta center as the Ta—C—R or Ta=C—R (R = CMe$_3$, Ph) angles become more obtuse.[15-17] For example, (silox)Np$_2$Ta=C(H)CMe$_3$ (**12**) exhibits 108 and 88 Hz ($J_{C\alpha H}$) couplings for the Np and neopentylidene ligands, respectively; the values for Np$_3$Ta=C(H)CMe$_3$ are 107 and 90 Hz.[11,15] The similarity in the coupling constants of these species apparently demonstrates the steric resemblance of Np (cone angle ≈ 120°[10]) to silox. Both (silox)$_2$NpTa=C(H)CMe$_3$ (**11**) (J_{CH} = 103 Hz (CH$_2$), J_{CH} = 95 Hz (=CH)) and (silox)$_2$Ta=CHPh(CH$_2$Ph) (**7**) (J_{CH} = 121 Hz (CH$_2$), J_{CH} = 109 Hz (=CH)) manifest analogous interactions. The lowered coupling constants of **11** relative to **7** are a consequence of the smaller size of the benzyl ligand (cone angle ≈ 109°). While the steric requirements of the ligands probably play the dominant role in establishing the Cα–H agostic interactions,[18] the electrophilicity of the Ta center also contributes. Since an R$_3$Si group can accept oxygen π-electron density, the silox ligand is not expected to be as potent a π-donor as an alkoxide, thereby enabling high electronic unsaturation of the metal center and substantial Cα–H donation.

Curiously, Cp$_2$Ta=CHPh(CH$_2$Ph)[19] does not exhibit values (J_{CH} = 123 Hz (CH$_2$), J_{CH} = 127 Hz (=CH)) paralleling those of **7** despite the contention that Cp is slightly larger than silox. Recall that the benzylidene ligand is held such that its substituents are directed toward each Cp; this "locked" position must prevent the CαH–Ta interactions prevalent for the silox species. Unfavorable steric interactions of the alkylidene substituents with the Cp ligands and the lack of available low-lying, empty Ta orbitals[20] on this electronically saturated (18 electron) complex both contribute to a diminished Cα–H donation with respect to **7**. Schrock[19] has previously noted that partial rotation (ϕ) of an alkylidene from this "locked" orientation results in a lowered J_{CH} (Cp$_2$Ta=CHR(X): R = H, X = CH$_3$, ϕ = 0 (3)°, J_{CH} = 132 Hz;[21] R = Ph, X = CH$_2$Ph, ϕ = 5.7 (5)°, J_{CH} = 127 Hz;[19] R = CMe$_3$, X = Cl, ϕ = 10.3 (5)°, J_{CH} = 121 Hz).[22] The silox ligands of **7** and **11** display equivalent resonances in both the ^{1}H and ^{13}C NMR at room temperature, indicating that the alkylidene ligand substituents either lie in the plane between the silox units or that alkylidene rotation is rapid. Low-temperature NMR experiments corroborated neither hypothesis since extensive broadening of the silox resonances due to stoppage of the *tert*-butyl rotations complicated interpretations. Calculations indicate that alkylidene rotation in such systems should have a small barrier;[23] the orbital requirements of oxygen donors are less restrictive than those of Cp, perhaps reflecting their lesser degree of π-donation to Ta. An important structural feature of Rothwell's (2,6-di-*tert*-butylphenoxide)$_2$Ta=CHSiMe$_3$(CH$_2$SiMe$_3$) complex[24] is its alkylidene unit, in which the substituents are directed toward the phenoxides, rendering these chemically inequivalent, but observed as equivalent by ^{1}H NMR. It is likely that both **7** and **11** are constrained in similar fashion.

From examination of the spectral data, it is tempting to conclude that all five-coordinate, bis(silox) complexes are tbp with axial siloxide ligation. Since no low-temperature data were obtained, fluxional square-pyramidal structures in which axial and basal sites are averaged can not be ruled out. The observed conformational isomers of (silox)$_2$Ta(CH$_2$Ph)$_3$ (**6**) suggest that such a fluxional process would be slow, but **6** may be a special case if an interlocking of the benzyl groups with the *tert*-butyl portions of the silox ligands is important. Structural studies of Ta(OAr′)$_2$Me$_3$[25] and Ta(OAr′)$_2$Cl$_3$[26] (OAr′ = 2,6-di-*tert*-butylphenoxide) reveal the tbp geometry of the former and the latter's square-pyramidal configuration, although its low-temperature ^{1}H NMR spectra indicates equivalent phenoxides. Clearly, subtle energetic differ-

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Table I. ^{1}H NMR and ^{13}C NMR Data for Silox (((CH_3)$_3$C′)$_3$SiO) Complexes (Benzene-d_6)

	^{1}H,[a] δ (#H)			^{13}C,[b] δ			
complex	(t-Bu)$_3$Si[c]	other[c]	assnmt	C[d]	C′	other	assnmt
(silox)H	1.15 (27)			31.6	23.5		
(silox)Na	1.03 (27)			29.8	22.7		
(silox)$_2$TaCl$_3$ (4)	1.19 (54)			30.0	24.9		
(silox)$_2$TaMe$_3$ (**5**)	1.23 (54)	0.90 (9)	Me	30.3	23.9	57.9	Me
(silox)$_2$Ta(CH$_2$Ph)$_3$ (**6**)	1.09 (54)	3.33 (6)	CH$_2$	30.6	24.0	82.8	CH$_2$
major		6.9–7.3	Ph			125.5	Ph
						128.5	
						131.3	
						143.2	
minors[e]	1.23	3.28	CH$_2$				
	1.24	3.17	CH$_2$				
		2.86	CH$_2$				
		6.9–7.3	Ph				
(silox)$_2$Ta=CHPh(CH$_2$Ph) (7)	1.10 (54)	3.12 (2)	CH$_2$	29.9	23.3	60.5, (J_{CH} = 121)	CH$_2$
		6.67–7.73 (10)	Ph			123.7	Ph
						124.7	
		8.42 (1)	CH			127.5	
						128.4	
						128.8	
						129.5	
						146.0	
						232.2 (J_{CH} = 109)	CH
(silox)$_2$TaCl$_2$(CH$_2$Ph) (8)	1.18 (54)	3.67 (2)	CH$_2$	30.1	24.7	125.2	Ph
		6.63–6.87 (3)	Ph			128.3	
						131.5	
		7.15–7.57 (2)	Ph			141.4	
						?	CH$_2$
(silox)TaNp$_3$Cl (**9**)[f]	1.17 (27)	1.24 (27)	t-Bu	30.3	24.0	34.5	C(CH_3)$_3$
		1.98 (6)	CH$_2$			107.1	CH$_2$
(silox)$_2$TaNp$_2$Cl (**10**)[f]	1.24 (54)	1.32 (18)	t-Bu	30.8	24.3	34.6	C(CH_3)$_3$
		2.20 (4)	CH$_2$			104.3	CH$_2$
(silox)$_2$NpTa=C(H)CMe$_3$ (**11**)[f]	1.17 (54)	1.38 (9)	t-Bu	30.2	23.5	34.7	C(CH_3)$_3$
		1.39 (9)	t-Bu			35.6	C(CH_3)$_3$
		1.84 (2)	CH$_2$			73.9 (J_{CH} = 103)	CH$_2$
		5.37 (1)	CH			234.3 (J_{CH} = 95)	CH
(silox)Np$_2$Ta=C(H)CMe$_3$ (**12**)[f,g]	1.16 (27)	1.26 (18)	t-Bu	29.9	23.3	34.8	C(CH_3)$_3$
		1.38 (9)	t-Bu	29.9	23.3	34.8	C(CH_3)$_3$
		0.42 (2, d, ^2J = 13)	CHH			97.0 (J_{CH} = 108)	CH$_2$
		1.80 (2, d, ^2J = 13)	CHH			239.5 (J_{CH} = 88)	CH

[a] Referenced to either Me$_4$Si at δ 0.00 or C$_6$D$_5$H at δ 7.15; coupling constants (J) given in Hz. [b] Referenced to C$_6$D$_6$ at δ 128.0; coupling constants given in Hz. [c] Ph resonances considered multiplets, other singlets unless noted. [d] Where applicable, J_{CH} = 125–126 Hz. [e] Assignment of minor species problematic due to overlapping silox and difficult integrations. [f] Tertiary Np and neopentylidene carbons unobserved. [g] Neopentylidene CH could not be identified with respect to trace impurities.

ences exist between these geometries.[27] In a similar manner, the spectra of (silox)TaNp$_3$Cl (**9**) may reflect either a tbp (silox, Cl$^-$ axial) or a fluxional square-pyramidal geometry.

Molecular Structure of (TpO)$_2$TaNp$_3$ (3)

Structural characterization of (TpO)$_2$TaNp$_3$ (**3**) was accomplished via standard X-ray methods (orthorhombic, $Pn2_1a$ (see Experimental Section), R = 0.054); Figure 2 depicts both a molecular view of **3** and a corresponding illustration of the effective size of the ligands surrounding the Ta through the use of appropriate van der Waals radii. This latter drawing portends the difficulties encountered by a substrate molecule that attacks the Ta center. Recall that **3** displays little reactivity with small molecules, despite being electronically unsaturated (10, 12, or 14 electrons), *if* the alkoxides can be construed as two- or four-electron donors. The neopentyl groups effectively fill the "pockets" between the phenyl portions of the 9-oxytriptycene ligands, resulting in a near-eclipsed conformation of the TpO units about this pseudo-tbp molecule. Although the TpO ligands should prefer equatorial sites or the axial site of a square pyramid[26,27] in order to maximize π-bonding interactions, such configurations would leave greater spaces between the phenyl portions of the alkoxides. The ability of small molecules, especially polar ones, to penetrate the hydrocarbon shell of **3** must be dramatically reduced by the close packing of the ligands.

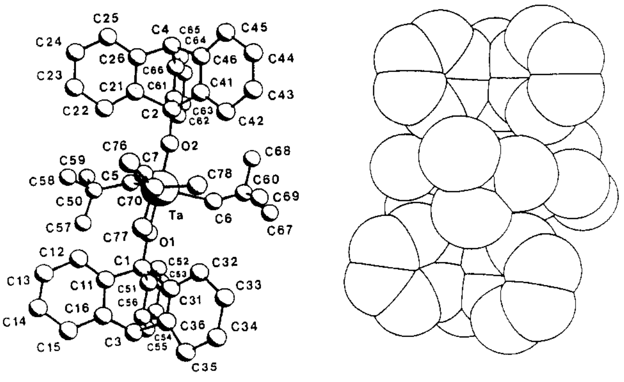

Figure 2. Molecular structure of (TpO)$_2$TaNp$_3$ (3) with accompanying space-filling view (van der Waals radii (Å): C (1.6), O (1.4), and Ta (1.9); hydrogens admitted for clarity).

Figure 3 illustrates the inner coordination sphere of (TpO)$_2$TaNp$_3$ (**3**), and Table II lists its pertinent bond distances and angles. The pseudo-tbp geometry is characterized by the near linear O–Ta–O angle (178.3 (8)°), O1–Ta–C and O2–Ta–C angles of 92.5 (31)° (average), and 87.6 (43)° (average), and the approximately trigonal ar-

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(27) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

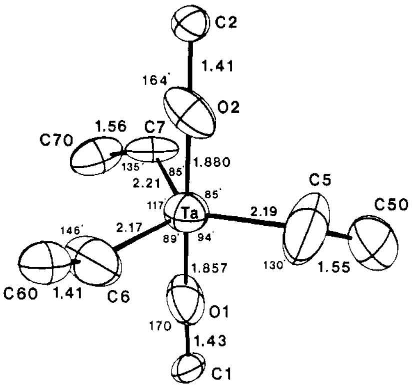

Figure 3. Inner coordination sphere of $(TpO)_2TaNp_3$ (3).

Table II. Selected Bond Distances (Å) and Angles (deg) for $(TpO)_2TaNp_3$ (3)

	Bond Distances		
Ta–O1	1.857 (10)	Ta–C5	2.186 (26)
Ta–O2	1.880 (8)	Ta–C6	2.167 (19)
		Ta–C7	2.207 (19)
O1–C1	1.430 (16)	C5–C50	1.55 (4)
O2–C2	1.411 (16)	C6–C60	1.41 (3)
		C7–C70	1.56 (3)
	Bond Angles		
O1–Ta–O2	178.3 (8)	O1–Ta–C5	93.7 (11)
Ta–O1–C1	170.3 (19)	O1–Ta–C6	89.0 (5)
Ta–O2–C2	163.9 (16)	O1–Ta–C7	94.8 (8)
C5–Ta–C6	115.0 (11)	O2–Ta–C5	85.0 (11)
C5–Ta–C7	127.3 (9)	O2–Ta–C6	92.6 (5)
C6–Ta–C7	117.0 (9)	O2–Ta–C7	85.2 (8)
Ta–C5–C50	130.0 (19)		
Ta–C6–C60	146.6 (15)		
Ta–C7–C70	135.1 (12)		

rangement of the neopentyl groups (C–Ta–C = 120 (7)° average). The pronounced linearity of the Ta–O–C angles (170.3 (19) and 163.9 (16)°) may be a consequence of the neopentyl ligands being internally "trapped" due to the clathrate-like properties of the TpO moieties. In conjunction with the short Ta–O distances (1.857 (10) and 1.880 (8) Å), this linearity may also be interpreted in terms of the substantial π-donating ability of TpO. These distances are 0.03–0.09 Å shorter than those of $Ta(OAr')_2Me_3$ (OAr′ = 2,6-di-*tert*-butylphenoxide, Ta–O = 1.930 (6) and 1.945 (6) Å) and $(Ar'O)\overline{Ta(OC_6H_3(t\text{-}Bu)CMe_2CH_2})Ph_2$ (Ta–O = 1.909 (4) and 1.926 (4) Å),[25] both pseudo-tbp complexes containing axial phenoxides. Presumably the greater steric demands or the lesser π-donating ability of the 2,6-di-*tert*-butylphenoxide ligands accounts for the difference. Both square-pyramidal $Ta(OAr')_2Cl_3$ ($Ta–O_{ax}$ = 1.836 (4), $Ta–O_{eq}$ = 1.872 (5) Å)[26] and $(Ar'O)_2Ta{=}C(H)SiMe_3(CH_2SiMe_3)$ (Ta–O = 1.854 (15), 1.845 (16) Å)[24] possess slightly shorter Ta–O distances, possibly due to the predictably greater axial π-donor phenoxide plus the electrophilic character of the former and the less sterically restrictive tetrahedral geometry of the latter.

The Ta–C bond distances (2.187 (20) Å average) of 3 are normal (Ta–C = 2.17 (6) Å average for $Ta(OAr')_2Me_3$),[25] but the accompanying Ta–C–C angles are fairly obtuse (Ta–C–C's = 130.0 (19), 146.4 (15), and 135.1 (12)°), lending credence to the congested nature of the molecule. The observed J_{CH} of 110 Hz for the α-CH_2 groups is in accord with a slight agostic interaction with the electrophilic Ta center.[15–18] Modeling the *tert*-butyl portions of the Np ligands proved to be difficult due to high thermal motion of the methyls (see Experimental Section). Examination of the triptycene portions of each alkoxide yielded no surprises; structural features paralleling those previously observed[28] are exhibited.

Conclusions

It is clear that the decomposition pathways manifested by the tritox ligand are suppressed with the utilization of either 9-oxytriptycene (TpO) or $(t\text{-}Bu)_3SiO^-$ (silox). Of the two, silox is the preferred bulky oxygen donor for several reasons. The clathrate-like behavior and poor solubility properties of TpO pose synthetic difficulties that are not easily circumvented. In addition, the planarity of the phenyl groups of TpO allows this alkoxide to react in a manner which belies its cone angle (150°). Consider the treatment of $Np_3Ta{=}C(H)CMe_3$ with each of the ligands above. Assuming the alcoholysis (or silolysis) of the Ta–Np bond is highly exothermic and that the reaction conditions reflect kinetic barriers that are predominantly steric in nature, the respective sizes of the ligands can be ordered. Note that even under extreme conditions (neat, >120 °C), (tritox)H did not react with $Np_3Ta{=}C(H)CMe_3$; presumably its bulk (cone angle ≈ 125°) prevented penetration of the complex's hydrocarbon shell. Fairly harsh conditions (75 °C, 48 h) were needed to replace one Np ligand with silox. Under no conditions could a second silox ligand be placed on the Ta via silanolysis of $(silox)Np_2Ta{=}C(H)CMe_3$ (**12**). Given Tolman's cone angle assessment of Np (120°),[10] silox may be estimated to have an effective cone angle slightly larger, but less than measured (125°). In contrast, while measurements indicate that TpO has a cone angle of about 150°, two TpO units may be attached to the Ta via alcoholysis at ambient temperatures, thus rendering this number meaningless. The unusual rigid shape and properties of TpO probably dictate how this species reacts under alcoholysis conditions, but it is safe to assume it is effectively much smaller than either tritox or silox.

One striking feature of almost all of the complexes described is their robust character; most are thermally stable to upwards of 200 °C! For example, $(silox)_2TaMe_3$ (**5**) may be heated in solution to 200 °C for 7 days without noticeable decomposition. In addition, **5**, $(silox)_2Ta{=}C(H)Ph(CH_2Ph)$ (**7**), $(silox)_2NpTa{=}C(H)CMe_3$ (**11**), and $(silox)Np_2Ta{=}C(H)CMe_3$ (**12**) are unreactive when exposed to excess PMe_3 at elevated temperatures. Although the steric problems associated with causing phosphine-promoted α-abstractions yielding methylidene, alkylidyne, or bis(neopentylidene) complexes are self-evident, it must be remembered that $NpM({=}C(H)CMe_3)_2L_2$ (M = Nb, Ta; L = PMe_3, PMe_2Ph)[29] species are generated from addition of L to $Np_3M{=}C(H)CMe_3$ under mild conditions. Chisholm[30] has annotated the observation that π-donors stabilize metal–alkyl bonds through interactions with orbitals responsible for Cα–H or Cβ–H activations. While this reasoning may hold true for **5**, **7**, and **11**, it may be unapplicable to **12**, since its J_{CH}'s are essentially the same as those of $Np_3Ta{=}(H)CMe_3$. A combination of steric and electronic arguments may be relevant in this case.

No difficulties pertaining to the displacement of silox by alkyllithiums have been encountered in any of the transformations indicated, despite the fact that a R_3SiO^- moiety may be a reasonable leaving group due to charge

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(28) (a) Iwamura, H.; Ito, T.; Ito, H.; Toriumi, K.; Kawada, Y.; Osawa, E.; Fujiyoshi, T.; Jaime, C. *J. Am. Chem. Soc.* **1984**, *106*, 4712. (b) Johnson, C. A.; Guenzi, A.; Nachbar, R. B., Jr.; Blount, J. F.; Wennerstrom, O.; Mislow, K. *Ibid.* **1982**, *104*, 5163.

(29) Fellmann, G. A.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964.

(30) Chisholm, M. H.; Tan, L.-S.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4879.

stabilization via the silicon. Groups 4[2] and 5[31] alkoxides also appear to be impervious to similar displacements. Investigations into the reactivity of these species with small molecules are currently underway.

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 hexane in order to solubilize the Na/benzophenone. Dichloromethane was distilled from CaH_2, followed by vacuum transfer from P_2O_5. Benzene-d_6, CD_2Cl_2, $CDCl_3$, and Me_2SO-d_6 were dried over activated 4-Å molecular sieves and stored under N_2. Argon was passed over MnO on vermiculite and activated 4-Å sieves. Tantalum pentachloride (Alfa) and TaF_5 (Cerac) were sublimed at 115 °C (10^{-4} torr) and 80 °C (10^{-4} torr), respectively, prior to use. Anthrone, anthranilic acid, and isoamyl nitrite (Alfa) were used as received. Tri-*tert*-butylmethanol ((tritox)H),[3] tri-*tert*-butyl silanol ((silox)H),[8] Np_2TaCl_3, Np_3TaCl_2, $Np_3Ta{=}C(H)CMe_3$,[11] Me_3TaCl_2, $TaMe_5$, and $(PhCH_2)_3TaCl_2$[12] were prepared via literature procedures.

^{1}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 instrument. Infrared spectra were run on a Perkin-Elmer 357 spectrophotometer; the spectra of the new compounds were not formally assigned, but used as fingerprints. Analyses were performed by Analytische Labortorien, Germany.

Reactions such as the treatment of Np_2TaCl_3 with (tritox)Li were conducted in sealed NMR tubes for convenient monitoring. For example, to a 5-mm NMR tube (sealed to a joint) charged with 20 mg (0.05 mmol) Np_2TaCl_3 and Li(tritox) (10 mg, 0.05 mmol) was added 0.3 mL of benzene-d_6. The solution was freeze–pump–thaw degassed, and the tube was sealed with a torch. After 12 h at 20 °C, the formation of (tritox)Np_2TaCl_2 (**1**) was tentatively noted by ^{1}H NMR: δ 2.67 (s, 4 H, $TaCH_2$), 1.43 (s, 27 H, $(t\text{-Bu})_3C$), 1.36 (s, 18 H, Np). At this time, **1** is approximately the concentration of starting Np_2TaCl_3. Over the course of 50 h, the resonances corresponding to **1** gradually decrease in intensity as a number of unidentifiable decomposition products, as well as NpH and leftover Np_2TaCl_3, grow in.

Procedures. 1. 9-Anthrol Acetate. To a flask containing 500 mL of THF at 25 °C was added 7.30 g of KH (0.182 mol), followed by slow addition of anthrone (34.9 g, 0.180 mol). Acetyl chloride (13.2 mL, 0.185 mol) was added via syringe over a 10-min period. The THF was stripped, the residue dissolved in toluene, and the KCl removed by filtration. The toluene was rotovapped off, and the crude product was recrystallized from ethanol to provide 34.5 g of pale yellow needles [81%, mp 133–135 °C (lit.[32] 133–134 °C)]: ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 3 H, CH_3), 7.30–7.55 (m, 4 H, Ph), 7.75–8.00 (m, 4 H, Ph), 8.23 (s, 1 H, CH).

2. 9-Acetyltriptycene (TpOAc). Fieser's preparation of triptycene[33] was followed by using the following amounts: 10.0 g of 9-anthrol acetate (42.4 mmol), 14.9 of isoamyl nitrite (127 mmol), and 11.6 g of anthranilic acid (84.7 mmol) dissolved in 70 mL of DME added over a 6-h period. The maleic anhydride treatment was not used. The crude orange solid obtained (6.5 g) was decolorized in CH_2Cl_2 and recrystallized from CH_2Cl_2/methanol to give 4.4 g of pale orange crystals (33%): ^{1}H NMR ($CDCl_3$) δ 2.62 (s, 3 H, CH_3), 5.33 (s, 1 H, CH), 6.90–7.20 (m, 6 H, Ph), 7.25–7.50 (m, 6 H, Ph).

3. 9-Hydroxytriptycene (TpOH). TpOAc (10.0 g, 32 mmol) was refluxed in 100 mL of 8 N KOH and 200 mL of MeOH for 3 h. The solution was allowed to cool slowly to 25 °C and the greenish precipitate collected by filtration. The solid was dissolved in CH_2Cl_2 and treated with decolorizing carbon. The decolorized material was recrystallized from toluene/heptane to yield 7.0 g of colorless prisms (81%): ^{1}H NMR ($CDCl_3$) δ 3.51 (s, 1 H, OH), 5.50 (s, 1 H, CH), 6.95–7.25 (m, 6 H, Ph), 7.4–7.75 (m, 6 H, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 125.5, 125.1, 123.2, 118.9 (=CH), 145.8, 143.7 (C), 80.7 (CO), 52.8 (CH).

4. TpOLi·Et$_2$O. To a flask containing TpOH (1.7 g, 6.3 mmol) was added 50 mL of Et_2O at −78 °C followed by 4.3 mL of 1.5 M MeLi in Et_2O (6.5 mmol). The reaction was allowed to warm to and stir at 25 °C for 12 h. The solution was reduced in volume to 15 mL, cooled to −78 °C, and filtered to collect 1.95 g of white powder (88%): ^{1}H NMR (CD_2Cl_2) δ 8.23 (d (J = 6.9 Hz), 3 H, =CH), 7.20 (d (J = 7.6), 3 H, =CH), 6.75 ("t" (J = 7.2), 3 H, =CH), 6.45 ("t" (J = 7.2), 3 H, =CH), 5.21 (s, 1 H, CH), 2.93 (q, 4 H, $CH_2(Et_2O)$), 0.77 (t (J = 7.0), 6 H, $CH_3(Et_2O)$); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 124.3 (2 C's), 122.4, 120.3 (=CH), 151.3, 144.5 (C), 83.4 (CO), 53.0 (CH), 64.6 ($CH_2(Et_2O)$), 14.2 ($CH_3(Et_2O)$).

5. TpOSiMe$_3$. To a 50-mL glass bomb containing TpOLi·Et$_2$O (2.0 g, 5.7 mmol) were distilled 20 mL of benzene and 4 mL of Me_3SiCl (excess) at −78 °C. The bomb was closed and heated at 90 °C for 2 days. The contents of the bomb were then transferred to a 50-mL flask. This slurry was filtered to remove LiCl and the volume of the filtrate reduced to 3 mL. A thick slurry of colorless crystals precipitated upon addition of 5 mL of hexane. Collection via filtration, washing with a 2-mL portion of cold hexane, and vacuum drying yielded 1.62 g of TpOSiMe$_3$ (83%): ^{1}H NMR (C_6D_6) δ 7.73–7.57 (m, 3 H, Ph), 7.27–7.03 (m, 3 H, Ph), 6.96–6.93 (m, 6 H, Ph), 5.07 (s, 1 H, CH), 0.49 (s, 9 H, $Si(CH_3)_3$).

6. (TpO)$_2$TaCl$_3$, 2. To a 50-mL flask containing TpOSiMe$_3$ (500 mg, 1.46 mmol) and $TaCl_5$ (262 mg, 0.732 mmol) was added 15 mL of benzene. The mixture was allowed to stir at 25 °C for 24 h, during which time a brown solid separated from solution. The solid was collected by filtration, washed with a 5-mL portion of benzene, and dried to yield 720 mg of light tan powder (119%). ^{1}H NMR showed a large amount of benzene was associated with **2**. Further drying (4 h, 10^{-4} torr) reduced the sample weight to 650 mg (107%, based on $(TpO)_2TaCl_3$ (**2**)): ^{1}H NMR (Me_2SO-d_6) δ 8.83 (dd (J = 7, 15 Hz), 3 H, =CH), 7.34 (d (J = 7), 3 H, =CH), 7.28 (s, variable amounts, C_6H_6), 6.86 (d (J = 7), 3 H, =CH), 6.55 (dd (J = 7, 15), 3 H, =CH), 5.52 (s, 1 H, CH); ^{13}C{^{1}H} NMR (Me_2SO-d_6) δ 125.5, 124.1, 123.2, 121.6 (=CH), 145.1, 142.8 (C), 128.2 (C_6H_6), 96.0 (CO), 51.2 (CH).

7. (TpO)$_2$TaNp$_3$, 3. To a flask containing $Np_3Ta{=}C(H)CMe_3$ (1.00 g, 2.15 mmol) and TpOH (1.16 g, 4.30 mmol) was added 15 mL of benzene. The reaction mixture was stirred for 2 days at 25 °C, during which time a tan solid separated from the orange solution. The solid was collected by filtration and then recrystallized from CH_2Cl_2/toluene to give 1.58 g of white product (79%): ^{1}H NMR (CD_2Cl_2) δ 8.14 (m, 6 H, =CH), 7.54 (m, 6 H, =CH), 7.20 (m, 12 H, =CH), 5.55 (s, 2 H, CH), 2.25 (s, 6 H, $TaCH_2$), 1.11 (s, 27 H, $C(CH_3)_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 126.1, 124.3, 123.8, 123.6 (=CH), 145.5, 144.0 (C), 100.3 ($TaCH_2$), 94.0 (CO), 53.4 (CH), 36.6 ($C(CH_3)_3$), 35.3 ($C(CH_3)_3$). Anal. Calcd for $C_{55}H_{58}O_2Ta$: C, 70.80; H, 6.37. Found: C, 70.91; H, 6.39.

8. Na(silox). To a slurry of NaH (1.00 g, 0.0417 mol) in 50 mL of THF at −78 °C was added (silox)H (8.8 g, 0.041 mol, dissolved in Et_2O). The reaction mixture was allowed to slowly warm to 25 °C and stirred for an additional 12 h to yield a clear colorless solution and a few particles of unreacted NaH. The solution was reduced in volume to 40 mL, filtered, further reduced by 20 mL, and cooled to −78 °C. The resulting crystals were collected by filtration and vacuum dried to yield a white powder (7.7 g, 79%).

9. (silox)$_2$TaCl$_3$, 4. To a flask containing Na(silox) (5.00 g, 21.0 mmol) and $TaCl_5$ (3.76 g, 10.5 mmol) was added 80 mL of toluene at −78 °C. The resulting yellow suspension was allowed to warm and stir at 25 °C for 12 h to give a clear colorless solution. The toluene was removed in vacuo, and 40 mL of hexane was added to the resulting solid. After filtration and eight 30 mL of hexane washes of the residual, the filtrate was reduced to 20 mL and cooled to −78 °C. Colorless crystals were collected via filtration and washed once with 5 mL of cold hexane (6.01 g, 80%). Anal. Calcd for $C_{24}H_{54}O_2Si_2Cl_3Ta$: C, 40.14; H, 7.58. Found: C, 40.18; H, 7.45.

10. (silox)$_2$TaMe$_3$, 5. (a) To a flask containing Me_3TaCl_2 (1.00 g, 3.37 mmol) and Na(silox) (1.61 g, 6.76 mmol) was added 80 mL of toluene at −78 °C. The mixture was allowed to warm and stir at 25 °C for 24 h, producing a dark brown solution. The toluene

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[31] Chamberlain, L.; Keddington, J.; Rothwell, I. P. *Organometallics* **1982**, *1*, 1098.

[32] Fieser, L. F.; Putnam, S. T. *J. Am. Chem. Soc.* **1947**, *69*, 1038.

[33] Fieser, L. F. "Organic Experiments"; D. C. Heath: New York, 1964; p 315.

was removed, 30 mL of hexane added, and the resulting mixture filtered to give a brown solid and a brown solution. The solid was extracted with five 20-mL portions of hexane. The filtrate and extracts were reduced in volume to 10 mL and filtered and the white, crystalline product washed with two 2-mL portions of cold hexane to afford 1.34 g (60%). **(b)** To a flask containing (silox)$_2$TaCl$_3$ (**4**, 200 mg, 0.279 mmol) in 30 mL of Et$_2$O was added 0.56 mL of 1.5 M MeLi (0.84 mmol) in ether at −78 °C. The reaction mixture was allowed to warm and stir for 2 h at 25 °C. The ether was stripped, and 15 mL of hexane was added to yield a colorless solution. Isolation was as in (a) (120 mg, 66%). Anal. Calcd for $C_{27}H_{62}O_2Si_2Ta$: C, 49.37; H, 9.67. Found: C, 49.20; H, 9.52.

11. (silox)$_2$Ta(CH$_2$Ph)$_3$, 6. To a flask containing Cl$_2$Ta(CH$_2$Ph)$_3$ (1.00 g, 1.90 mmol) and Na(silox) (0.904 g, 3.80 mmol) was added 20 mL of benzene. After stirring the mixture for 24 h at 25 °C, a colorless solid had precipitated from the orange/brown solution. The benzene was removed, 15 mL of hexane was added, and the resulting slurry was filtered to provide a white solid and a brownish solution. After the solid was extracted with 15 10-mL portions of hexane and the filtrate volume was reduced to 5 mL, opalescent white flakes were collected via filtration and washed with two 2-mL portions of cold hexane to yield 1.06 g (62%). Analysis was consistent with (silox)$_2$Ta=CHPh(CH$_2$Ph) (**7**), indicating that **6** is somewhat thermally sensitive.

12. (silox)$_2$Ta=CHPh(CH$_2$Ph), 7. To a 5-mL glass bulb equipped with a needle valve was added (silox)$_2$Ta(CH$_2$Ph)$_3$ (**6**, 200 mg, 0.224 mmol) and 2 mL of benzene. The reactor was heated at 125 °C for 36 h and the solvent removed to yield **7** as a dark red oil. No further purification was needed. Anal. Calcd for $C_{38}H_{67}O_2Si_2Ta$: C, 57.55; H, 8.51. Found: C, 57.64; H, 8.39.

13. (silox)$_2$TaCl$_2$(CH$_2$Ph), 8. To a flask containing (silox)$_2$TaCl$_3$ (**4**, 300 mg, 0.418 mmol) was added 30 mL of Et$_2$O at −78 °C followed by 0.65 mL of PhCH$_2$MgCl (2.0 M, 1.3 mmol in THF). Upon warming and stirring for 20 h at 25 °C, a canary yellow solution was produced. The solvent was removed, and 10 mL of hexane was distilled in. A white solid was removed by filtration, and the volume of the filtrate was reduced to 2 mL. Cooling this solution to −78 °C resulted in the formation of yellow crystals which were collected by filtration and washed with 1 mL of cold hexane to afford 120 mg of **8** (37%). Anal. Calcd for $C_{31}H_{61}O_2Si_2Cl_2Ta$: C, 48.12; H, 7.94. Found: C, 48.13; H, 7.81.

14. (silox)TaNp$_3$Cl, 9. To a small glass bulb sealed to a joint were added Np$_3$TaCl$_2$ (930 mg, 2.00 mmol), Na(silox) (476 mg, 2.00 mmol), and 5 mL of toluene. The reactor was degassed, sealed with a torch, and placed in a 100 °C bath for 18 h. The bomb was then opened and the contents transferred to a flask. The toluene was removed, 15 mL of hexane was distilled in, and the resulting suspension was filtered to give a colorless solid and yellow solution. The filtrate was reduced in volume to 2 mL and cooled to −78 °C, and the white crystals were collected by filtration. After the solution was washed with two 1-mL portions of cold hexane and drying in vacuo, 400 mg of **9** remained (31%). Anal. Calcd for $C_{27}H_{60}OSiClTa$: C, 50.26; H, 9.37. Found: C, 50.28; H, 9.32.

15. (silox)$_2$TaNp$_2$Cl, 10. To a flask containing Np$_2$TaCl$_3$ (410 mg, 0.956 mmol) and Na(silox) (455 mg, 1.91 mmol) was added 10 mL of benzene. The mixture was allowed to stir at 25 °C for 20 h. The benzene was replaced with 10 mL of hexane and the resulting slurry filtered, resulting in a white solid and yellow-orange filtrate. Removal of the hexane yielded 700 mg of waxy orange solid **10** (93%). This material could not be further purified (~90% **10** by ^{1}H NMR, ~5% Np$_2$TaCl$_3$) due to extreme solubility.

16. (silox)$_2$NpTa=C(H)CMe$_3$, 11. To a 50-mL bomb reactor containing Np$_3$TaCl$_2$ (465 mg, 1.00 mmol) and Na(silox) (476 mg, 2.00 mmol) was added 5 mL of benzene. The reaction was stirred at 60 °C for 2 days and an additional 14 days at 120 °C. The dark brown solution was transferred to a sublimator, the solvent was removed, and the residue was sublimed at 110 °C (10^{-4} torr) to produce 250 mg of waxy yellow crystals (33%). The addition of three NpLi to (silox)$_2$TaCl$_3$ (**4**) also produced **11** (70% by ^{1}H NMR) but purification proved too difficult. Anal. Calcd for $C_{34}H_{75}O_2Si_2Ta$: C, 54.23; H, 10.04. Found: C, 54.13; H, 9.97.

17. (silox)Np$_2$Ta=C(H)CMe$_3$, 12. To a 10-mL glass bulb sealed to a joint was added Np$_3$Ta=C(H)CMe$_3$ (465 mg, 1.00 mmol), (silox)H (216 mg, 1.00 mmol), and 2 mL of toluene. The bulb was degassed and sealed with a torch. The reactor was heated at 75 °C for 2 days, the resulting brown solution transferred to a sublimator, the solvent stripped, and the residue sublimed at 100 °C (10^{-4} torr) for 1 day to afford 500 mg waxy orange solid (82%). Anal. Calcd for $C_{27}H_{59}OSiTa$: C, 53.27; H, 9.77. Found: C, 53.05; H, 9.60.

Table III. Fractional Coordinates and Thermal Parameters[a] for (TpO)$_2$TaNp$_3$ (3)

atom	x	y	z	B,[a] Å^2
Ta	0.2768 (0)	0.7495 (4)	0.5084 (0)	4.9 (1)
O1	0.2441 (6)	0.7493 (20)	0.4251 (4)	5.5 (5)
Cl	0.2284 (10)	0.7627 (24)	0.3598 (6)	3.6 (7)
C3	0.1992 (10)	0.7560 (27)	0.2401 (6)	4.6 (7)
C11	0.1349 (9)	0.7587 (30)	0.3438 (6)	4.2 (7)
C12	0.0696 (10)	0.7417 (32)	0.3867 (7)	6.0 (9)
Cl3	−0.0131 (11)	0.7404 (36)	0.3646 (8)	6.6 (10)
Cl4	−0.0283 (9)	0.7488 (34)	0.3027 (8)	6.1 (9)
Cl5	0.0368 (11)	0.7360 (23)	0.2584 (7)	5.5 (10)
Cl6	0.103 (10)	0.7353 (17)	0.2792 (6)	2.8 (8)
C31	0.2650 (11)	0.6616 (13)	0.3246 (7)	4.9 (8)
C32	0.3140 (14)	0.5940 (16)	0.3551 (11)	7.3 (12)
C33	0.3451 (14)	0.5175 (15)	0.3129 (11)	7.1 (13)
C34	0.3228 (14)	0.5185 (17)	0.2456 (12)	7.2 (11)
C35	0.2717 (13)	0.5897 (15)	0.2164 (12)	6.8 (12)
C36	0.2523 (12)	0.6602 (13)	0.2653 (9)	5.6 (10)
C51	0.2647 (10)	0.8383 (12)	0.3244 (8)	4.3 (8)
C52	0.3156 (10)	0.9149 (12)	0.3466 (7)	4.0 (7)
C53	0.3443 (13)	0.9889 (15)	0.3124 (9)	6.4 (11)
C54	0.3267 (13)	0.9896 (14)	0.2507 (10)	6.5 (11)
C55	0.2779 (11)	0.9150 (15)	0.2255 (7)	5.2 (9)
C56	0.2452 (10)	0.8362 (12)	0.2585 (8)	4.4 (8)
O2	0.3072 (5)	0.7522 (20)	0.5933 (4)	5.0 (5)
C2	0.3112 (10)	0.7356 (23)	0.6584 (5)	3.6 (7)
C4	0.3207 (10)	0.7474 (33)	0.7810 (5)	5.1 (7)
C21	0.2239 (9)	0.7468 (27)	0.6921 (6)	3.7 (6)
C22	0.1486 (9)	0.7553 (34)	0.6624 (7)	4.8 (7)
C23	0.0752 (10)	0.7412 (39)	0.6993 (7)	6.2 (8)
C24	0.0826 (11)	0.7498 (31)	0.7650 (8)	5.8 (8)
C25	0.1608 (10)	0.7433 (35)	0.7943 (7)	5.4 (8)
C26	0.2311 (9)	0.7388 (30)	0.7568 (7)	4.7 (7)
C41	0.3604 (10)	0.6623 (13)	0.6838 (7)	4.6 (8)
C42	0.3938 (12)	0.5868 (15)	0.6425 (9)	6.5 (11)
C43	0.4309 (15)	0.5067 (16)	0.6765 (10)	7.6 (13)
C44	0.4346 (13)	0.5067 (12)	0.7411 (11)	5.3 (11)
C45	0.4007 (12)	0.5869 (12)	0.7867 (9)	5.1 (9)
C46	0.3639 (11)	0.6586 (12)	0.7511 (7)	4.2 (7)
C61	0.3527 (11)	0.8425 (12)	0.6872 (7)	4.3 (8)
C62	0.3879 (9)	0.9201 (12)	0.6583 (6)	3.6 (7)
C63	0.4282 (12)	0.9916 (13)	0.6882 (8)	5.0 (9)
C64	0.4353 (12)	0.9889 (16)	0.7536 (8)	6.2 (10)
C65	0.4006 (12)	0.9168 (15)	0.7795 (8)	5.7 (10)
C66	0.3587 (11)	0.8363 (12)	0.7499 (8)	4.9 (8)
C5	0.2468 (19)	0.9048 (19)	0.5217 (13)	8.2 (14)
C50	0.1640 (21)	0.9609 (20)	0.5101 (9)	8.3 (14)
C57	0.1342 (13)	0.9698 (17)	0.4449 (9)	7.2 (12)
C58	0.0861 (19)	0.9078 (35)	0.5381 (17)	13.6 (25)
C59	0.1702 (33)	1.0618 (34)	0.5396 (21)	15.0 (27)
C6	0.4036 (11)	0.7200 (20)	0.4786 (7)	6.4 (12)
C60	0.4893 (11)	0.7299 (24)	0.4925 (6)	4.8 (10)
C67	0.5564 (14)	0.7235 (36)	0.4513 (9)	9.0 (16)
C68	0.5193 (11)	0.7369 (33)	0.5597 (7)	6.5 (11)
C69	0.4844 (20)	0.6211 (24)	0.4832 (11)	9.3 (16)
C7	0.1995 (11)	0.6217 (15)	0.5346 (7)	4.6 (8)
C70	0.1891 (16)	0.5149 (17)	0.5094 (8)	6.3 (10)
C77	0.1583 (13)	0.5075 (17)	0.4434 (8)	6.5 (11)
C78	0.2706 (14)	0.4636 (22)	0.5101 (10)	7.4 (13)
C79	0.1248 (15)	0.4664 (20)	0.5517 (9)	8.0 (14)

[a] From the anisotropic thermal parameters in the form exp$[-(h^2\beta_{11} + k^2\beta_{22} + 1^2\beta_{33} + 2hk\beta_{12} + 2hl\beta13 + 2kl\beta_{23})]$, the B(equivalent)'s are derived: $B(\mathrm{equiv}) = 4.0\ [V^2 \det(\beta_{ij})]^{1/3}$.

18. Reaction of Np$_3$Ta=C(H)CMe$_3$ with (silox)D. To a 50-mL glass bomb reactor holding (silox)D (217 mg, 1.00 mmol, prepared from Na(silox) and D$_2$O in a D$_2$O washed vessel and purified by 60 °C (10^{-4} torr) sublimation) and Np$_3$Ta=C(H)CMe$_3$ (465 mg, 1.00 mmol) was added 5 mL of toluene. The bomb was degassed, closed, and placed in a 75 °C bath for 3 days. The volatiles were then vacuum transferred, and a 1-mL aliquot was removed and submitted for GC–MS analysis. Sublimation yielded 470 mg of **12** (77%).

Single-Crystal X-ray Diffraction Analysis of $(TpO)_2TaNp_3$ (3). Slow evaporation of a toluene solution containing $(TpO)_2TaNp_3$ (**3**) at 25 °C produced several clear, colorless crystals, from which an irregularly shaped one, roughly 0.3 × 0.2 × 0.2 mm, was selected and sealed in a thin-walled capillary. Preliminary X-ray diffraction photographs displayed orthorhombic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer measured 2θ values at 25 °C, were $a = 16.024$ (2) Å, $b = 13.607$ (4) Å, and $c = 21.377$ (1) Å. The cell volume is 4661.0 Å^3 with calculated density of 1.329 g/cm^3 ($Z = 4$). All unique diffraction maxima ($+h,+k,+l$) 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 K$\bar{\alpha}$ radiation (0.71069 Å). After correction for Lorentz, polarization, and background effects, 2651 (71%) of the 3750 reflections collected were judged observed ($|F_o| \geq 3\sigma(F_o)$).[34] Systematic extinctions were consistent with either *Pnma* or $Pn2_1a$. The Ta was positioned from a Patterson synthesis.[35] Assuming space group *Pnma*, all non-hydrogen light atoms, except those in the Np groups, were revealed in successive Fourier syntheses. Locating the Np groups in the electron density syntheses proved difficult thereby prompting consideration of the alternate space group. In space group $Pn2_1a$, these remaining non-hydrogen light atoms were easily located. Block-diagonal least-squares refinements in $Pn2_1a$ (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 58 anisotropic non-hydrogen atoms, and all hydrogen atoms included at calculated positions, have converged to a residual (R) of 0.054 and a weighted residual (R_w) of 0.059 for the indicated reflections.[36] The fractional coordinates and thermal parameters are listed in Table III. A refinement in *Pnma* was carried out for comparison ($R = 0.064$, $R_w = 0.069$) with that of $Pn2_1a$ (alternate setting of $Pna2_1$). The results of a Hamilton's test[37] indicated that the difference in R_w's is significant to the 0.005 level; statistically, $Pn2_1a$ was concluded to be the correct space group.

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Registry No. **1**, 97733-25-0; **2**, 97749-47-8; **3**, 97733-15-8; **4**, 97733-17-0; **5**, 97733-18-1; **6**, 97733-19-2; **7**, 97733-20-5; **8**, 97749-48-9; **9**, 97733-21-6; **10**, 97733-22-7; **11**, 97733-23-8; **12**, 97733-24-9; TpOAc, 97733-14-7; TpOH, 73597-16-7; $TpOSiMe_3$, 97749-46-7; (silox)H, 56889-90-8; Na(silox), 97733-16-9; (silox)D, 97733-26-1; (tritox)Li, 89958-97-4; NpLi, 7412-67-1; $TpOLi{\cdot}Et_2O$, 97749-45-6; $TaCl_5$, 7721-01-9; $Np_3Ta{=}C(H)CMe_3$, 54294-45-0; Me_3TaCl_2, 3020-02-8; $Cl_2Ta(CH_2Ph)_3$, 59326-13-5; Np_3TaCl_2, 38010-73-0; Np_2TaCl_3, 61645-40-7; anthrone, 90-44-8; 9-anthrol acetate, 1499-12-3; anthranilic acid, 118-92-3.

Supplementary Material Available: Tables of bond distances, bond angles, observed and calculated structure factors, fractional coordinates, and thermal parameters and a thermal ellipsoid skeletal drawing showing the entire neopentyl groups (22 pages). Ordering information is given on any current masthead page.

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(34) 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.

(35) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(36) $R = \sum||F_o| - |F_c||/(\sum|F_o|)$; $R_w = \{\sum w|F_o| - |F_c|)^2/(\sum w|F_o|_2\}^{1/2}$.

(37) Hamilton, W. C. "Statistics in Physical Science"; Ronald Press: New York, 1964.