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Article

A New Route to Chelating Bis(aryloxide) Ligands and Their Applications to Tantalum and Titanium Organometallic Compounds[†]

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A new route to sterically tuned, chelating bis(aryloxide) ligands is described and demonstrated by the synthesis of 2,2′-ethylenebis(6-isopropylphenol) (**1**, H_2BIPP) and transition metal complexes of its dianion. The utility of these ligands in titanium and tantalum organometallic chemistry is shown in the alkylation of (BIPP)$TiCl_2$ (**7**) to form (BIPP)$TiMe_2$ (**8**) and (BIPP)$Ti(CH_2Ph)_2$ (**9**) and in the alkylation of (BIPP)$TaCl_3$ (**10**) and its base adducts to form (BIPP)$TaMe_3$ (**14**) and (BIPP)$Ta(CH_2Ph)_3$ (**13**). Structural comparisons of the chelating 2,2′-ethylenebis(6-isopropylphenoxide) (BIPP) ligand with its analogous, nonchelating bis(2,6-dialkylaryloxide) ligand set are examined in the X-ray diffraction studies of (BIPP)$TaCl_3$(THF)·THF (**11**·THF) and (BIPP)$Ta(CH_2C_6H_5)_3$ (**13**).

Introduction

Despite the abundance of aryloxide ligands throughout transition metal chemistry,[1] there are relatively few examples of chelating bis(aryloxide) ligands and even fewer instances of chelating bis(aryloxide) ligands with ethylene-bridged aryl rings. Okuda and co-workers have demonstrated that ethylene-bridged 2,2′-ethylenebis(6-*tert*-butyl-4-methylphenol) (ebmpH_2) is useful in the polymerization of ethylene when bound to titanium.[2] In addition to its potential general utility as a ligand for Lewis acid catalysts, we envision ethylene-bridged bis(aryloxide) ligands as playing an important role in circumventing the problems associated with cyclometalation of certain 2,6-dialkylaryloxide ligands.[3−8] Cyclometalation of an *ortho*-alkyl group of such ligands is not uncommon upon reducing d^0 group 5 transition metal complexes with ancillary 2,6-dialkylaryloxide ligands.

In our preparative approach to certain d^2 niobium and tantalum bis(2,6-diisopropylaryloxide) complexes, we also encountered cyclometalation reactivity of the isopropyl groups on these ligands and thus set out to design chelating ligands with steric and electronic properties similar to those of the bis(2,6-diisopropylaryloxide) ligand set but with potentially lower cyclometalation reactivity. In this report, we describe the synthesis of an ethylene-linked bis(aryloxide) ligand and the preparation and properties of some of its complexes of tantalum and titanium.

Results and Discussion

Synthesis of 2,2′-Ethylenebis(6-isopropylphenol) (1, H_2BIPP). The synthesis of 2,2′-ethylenebis(6-isopropylphenol), abbreviated H_2BIPP, is summarized in Scheme 1. We envisioned a synthetic approach that would allow for a sterically tunable and inexpensive ethylene-linked bis(aryloxide) ligand. Accordingly, this synthesis was accomplished starting with a 2-substituted phenol, which allows the preparation of chelating analogues of the analogous bis(2,6-dialklaryloxide) ligand set. This approach was developed using the isopropyl-substituted material, 2-isopropylphenol, but other 2-alkylphenols can be used (e.g. 2-*tert*-butylphenol) to afford a variety of substituted bis(phenol) ligands.

The alcohol was protected as a methoxy group via deprotonation with potassium, followed by quenching with

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(1) For a comprehensive review of transition metal aryloxide chemistry, see: Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: San Diego, CA, 2001.

(2) Fokken, S.; Spaniol, T. P.; Okuda, J.; Sernetz, F. G.; Muelhaupt, R. *Organometallics* **1997**, *16*, 4240−4242.

(3) Mulford, D. R.; Clark, J. R.; Schweiger, S. W.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 4448−4458.

(4) Steffey, B. D.; Chamberlain, L. R.; Chesnut, R. W.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1989**, *8*, 1419−1423.

(5) Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. P.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6471−6478.

(6) Chesnut, R. W.; Steffy, B. D.; Rothwell, I. P. *Polyhedron* **1988**, *9*, 753−756.

(7) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 4611−4621.

(8) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 9632−9633.

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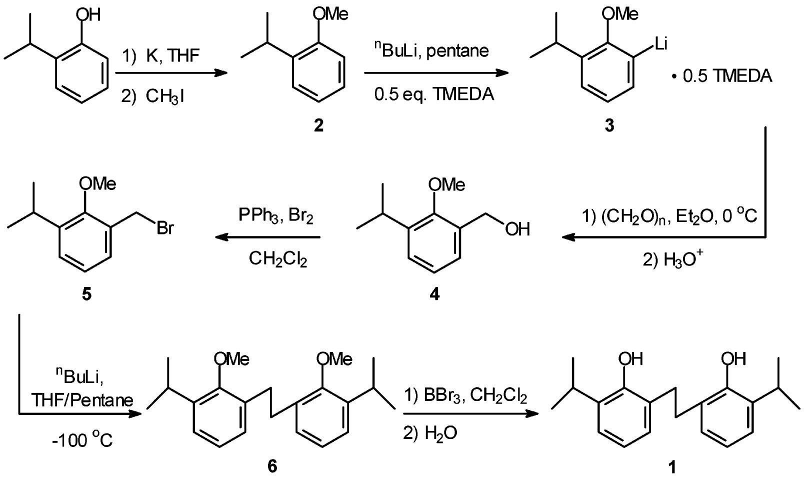
Scheme 1

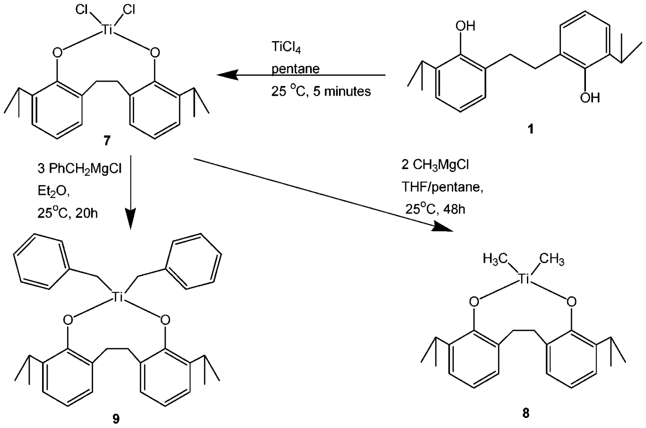


methyl iodide to provide 2-isopropylanisol (**2**) in 87% yield. The methoxy protecting group was used because of its robust nature, and the final product allows for the harsh cleaving conditions required to remove it. The *ortho*-lithiated product (3-isopropyl-2-methoxyphenyl)lithium·0.5TMEDA (**3**) was synthesized from **2** using *n*-butyllithium under standard conditions.[9,10] Compound **3** was isolated as a white powder and was stable indefinitely at room temperature under a nitrogen atmosphere. The isolation of **3** was not necessary for the effective synthesis of H_2BIPP (**1**), as **3** could be converted to the benzyl alcohol **4** in situ. However, the utility of **3** for other ligand preparations and its thermal stability resulted in its isolation as the standard synthetic procedure.

The benzyl alcohol **4** was synthesized from **3** upon its reaction with paraformaldehyde, following an acid workup, which afforded 2-(hydroxymethyl)-6-isopropylanisole (**4**) in high (81%) yield. Bromination of the benzyl alcohol with bromine/triphenylphosphine was effected under standard conditions to provide 2-(bromomethyl)-6-isopropylanisole (**5**) in 86% yield.[11] We found that the workup of **5** was best carried out while being stirred rapidly with a mechanical stirrer to minimize the size of the triphenylphosphine oxide clumps that precipitated during this procedure. 2,2′-Ethylenebis(6-isopropylanisole) (Me_2BIPP, **6**) was synthesized through the low-temperature homocoupling of **5** with *n*-butyllithium. Compound **6** was then deprotected using boron tribromide, followed by an acidic workup, to yield 2,2′-ethylenebis(6-isopropylphenol) (**1**, H_2BIPP) in an overall yield of 44.3% for the six-step synthesis.

Transition Metal−BIPP Complexes. To examine the chelating bis(aryloxide) compound and compare it structurally with the analogous bis(2,6-diisopropylphenoxide) ligand set which has shown considerable utility,[12−19] we prepared both tantalum and titanium compounds of this ligand from their respective d^0 halides. Scheme 2 outlines reactions to form the titanium BIPP complexes. The titanium complex (BIPP)$TiCl_2$ (**7**) was synthesized by the method of Okuda and co-workers,[2] by adding a solution of H_2BIPP (**1**) in pentane to a concentrated solution of titanium tetrachloride in pentane at room temperature. The product precipitated from the reaction solution as a dark red solid within seconds of adding the ligand. Filtration of the precipitate afforded analytically pure product with no further purification required. Compound **7** was soluble in several organic solvents including pentane, from which crystals could be grown. Reacting **7** with the methyl and benzyl Grignards afforded (BIPP)$TiMe_2$ (**8**) and (BIPP)$Ti(CH_2C_6H_5)_2$ (**9**), respectively, in moderate yields as highly soluble red to orange solids.

Scheme 2



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[9] Filippov, I. *Metal-Mediated Hydrodenitrogenation Catalysis: Designing New Models*; Ph.D. Dissertation; University of Arizona: Tucson, AZ, 1998; p 218.

[10] Graybill, B. M.; Shirley, D. A. *J. Org. Chem.* **1966**, *31*, 1221−1224.

[11] Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964−965.

[12] Fox, P. A.; Bruck, M. A.; Gray, S. D.; Gruhn, N. E.; Grittini, C.; Wigley, D. E. *Organometallics* **1998**, *17*, 2120.

[13] Weller, K. J.; Filippov, I.; Briggs, P. M.; Wigley, D. E. *Organometallics* **1998**, *17*, 322.

[14] Weller, K. J.; Fox, P. A.; Gray, S. D.; Wigley, D. E. *Polyhedron* **1997**, *16*, 3139.

[15] Weller, K. J.; Filippov, I.; Briggs, P. M.; Wigley, D. E. *J. Organomet. Chem.* **1997**, *528*, 225.

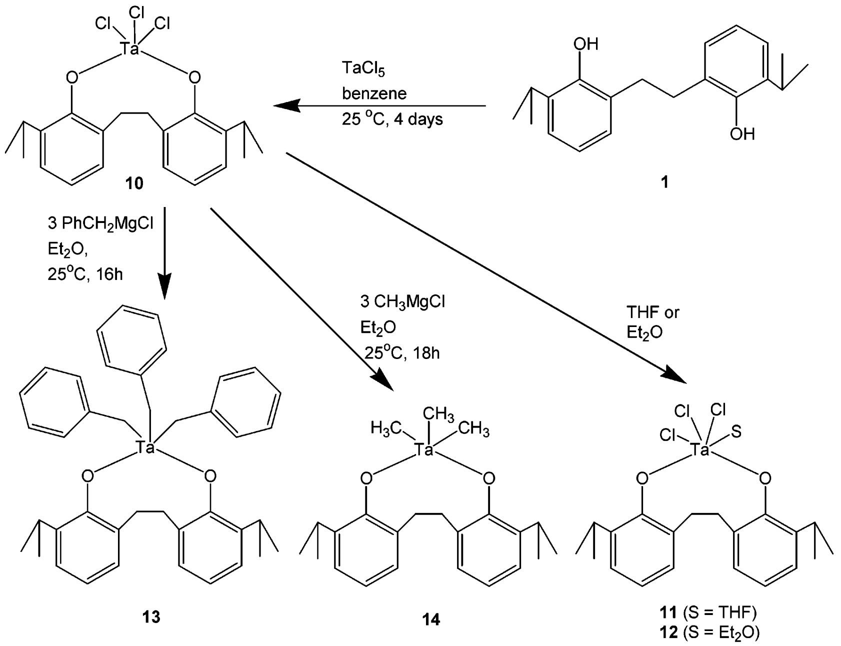
[16] Weller, K. J.; Gray, S. D.; Briggs, P. M.; Wigley, D. E. *Organometallics* **1995**, *14*, 5588.

[17] Gray, S. D.; Weller, K. J.; Bruck, M. A.; Briggs, P. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10678.

[18] Allen, K. D.; Bruck, M. A.; Gray, S. D.; Kingsborough, R. P.; Smith, D. P.; Weller, K. J.; Wigley, D. E. *Polyhedron* **1995**, *14*, 3315.

[19] Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275.

Scheme 3



All three titanium compounds, **7**−**9**, were thermally stable for at least several months at room temperature under a nitrogen atmosphere. The ^{1}H and ^{13}C NMR spectra of all three compounds showed only single, sharp resonances corresponding to the ethylene backbone of the BIPP ligand. The methyl and benzyl groups of **8** and **9** were also observed to be equivalent by ^{1}H and ^{13}C NMR spectroscopy.

Scheme 3 outlines reactions to form the tantalum BIPP complexes. When a solution of H$_2$BIPP in THF or Et$_2$O was added to a solution of TaCl$_5$ in the corresponding THF or Et$_2$O solvent, the adducts (BIPP)TaCl$_3$L could be isolated as a bright yellow powders upon precipitation with pentane (L = THF (**11**) or Et$_2$O (**12**)). Solid samples of both products isolated in this manner contained nonstoichiometric amounts of coordinating solvent which could be substantially removed under high vacuum over an extended period of time, such that the formulation of **11** and **12** approached (BIPP)TaCl$_3$L. Compound **11** was poorly soluble in most solvents except THF. Pure crystals of **11** grown from THF at −35 °C and of **12** grown from Et$_2$O at −35 °C contained a single molecule of lattice solvent, forming (BIPP)TaCl$_3$(THF)·THF (**11**·THF) and (BIPP)TaCl$_3$(OEt$_2$)·OEt$_2$ (**12**·OEt$_2$), respectively.

Base-free (BIPP)TaCl$_3$ (**10**) was synthesized in 85% yield by the reaction of H$_2$BIPP and TaCl$_5$ in a benzene slurry, over a 4 day period at room temperature. Shorter reactions times yielded an intermediate product (**A**), which over time converted to **10**. When the synthesis of base-free (BIPP)-TaCl$_3$ was attempted at elevated temperatures, only intractable decomposition products were obtained.

An examination of the H$_2$BIPP and TaCl$_5$ reaction mixture in benzene revealed the following. When a benzene solution of H$_2$BIPP was first added to a benzene slurry of TaCl$_5$, the solution rapidly turned dark yellow-brown. Although (BIPP)-TaCl$_3$ (**10**) subsequently formed in high yield from this solution, examining the reaction mixture after less than 4 days reaction time revealed a mixture of (BIPP)TaCl$_3$ (**10**) and another product (**A**). Subsequent examination of the same reaction mixture revealed the slow conversion of **A** to **10** as the reaction proceeded to completion. Compound **A** is characterized by a simple ^{1}H NMR spectrum, similar to that of **10**. Although **A** was not isolated or fully characterized, its ^{1}H NMR and reactivity data suggest its possible formulation as the bis(BIPP) complex (BIPP)$_2$TaCl, which is capable of subsequent reaction with TaCl$_5$ to afford 2 equiv of (BIPP)TaCl$_3$ (**10**). However, other formuations of **A** are possible, including a monomer/μ-Cl dimer relationship between **10** and **A**.

The proton NMR of compound (BIPP)TaCl$_3$(THF) (**11**) in THF-d_8 showed two sharp septet resonances indicating inequivalent isopropyl methine protons, consistent with the two ^{13}C resonances observed for the corresponding carbon atoms. These NMR data suggest that the coordinated THF molecule is bound trans to one of the BIPP oxygen donors, and cis to the other, thereby rendering the ends of the BIPP ligand inequivalent. As described below, the X-ray structural study of this adduct reveals a *mer* isomer of **11** in the solid state, consistent with this observed solution structure.

The organometallic compounds (BIPP)Ta(CH$_2$C$_6$H$_5$)$_3$ (**13**) and (BIPP)TaMe$_3$ (**14**) were synthesized by reacting the appropriate Grignard reagent with (BIPP)TaCl$_3$ in diethyl ether. The highly soluble benzyl derivative (BIPP)Ta-(CH$_2$C$_6$H$_5$)$_3$ (**13**) was isolated as a crystalline orange solid, which was thermally stable for at least several months at room temperature under nitrogen atmosphere. In contrast, while the methyl compound (BIPP)TaMe$_3$ (**14**) was observable by ^{1}H and ^{13}C NMR spectroscopy and could be isolated as a mixture, attempts to isolate this compound in pure form were unsuccessful. Attempts to isolate partially substituted compounds (BIPP)Ta(CH$_2$C$_6$H$_5$)$_n$Cl$_{3-n}$ and (BIPP)TaMe$_n$Cl$_{3-n}$ using a lower mole ratio of Grignard to metal halide typically resulted in intractable mixtures.

Table 1. Details of the X-ray Diffraction Studies for (BIPP)$TaCl_3$(THF)·THF (**11**·THF) and (BIPP)$Ta(CH_2C_6H_5)_3$ (**13**)

param	**11**·THF	13
	Crystal Parameters	
molecular formula	$C_{28}H_{40}Cl_3O_4Ta$	$C_{41}H_{45}O_2Ta$
M_r	727.90	750.72
$F(000)$	1456	1520
cryst color	yellow	orange
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
unit cell vol, Å^3	3039.5(4)	3421.8(2)
a, Å	10.5486(9)	10.2826(3)
b, Å	17.1174(14)	16.6334(6)
c, Å	16.9328(15)	20.0078(7)
β, deg	96.215(4)	90.7020(10)
Z	4	4
D(calcd), g cm^{-3}	1.591	1.457
cryst dimens, mm	0.33 × 0.20 × 0.15	0.2 × 0.3 × 0.4
Ω width, deg	0.3	0.3
exposure time, s	10	10
abs coeff, cm^{-1}	39.10	32.46
data collcn temp, K	170(2)	443(2)
	Data Collection	
diffractometer	Bruker SMART 1000 CCD	Bruker SMART 1000 CCD
monochromator	graphite	graphite
Mo Kα radiation λ, Å	0.710 73	0.710 73
2θ range, deg	2−60	2−60
tot. no. of refclns measd	78 412 reflections (26 397 unique)	24 443 reflections (8502 unique)
corrs	empirical abs and decay using SADABS (SHELDRICK)	empirical abs and decay using SADABS (SHELDRICK)
	Solution and Refinement	
solution	direct methods	direct methods
refinement	full-matrix least squares	full-matrix least squares
minimization function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
reflcns used in refinement; $I > 2\sigma(I)$	8175 (69%)	6406 (75%)
param refined	308	405
R $(=\Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert)$ $(I > 2\sigma(I))$	R1 = 0.0698	R1 = 0.0259
R_w $(=[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w(F_o)^2]^{1/2})$ $(I > 2\sigma(I))$	wR2 = 0.1788	wR2 = 0.0462
convergence, largest shift	0.005σ	0.003σ
Δ/σ(max), e/Å^3	2.535	1.074
Δ/σ(min), e/Å^3	−1.656	−0.669
software	SHELXS in Bruker SHELXTL (version 5.0)[20]	SHELXS in Bruker SHELXTL (version 5.0)[20]

The ^1H and ^{13}C NMR spectra of tantalum BIPP compounds **11**−**14** all exhibited single, sometimes broad, resonances corresponding to the ethylene backbone of the BIPP ligand. This observation likely reflects the fluxionality of the five-coordinate benzyl (**13**) and methyl (**14**) compounds and the lability of the ether base in compounds **11** and **12**.

X-ray Crystallographic Studies of BIPP Compounds. Yellow, block-shaped crystals of (BIPP)$TaCl_3$(THF)·THF (**11**·THF) and orange, block crystals of (BIPP)$TaBn_3$ (**13**) suitable for X-ray structural studies were grown at −35 °C from THF and Et_2O solutions, respectively. (BIPP)$TaCl_3$(THF)·THF (**11**·THF) grew as a pseudomirrorhedral twin and was solved accordingly.[20] A summary of the crystal data and structural analysis is given in Table 1. Relevant bond distances, bond angles, and torsion angles for **11**·THF are provided in Table 2, and those for **13** are provided in Table 3. Figures 1 and 2 present ORTEP drawings (50% thermal probability ellipsoids) of (BIPP)$TaCl_3$(THF)·THF (**11**·THF) and (BIPP)$TaBn_3$ (**13**), respectively.

Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in (BIPP)$TaCl_3$(THF)·THF (**11**·THF)

	Bond Distances		
Ta(1)−O(1)	1.8405(56)	Ta(1)−Cl(1)	2.363(2)
Ta(1)−O(2)	1.8618(57)	Ta(1)−Cl(2)	2.371(3)
Ta(1)−O(3)	2.192(6)	Ta(1)−Cl(3)	2.388(3)
	Bond Angles		
O(1)−Ta(1)−O(2)	99.86(25)	O(1)−Ta(1)−Cl(3)	166.88(19)
Ta(1)−O(1)−C(1)	171.05(59)	O(1)−Ta(1)−O(3)	84.6(2)
Ta(1)−O(2)−C(11)	170.97(59)	O(2)−Ta(1)−Cl(1)	91.11(19)
C(6)−C(10)−C(20)	111.1(8)	O(2)−Ta(1)−Cl(2)	96.36(19)
C(16)−C(20)−C(10)	112.9(8)	O(2)−Ta(1)−Cl(3)	93.19(19)
O(1)−Ta(1)−Cl(1)	92.4(2)	O(2)−Ta(1)−O(3)	174.6(2)
O(1)−Ta(1)−Cl(2)	89.6(2)		
	Torsion Angles		
C(6)−C(10)−C(20)−C(16)	161.5(9)	O(1)−Ta(1)−O(2)−C(11)	27.4(4)
Ta(1)−O(1)−C(1)−C(6)	33(4)	O(2)−Ta(1)−O(1)−C(1)	9(4)
Ta(1)−O(2)−C(11)−C(16)	40(4)		

Molecular Structure of (BIPP)$TaCl_3$(THF)·THF (11·THF). The molecular geometry of **11**·THF shown in Figure 1 can be described as a distorted octahedral structure, having a *mer* geometry, with the tantalum atom situated slightly below the O(1)−Cl(1)−Cl(2)−Cl(3) plane. Table 2 reveals that the O(1)−Ta(1)−O(2) bite angle formed by the BIPP ligand is 99.86(25)°, which is only slightly larger than an analogous compound without linked aryloxide ligation, $(DIPP)_2TaCl_3$(pyridine) (DIPP = 2,6-diisopropylphenoxide), which displays an O−Ta−O bond angle of 95.0(2)°.[21] The Ta(1)−O(1)−C(1) and Ta(1)−O(2)−C(11) angles are 171.05-

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(20) Sheldrik, G. M. In *SHELLXTL*, 5.1 ed.; Sheldrik, G. M., Ed.; Bruker AXS: Madison, WI, 1997.

(21) Clark, J. R.; Pulvirenti, A. L.; Fanwick, P. E.; Sigalas, M.; Eisenstein, O.; Rothwell, I. P. *Inorg. Chem.* **1997**, *36*, 3623−3631.

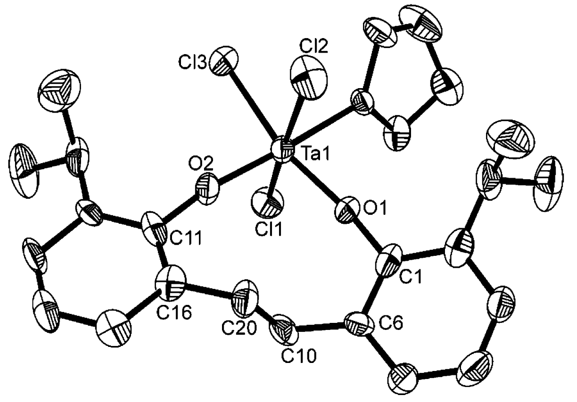

Figure 1. ORTEP drawing (BIPP)TaCl$_3$(THF)·THF (**11**·THF) with 50% thermal ellipsoids. The lattice THF molecule has been removed for clarity.

Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in (BIPP)Ta(CH$_2$C$_6$H$_5$)$_3$ (**13**)

	Bond Distances		
Ta(1)−O(1)	1.8375(18)	Ta(1)−O(2)	1.8731(17)
	Bond Angles		
O(1)−Ta(1)−O(2)	117.20(8)	O(1)−Ta(1)−C(35)	107.33(10)
Ta(1)−O(1)−C(1)	159.49(17)	O(2)−Ta(1)−C(21)	139.80(9)
Ta(1)−O(2)−C(2)	159.24(18)	O(2)−Ta(1)−C(28)	88.46(9)
C(6)−C(10)−C(20)	113.6(2)	O(2)−Ta(1)−C(35)	89.21(9)
C(16)−C(20)−C(10)	112.8(2)	Ta(1)−C(21)−C(22)$_{ipso}$	119.6(7)
O(1)−Ta(1)−C(21)	102.98(9)	Ta(1)−C(28)−C(29)$_{ipso}$	105.91(18)
O(1)−Ta(1)−C(28)	107.77(10)	Ta(1)−C(35)−C(36)$_{ipso}$	107.95(17)
	Torsion Angles		
C(6)−C(10)−C(20)−C(16)	164.1(2)	O(1)−Ta(1)−O(2)−C(11)	4.6(5)
Ta(1)−O(1)−C(1)−C(6)	17.9(7)	O(2)−Ta(1)−O(1)−C(1)	1.7(5)
Ta(1)−O(2)−C(11)−C(16)	18.6(6)		

(59) and 170.97(59)°, respectively, which, again, are similar to the angles of 173.8(5) and 174.0(5)° of the analogous, nonlinked or nonchelating bis(aryloxide) complex (DIPP)$_2$TaCl$_3$(pyridine). Thus, the apparent flexibility of the BIPP ligand through its ethylene bridge allows the molecule to attain a near-octahedral structure very similar to its nonchelated analogue.

Molecular Structure of (BIPP)TaBn$_3$ (13). As shown in Figure 2 and in Table 3, the structural properties of the BIPP ligand in compound **13** are similar to those described for **11**·THF above. The molecular structure of **13** can be described as distorted trigonal bipyramidal in which Ta(1), O(1), O(2), and C(21) comprise the equatorial plane, while the benzyl groups containing C(28) and C(35) occupy the axial positions. This structure differs significantly from the analogous nonlinked bis(aryloxide) tris(benzyl) compound reported by Rothwell and co-workers, (DMP)$_2$Ta(CH$_2$Ph)$_3$ (DMP = 2,6-dimethylphenoxide).[22] While (DMP)$_2$Ta(CH$_2$Ph)$_3$ is characterized by a trigonal bipyramidal geometry, the aryloxide ligands occupy axial sites with the three benzyl groups residing in the equatorial plane. The O(1)−Ta(1)−O(1) angle created by the BIPP ligand in **13** is 117.20(8)°, which is close to idealized trigonal bipyramidal geometry. The equatorial benzyl group, however, is distorted somewhat from an ideal TBP with O(1)−Ta(1)−C(21) and O(2)−Ta(1)−C(21) angles of 102.98(9) and 139.80(9)°, respectively.

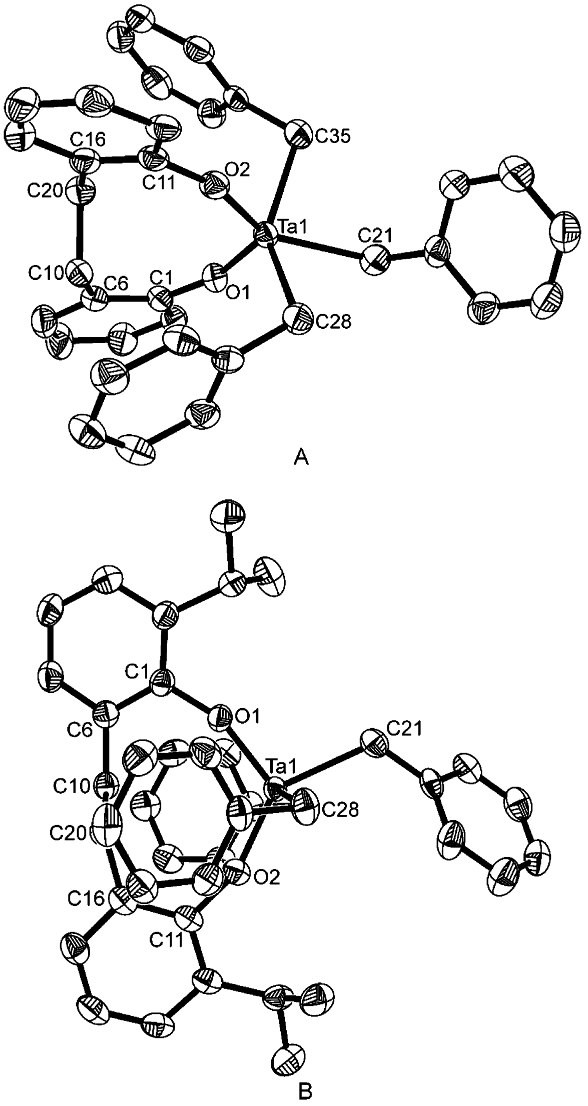

Figure 2. ORTEP drawings of (BIPP)Ta(CH$_2$C$_6$H$_5$)$_3$ (**13**) with 50% thermal ellipsoids. In view A, the isopropyl groups have been removed for clarity. View B looks down the pseudoaxis of the trigonal bipyramid normal to the equatorial plane

This latter feature demonstrates the distortion toward the square pyramidal geometry, in which the BIPP ligand occupies the axial and one basal position, while the benzyl ligands all occupy basal sites.

The Ta(1)−O(1)−C(1) and Ta(1)−O(2)−C(11) bond angles of 159.49(17) and 159.24(18)° in **13** correspond to Ta−O bond lengths of 1.8375(18) Å for Ta(1)−O(1) and 1.8731(17) Å for Ta(1)−O(2). These Ta−O−C$_{ipso}$ angles in **13** are consistent with the analogous nonlinked, bis(aryloxide) complex (DMP)$_2$Ta(CH$_2$Ph)$_3$, which exhibits by Ta−O−C$_{ipso}$ angles of 158.9(4) and 150.6(4)°.

One striking feature of the axial benzyl ligands in **13** is the rotational orientation of their Ta−Cα−C$_{ipso}$ angles with respect to the TBP equatorial plane, such that the phenyl rings are situated above and below the rough plane formed by the chelating BIPP ligand and tantalum center. This feature may simply reflect the most efficient packing of the axial ligands about the metal. Further, the Ta−Cα−C$_{ipso}$ angles of these axial benzyl ligands, 105.91(18)° for Ta-

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(22) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 155−162.

(1)−C(28)−C(29)$_{ipso}$ and 107.95(17)° for Ta(1)−C(35)−C(36)$_{ipso}$, stand in contast to the larger Ta(1)−C(21)−C(22)$_{ipso}$ angle of 119.6(7)° for the equatorial benzyl. These more acute axial Ta−Cα−C$_{ipso}$ angles suggest an allylic contribution to the benzyl ligand structure, though the similar carbon−carbon bond lengths in the benzyl aryl might suggest otherwise.

One measure of BIPP ligand structure is the C(6)−C(10)−C(20)−C(16) torsion angle, which simply indicates the orientation about the ethylene linker between the aryl rings. The C(6)−C(10)−C(20)−C(16) torsion angle in **13** is 164.1(2)°, which drives the BIPP phenyl rings nearly coplanar (dihedral angle 16.59(16)°), similar to its structure in **11**·THF, where this torsion angle is 161.5(9)°.

Bond Length/Bond Angle Comparisons between Tantalum BIPP Complexes. Tables 2 and 3 allow a ready comparison of bond angles and distances between (BIPP)-$TaCl_3(THF)$·THF (**11**·THF) and (BIPP)Ta(CH_2Ph)$_3$ (**13**). Comparing the O(1)−Ta(1)−O(2) bite angles of 99.86(25)° for **11**·THF and 117.20(8)° for **13,** we see that although the ligand is constrained to be cis, it is flexible enough to allow for both octahedral and trigonal geometries. One obvious difference between the two BIPP ligands that allows them to form bite angles of this range is the flexibility of the Ta−O−C$_{ipso}$ bond angles. The Ta−O(1)−C(1) and Ta−O(2)−C(2) angles in **11**·THF are 171.05(59) and 170.97(59)°, respectively, whereas the same angles in **13** are 159.49(17) and 159.24(18)°.

Other more subtle but important differences between the two compounds are the “chelate” Ta−O(1)−C(1)−C(6) and Ta−O(2)−C(11)−C(16) torsion angles. The octahedral compound **11**·THF has Ta−O(1)−C(1)−C(6) and Ta−O(2)−C(11)−C(16) torsion angles of 33(4) and 40(4)°, respectively, while the trigonal compound, **13**, has angles of 17.9(7) and 18.6(6)°. These data appear to correlate an increasing BIPP bite angle with increasingly planar aryl rings, which become increasingly necessary to accommodate a larger bite angle. Thus, the more the Ta−O(1)−C(1)−C(6) and Ta−O(2)−C(11)−C(16) angles approach 0°, the greater the O−Ta−O angle that ligand must span as the aryl ring planes approach coplanarity with the chlelate ring plane.

Conclusions

A new route to ethylene bis(aryloxide) ligands has been developed. The new H_2BIPP (**1**) ligand readily reacts with the d^0 chlorides of tantalum and titanium to form the complexes (BIPP)$TaCl_3$ and (BIPP)$TiCl_2$, respectively. These compounds react with Grignard reagents to afford the corresponding alkyl complexes. In (BIPP)Ta(CH_2Ph)$_3$ (**13**), the ethylene bridge constrains the aryloxide portions of the BIPP ligand to reside in a TBP equatorial plane rather than in the axial positions as observed in the unlinked analogue. A structural comparison between (BIPP)$TaCl_3$ (THF) (**11**) where the BIPP ligand is bound cis-octahedral and (BIPP)-$TaBn_3$ (**13**) where the BIPP ligand is bound in diequatorial-TBP positions shows that ethylene-linked phenoxides are more flexible than anticipated. This flexibility appears to arise to a large extent through the wide range of accessible Ta−O−C$_{ipso}$ angle.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[23] or in a Vacuum Atmospheres HE-493 drybox at room temperature, unless otherwise indicated. Solvents were distilled under N_2 from an appropriate drying agent and were transferred to the drybox without exposure to air. 2-Isopropylphenol (**1**), TMEDA (redistilled, 99.5%), triphenylphosphine, BBr_3 (1 M in CH_2Cl_2), Br_2, *n*-butyllithium (1.6 M in hexanes), CH_3I (99.5%), and paraformaldehyde were purchased from Aldrich (Milwaukee, WI). Reagents TMEDA, triphenylphosphine, BBr_3, Br_2, *n*-butyllithium, and CH_3I were used as received, while 2-isopropylphenol (**1**) was dried over 4 Å molecular sieves and distilled prior to use. Paraformaldehyde was dried in vacuo for 4 h prior to use. Tantalum pentachloride ($TaCl_5$) was obtained form CERAC, Inc. (Milwaukee, WI), and used as received. Titanium tetrachloride ($TiCl_4$) was purchased from Aldrich and used as received. All Grignard reagents were also purchased from Aldrich and used as received. In all preparations, BIPP = the 2,2′-ethylenebis(6-isopropylphenoxide) dianion.

Physical Measurements. ^1H NMR and ^{13}C NMR spectra were recorded at probe temperature using either a Varian Unity 300 spectrometer or a Bruker AM-250 spectrometer in C_6D_6 or THF-d_8 solvent. Chemical shifts are referenced to the protio impurities (δ 7.15, C_6D_6; δ 3.58, THF-d_8) or solvent ^{13}C resonances (δ 128.4, C_6D_6; δ 67.6, THF-d_8) and are reported downfield of Me_4Si. Carbon ^{13}C assignments were assisted by HETCOR and HMBC spectra acquired at 30 °C without sample spinning. Microanalyses were preformed by Desert Analytics, Tucson, AZ. Microanalytical samples were routinely handled under nitrogen, and all samples were combusted with WO_3.

Preparations. 2-Isopropylanisole (2). In a typical experiment, a large Schlenk tube equipped with a magnetic stir bar was charged with 500 mL of THF and 28.53 g (0.729 mol) of potassium chunks. The mixture was cooled in an ice bath and vigorously stirred, while a solution of 99.99 g (0.734 mol) of isopropylphenol (**1**) in 100 mL of THF was slowly added. The resulting reaction mixture was stirred for 2−3 h at 0 °C under a slow purge of N_2, after which time it was allowed to warm to room temperature and stirred for an additional 3−4 h until all of the potassium had reacted. After this time, the solution was again cooled to 0 °C in an ice bath, and 105.57 g (0.743 mol) of CH_3I was added slowly. The resulting mixture was stirred overnight at room temperature, over which time a white solid precipitated. This slurry was extracted with water to remove the potassium iodide that had formed during the reaction. The aqueous layer was extracted with 50 mL of diethyl ether, and this ether extract was combined with the THF layer. The combined organic layers were washed with a saturated NaCl solution (2 × 100 mL) and dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo to afford a yellow liquid. Distillation of this liquid from sodium at atmospheric pressure gave 83.31 g (0.555 mol, 87%) of a clear, colorless liquid **2** with a boiling point of 190−192 °C. ^1H NMR (C_6D_6): δ 7.20−6.55 (m, 4 H, H_{aryl}), 3.50 (spt, 1 H, C*H*Me_2), 3.34 (OC*H_3*), 1.24 (d, 6 H, CH*Me_2*). ^{13}C NMR (C_6D_6): δ 157.15, 137.01, 126.86, 126.31, 120.97, 110.50, 54.78, 27.10, 22.91.

(3-Isopropyl-2-methoxyphenyl)lithium·0.5TMEDA (3). A 500 mL Schlenk flask equipped with a magnetic stir bar was charged

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[23] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley and Sons: New York, 1986.

with 208 mL (0.333 mol) of 1.6 M *n*-butyllithium in hexanes. This solution was stirred and cooled to 0 °C in an ice bath, after which 19.36 g (0.167 mol) of TMEDA was added dropwise via syringe to yield a thick white suspension. The suspension was stirred at 0 °C for 1 min, after which 50.00 g (0.333 mol) of 2-isopropylanisole (**2**) was added via syringe. After the addition of **2** was complete, the mixture was allowed to warm to room temperature to afford a clear, golden-yellow solution. This solution was stirred at room-temperature overnight to yield a thick, white precipitate. The precipitate was filtered off, washed with 50 mL of pentane, and dried in vacuo to afford 54 g (0.252 mol, 76%) of **3** as a fine, white powder. ^{1}H NMR (C_6D_6): δ 8.08 (pseudo dd (ABC mult), 1 H, H_{aryl}), 7.26 (pseudo t (ABC mult), 1 H, C(4)H, H_{aryl}), 7.17 (pseudo dd (ABC mult), 1 H, H_{aryl}), 3.31 and 3.28 (overlapped spt and br s, respectively, 4 H total, C*H*Me$_2$, ArO*Me*), 1.92 (s, 2 H, $Me_2NC\mathit{H_2}C\mathit{H_2}NMe_2$), 1.83 (s, 6 H, $\mathit{Me_2}NCH_2CH_2N\mathit{Me_2}$), 1.24 (d, 6 H, CH*Me*$_2$). ^{13}C NMR ($C_6D_6$): δ 167.8, 163.3, 139.5, 136.5, 125.2, 125.1, 60.1, 57.5, 45.9, 27.3, and 24.2. Anal. Calcd for $C_{13}H_{21}NOLi$ (includes 0.5 TMEDA): C, 72.88; H, 9.88; N, 6.53. Found: C, 72.61; H, 9.47; N, 5.88.

2-(Hydroxymethyl)-6-isopropylanisole (4). A 500 mL, two-neck round-bottom flask, equipped with a magnetic stir bar and a nitrogen inlet adapter, was charged with a solution of 25.0 g (0.117 mol) of **3** in 250 mL of diethyl ether. A solid addition tube containing 3.50 g (0.117 mol) of paraformaldehyde was attached to the flask. The reaction mixture was cooled to 0 °C in an ice bath, and the paraformaldehyde was added while the solution was stirred. After addition was complete, the reaction was stirred for another 10−15 h, while slowly warming to room temperature, over which time a white solid precipitated. The mixture was carefully hydrolyzed by adding 150 mL of 0.5 M aqueous HCl to the reaction mixture with vigorous stirring, which caused the precipitate to dissolve. The organic layer was separated, washed with 2 × 150 mL of saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and filtered, and the reaction volatiles were removed in vacuo to give a pale yellow oil. Distillation of this oil under reduced pressure yielded 17.0 g (94.4 mmol, 80.6%) of **4** as a clear, colorless oil with a boiling point of 119−121 °C (5 mmHg). ^{1}H NMR (C_6D_6): δ 7.21 (pseudo dd (ABC mult), 1 H, H_{aryl}), 7.08 (pseudo dd (ABC mult), 1 H, H_{aryl}), 7.00 (pseudo t, (ABC mult), 1 H, C(4)H, H_{aryl}), 4.62 (s, 2 H, ArC*H*$_2$OH), 3.41 (s, 3 H, ArO*Me*), 3.31 (spt, 1 H, C*H*Me$_2$), 2.20 (br s, 1 H, ArCH$_2$O*H*), 1.16 (d, 6 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 155.7, 141.8, 134.5, 126.8, 126.2, 124.8 (C(4), C_{aryl}), 61.7 (ArO*C*H$_3$), 61.0 (Ar*C*H$_2$OH), 26.5 (*C*HMe$_2$), 24.0 (CH*Me*$_2$). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.94. Found: C, 73.35; H, 8.68.

2-(Bromomethyl)-6-isopropylanisole (5). A 500 mL, three-neck round-bottom flask equipped with a magnetic stir bar, nitrogen inlet adapter, and a thermometer was charged with a solution of 83.3 g (0.318 mol) of triphenylphosphine in 250 mL of CH_2Cl_2. The reaction mixture was cooled to 0 °C in an ice bath and vigorously stirred, while a solution of 51.05 g (0.313 mol) of Br_2 in 50 mL of CH_2Cl_2 was added dropwise at a sufficiently slow rate to maintain the reaction temperature below 10 °C. A pale yellow solid precipitated as the reaction proceeded. After the addition was complete a solution of 28.31 g (0.151 mol) of **4** in 50 mL of CH_2Cl_2 was added, while maintaining the reaction temperature below 10 °C. After the addition was complete the reaction mixture was allowed to warm to room temperature. After being stirred for 3 h, the mixture was transferred into a 2 L Erlenmeyer flask, and 500 mL of diethyl ether was added followed by 1 L of pentane while the reaction mixture was stirred vigorously with an overhead mechanical stirrer. This mixture was then filtered through a pad of silica gel, and the reaction solids were washed with 2 × 50 mL of a diethyl ether/pentane (1:2 v/v) mixture. The volatile components were removed from the combined filtrate in vacuo to yield a pale yellow oil. Distillation of this oil under reduced pressure provided 32.56 g (0.134 mol, 86%) of **5** as a clear colorless liquid with a boiling point of 135−137 °C (13 mmHg). ^{1}H NMR (C_6D_6): δ 6.98−7.03 (mult, 2 H, C(3)H and C(5)H, H_{aryl}), 6.86 (pseudo t (ABC mult), 1 H, C(4)H, H_{aryl}), 4.33 (s, 2 H, ArC*H*$_2$Br), 3.55 (s, 3 H, ArO*Me*), 3.23 (spt, 1 H, C*H*Me$_2$), and 1.08 (d, 6 H, CH*Me*$_2$). ^{13}C (C_6D_6): δ 156.2, 142.4, 131.6, 129.3, 127.6, 124.9, 61.7, 28.6, 26.5, 23.8 (CH*Me*$_2$). Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.34; H, 6.21. Found: C, 54.67; H, 6.24.

1,2-Bis(3-isopropyl-2-methoxyphenyl)ethane (Me$_2$BIPP, 6). A 500 mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of 32.56 g (0.134 mol) of **5** in 100 mL of THF/pentane (3:1 v/v). This solution was stirred and cooled to −100 °C (diethyl ether/liquid-N_2 slush), and 84 mL (0.134 mol) of 1.6 M *n*-butyllithium in hexanes was slowly added over a period of 0.5 h to afford a white suspension. After the addition was complete, the mixture was stirred at −100 °C for 1 h, allowed to warm to −78 °C (diethyl ether/dry ice), and stirred at that temperature for 3 h. The resulting mixture was then carefully cannula-transferred into a 500 mL separatory funnel containing 150 mL of water. The organic layer was washed with water followed by 2 × 150 mL of saturated aqueous NaCl and dried over anhydrous $MgSO_4$. The solution volatiles, after filtration, were evaporated under reduced pressure to yield a pale yellow, viscous oil. Distillation of this oil under reduced pressure provided 15.56 g (0.048 mol, 71%) of **6** as a colorless oil, bp 185−190 °C (10 mmHg). ^{1}H NMR (C_6D_6): δ 7.17−7.02 (m, 6 H, H_{aryl}), 3.47 (s, 6 H, OC*H*$_3$), 3.41 (spt, 2 H, C*H*Me$_2$), 3.07 (s, 4 H, CH_2CH_2), 1.21 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 156.37, 142.07, 135.51, 128.50, 124.91, 124.76, 61.37, 32.20, 26.77, 25.15. Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 81.03; H, 9.69.

1,2-Bis(3-isopropyl-2-hydroxyphenyl)ethane (H$_2$BIPP, 1). A solution of 14.74 g (0.045 mol) of **6** in 250 mL of CH_2Cl_2 was added to a Schlenk tube containing a magnetic stir bar. The solution was stirred and cooled to −78 °C after which 90 mL (0.090 mol) of a 1 M BBr_3 solution in CH_2Cl_2 was slowly added. A white precipitate formed as the BBr_3 solution was added. The resulting slurry was stirred overnight and allowed to slowly warm to room temperature. The resulting brown-yellow solution was transferred into a separatory funnel and carefully hydrolyzed with water, which resulted in precipitation of a pale yellow solid. The solid was redissolved by adding a minimal amount of Et_2O. The organic layer was separated, washed with 2 × 100 mL of saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, filtered, and evaporated in vacuo to yield a brownish yellow oil. This oil was dissolved in 30 mL of pentane and filtered through a pad of alumina. The solvent was evaporated from the filtrate in vacuo to give 11.74 g (0.039 mol, 87%) of **1** as a pale brown oil. ^{1}H NMR (C_6D_6): δ 7.07−6.86 (m, 6 H, H_{aryl}), 5.58 (s, 2 H, O*H*), 2.95 (spt, 2 H, C*H*Me$_2$), 2.81 (s, 4 H, CH_2CH_2), 1.16 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 151.42, 134.28, 127.78, 124.70, 121.22, 121.14, 32.60, 27.20, 22.86. Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.16; H, 9.06.

(BIPP)TiCl$_2$ (7). A solution of 0.639 g (3.37 mmol) of $TiCl_4$ in 3 mL of pentane was prepared. A solution of 0.997 g (3.34 mmol) of H$_2$BIPP dissolved in 3 mL of pentane was prepared and was added dropwise to the vigorously stirred $TiCl_4$ solution. When the evolution of gas was complete, the reaction mixture was allowed to stir for another 4 h, after which time the reaction mixture was cooled to −40 °C. After 10 days at this temperature, the resulting solid which had precipitated was filtered off and dried in vacuo to afford 1.20 g (2.90 mmol, 87%) of analytically pure product as a dark red powder. ^{1}H NMR (C_6D_6): δ 6.91−6.77 (m, 6 H, H_{aryl}), 3.72 (spt, 2 H, C*H*Me_2), 2.49 (s, 4 H, CH_2CH_2), 1.27 (d, 12 H, CH*Me$_2$*). ^{13}C NMR (C_6D_6): δ 167.42 (C_{ipso}), 131.17, 133.53 (C_o), 127.38, 125.52 (C_m), 124.65 (C_p), 33.00 (CH_2CH_2), 28.49 (*C*HMe_2), 22.90 (CH*Me$_2$*). Anal. Calcd for $C_{20}H_{24}Cl_2O_2Ti$: C, 57.86; H, 5.83. Found: C, 57.42; H, 6.11.

(BIPP)TiMe$_2$ (8). A solution of 0.25 g (0.61 mmol) of **7** in 2 mL of pentane was prepared. A 0.401 mL (1.20 mmol) portion of 3 M MeMgCl in THF was diluted to 1 mL in pentane and was added dropwise to the rapidly stirring solution of **7**. After being stirred for 48 h at room temperature, the reaction mixture was filtered through Celite, and the resulting yellow filtrate was cooled to −40 °C. After 5 h at −40 °C, 0.08 g (0.21 mmol, 36%) of analytically pure red crystals had formed, which was collected and dried in vacuo. ^{1}H NMR (C_6D_6): δ 7.13−6.92 (m, 6 H, H_{aryl}), 4.10 (spt, 2 H, C*H*Me_2), 2.31 (s, 4 H, CH_2CH_2), 1.48 (d, 12 H, CH*Me$_2$*), 1.33 (TiC*H$_3$*). Anal. Calcd for $C_{22}H_{30}O_2Ti$: C, 70.59; H, 8.08. Found: C, 70.21; H, 8.02

(BIPP)Ti(CH$_2$C$_6$H$_5$)$_2$ (9). A solution of 0.30 g (0.73 mmol) of **7** in 5 mL of Et_2O was prepared. A 1.44 mL (1.44 mmol) sample of 1 M ($CH_2C_6H_5$)MgCl in THF was diluted to 3 mL with Et_2O and added dropwise to the vigorously stirred solution of **7**. After being stirred for 20 h at room temperature, the solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo to afford a red oil. This oil was triturated with pentane to afford an orange solid, which was filtered off and dried in vacuo giving 0.186 g (0.35 mmol, 49%) of **9** as a red orange powder. ^{1}H NMR (C_6D_6): δ 7.12−6.76 (m, 16 H, H_{aryl}), 3.88 (spt, 2 H, C*H*Me_2), 2.80 (s, 4 H, CH_2CH_2), 2.17 (C*H$_2$*C_6H_5), 1.42 (d, 12 H, CH*Me$_2$*). ^{13}C NMR (C_6D_6): δ 162.16 (C_{ipso}, BIPP), 141.91 (C_{ipso}, benzyl), 136.15, 132.90 (C_o, BIPP), 129.35, 128.78 (Co, Cm, Benzyl), 127.61 (C_p, benzyl), 124.46, 124.25 (C_m, BIPP), 122.63 (C_p, BIPP), 81.69 (*C*H$_2C_6H_5$), 33.04 (*C*HMe_2), 27.62(CH_2CH_2), 23.59 (CH*Me$_2$*). Anal. Calcd for $C_{23}H_{38}O_2Ti$: C, 77.56; H, 7.27. Found: C, 76.82; H, 7.66.

(BIPP)TaCl$_3$ (10). A suspension of 4.11 g (11.5 mmol) of $TaCl_5$ in 25 mL of benzene was prepared and vigorously stirred. A solution of 3.45 g (11.5 mmol) of H_2BIPP dissolved in 25 mL of benzene was slowly added (over ca. 5 min) to the stirred $TaCl_5$ suspension. The evolution of gas was observed, after which time the reaction was stirred at room temperature for an additional 4 days. After this time, the precipitate which had formed was filtered off and dried in vacuo to give 5.68 g (9.73 mmol, 85%) of product **10** as a yellow solid. ^{1}H NMR (THF-*d*$_8$): δ 7.28−6.90 (m, 6 H, H_{aryl}), 4.35 and 3.87 (spt, 1 H each, C*H*Me_2), 3.58 (br s, THF), 2.90 (br s, 4 H, CH_2CH_2), 1.73 (br s, THF), 1.30 (d, 12 H, CH*Me$_2$*). Anal. Calcd for $C_{20}H_{24}Cl_3O_2Ta$: C, 41.15; H, 4.14. Found: C, 41.29; H, 4.11.

(BIPP)TaCl$_3$(THF) (11). A solution of 0.198 g (0.55 mmol) of $TaCl_5$ in 3 mL of THF was prepared and rapidly stirred while a solution of 0.165 g (0.55 mmol) of H_2BIPP in 3 mL of THF was added over about a 5 min period. The reaction was allowed to stir for an additional 8 h, after which time the product was precipitated with pentane. The resulting yellow powder was filtered off, washed with pentane (3 × 5 mL), and dried in vacuo to afford 0.302 g (83%) of **11** which contained a nonstoichometric amounts of THF. This solvent could be substantially removed under high vacuum over an extended period of time, such that the formulation of **11** approached (BIPP)$TaCl_3$(THF). Pure crystals which contained one lattice THF molecule, (BIPP)$TaCl_3$(THF)·THF (**11**·THF), were obtained by crystallization of the yellow product at −35 °C from concentrated THF solutions.

The THF adduct (BIPP)$TaCl_3$(THF) (**11**) was also prepared in nearly quantitative yield (ca. 95%) by dissolving (BIPP)$TaCl_3$ (**10**) in neat THF, followed by removal of the solvent in vacuo to afford yellow crystals. The NMR properties of this compound were essentially identical with those of the base free (BIPP)$TaCl_3$ in THF, other than integration intensities. ^{1}H NMR (THF-*d*$_8$): δ 7.30−6.90 (m, 6 H, H_{aryl}), 4.35 and 3.87 (spt, 1 H each, C*H*Me_2), 3.6 (br, 4 H, Hα THF), 2.90 (br, 4 H, CH_2CH_2), 1.7 (br, 4 H, Hβ THF), 1.30 (d, 12 H, CH*Me$_2$*). Anal. Calcd for $C_{28}H_{40}Cl_3O_4Ta$ (includes lattice THF): C, 46.20; H, 5.54. Found: C, 46.34; H, 5.70.

(BIPP)TaCl$_3$(Et$_2$O) (12). A solution of 0.168 g (0.47 mmol) of $TaCl_5$ in 3 mL of diethyl ether was prepared and rapidly stirred while a solution of 0.142 g (0.47 mmol) of H_2BIPP in 3 mL of diethyl ether was added over a 5 min period. The reaction was allowed to stir for an additional 8 h, after which time the product was precipitated with pentane. The resulting yellow powder was filtered out, washed with pentane (3 × 5 mL), and dried in vacuo to afford 0.265 g of **12** which contained a nonstoichometric amounts of ether. This solvent could be substantially removed under high vacuum over an extended period of time, such that the formulation of **12** approached (BIPP)$TaCl_3$(OEt_2). Pure crystals which contained one lattice ether molecule, (BIPP)$TaCl_3$(OEt_2)·OEt_2 (**12**·OEt_2), were obtained by crystallization of the yellow product at −35 °C from concentrated diethyl ether solutions.

The Et_2O adduct (BIPP)$TaCl_3$(Et_2O) (**12**) was also prepared in nearly quantitative yield (ca. 95%) by dissolving (BIPP)$TaCl_3$ (**10**) in neat Et_2O, followed by removal of the solvent in vacuo to afford yellow crystals. ^{1}H NMR (C_6D_6, 70 °C): δ 7.13−6.84 (m, 6 H, H_{aryl}), 4.19 (br s, 6 H, C*H*Me_2 and MeC*H$_2$*O), 2.93 (br s, 4 H, CH_2CH_2), 1.31 (br d, 12 H, CH*Me$_2$*), 1.05 (t, 6 H, *Me*CH_2O). ^{13}C NMR (C_6D_6 70°C): δ 159.00 (C_{ipso}), 141.78 (C_o), 135.42 (C_o), 127.12 (C_m), 125.93 (C_p), 124.82 (C_m), 69.49 (CH_2O, ether), 34.42 (CH_2CH_2), 26.54 (*C*HMe_2), 24.32 (CH*Me$_2$*), 12.50 (CH_3, ether). Anal. Calcd for $C_{28}H_{44}Cl_3O_4Ta$ (includes lattice Et_2O): C, 45.95; H, 6.06; Cl, 14.53. Found: C, 46.06; H, 5.44; Cl, 14.01.

(BIPP)Ta(CH$_2$C$_6$H$_5$)$_3$ (13). A solution of 0.253 g (0.43 mmol) of (BIPP)$TaCl_3$ (**10**) in 8 mL of Et_2O was prepared. A 1.28 mL (1.28 mmol) sample of 1 M ($CH_2C_6H_5$)MgCl in THF was diluted to 5 mL with Et_2O and was added dropwise to the stirred solution of **10**. After being stirred for 16 h, the solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The residue was extracted with pentane, and the extract was filtered through Celite. The filtrate was cooled to −40 °C to afford 0.125 g (0.17 mmol, 39%) of **13** as X-ray-quality orange crystals. ^{1}H NMR (C_6D_6): δ 7.09−6.65 (m, 21 H, H_{aryl}), 3.51 (spt, 2 H, C*H*Me_2), 3.40 (s, 4 H, CH_2CH_2), 1.38 (s, 6 H, C*H$_2$*C_6H_5), 1.29 (d, 12 H, CH*Me$_2$*). ^{13}C NMR (C_6D_6): δ 157.94 (C_{ipso}, BIPP), 145.77 (C_{ipso}, benzyl), 137.79, 131.13 (C_o, BIPP), 129.21, 128.15 (C_o, C_m, benzyl), 127.37 (C_p, benzyl), 124.45, 124.11 (C_m, BIPP), 123.98 (C_p, BIPP), 80.7 (*C*H$_2C_6H_5$), 30.57 (*C*HMe_2), 27.31 (CH_2CH_2), 23.22 (CH*Me$_2$*). Anal. Calcd for $C_{41}H_{45}O_2Ta$: C, 65.59; H, 6.04. Found: C, 65.05; H, 5.96.

(BIPP)TaMe$_3$ (14). A solution of 0.247 g (0.42 mmol) of (BIPP)$TaCl_3$ (**10**) in 10 mL of Et_2O was prepared. A 0.428 mL (1.28 mmol) sample of 3 M MeMgCl in THF was diluted to 5 mL with Et_2O and added dropwise to the vigorously stirred solution of **10**. After being stirred for 18 h, the reaction mixture was filtered through Celite and the solvent was removed from the filtrate in vacuo. The residue was extracted with pentane and filtered through Celite. The resulting filtrate was cooled to −40 °C. After ca. 24 h at this temperature, 0.073 g of a pale yellow powder had precipitated a mixture of products which could not be separated further. The major product via NMR (~80%) is consistent with the structure of **14**. ^{1}H NMR (C_6D_6): δ 7.13−6.84 (m, 6 H, H_{aryl}), 3.81 (spt, 2 H, C*H*Me$_2$), 2.63 (s, 4 H, CH_2CH_2), 1.40 (s, 9 H, Ta*Me*$_3$), 1.26 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 157.45 (C_{ipso}), 139.69, 131.78 (C_o), 126.98, 125.13, 124.45 (C_m, C_p), 65.09 (Ta*Me*), 33.84 (*C*HMe$_2$), 27.00 (CH_2CH_2), 23.71 (CH*Me*$_2$).

Crystallography

X-ray Structural Determination of (BIPP)TaCl$_3$(THF)·THF (11·THF). A yellow cube crystal of $C_{28}H_{40}Cl_3O_4Ta$ was crystallized from THF solution at −35 °C and was mounted on a glass fiber in a random orientation. Examination of the crystal on a Bruker AXS SMART 1000 CCD detector X-ray diffractometer revealed the crystal to be a pseudomirrorhedral twin. The initial data set of 78 412 reflections (26 397 unique) was separated into three data sets (A, B, and overlapping) using the “twin” software package (Bruker SHELXTL software package).[20] The two independent data sets were then solved and merged using a BASF parameter of 0.64210. Systematic absences and intensity statistics indicated the space group to be $P2_1/c$ (No. 14), which was consistent with refinement. Hydrogen atoms were added at idealized positions, constrained to ride on the atom to which they are bonded, and given thermal parameters equal to 1.2 or 1.5 times U_{iso} of that bonded atom. Scattering factors and anomalous dispersion were taken from the *International Tables* Vol. C, Tables 4.2.6.8 and 6.1.1.4. Details of the structural determination and refinement are reported in Table 1.

X-ray Structural Determination of (BIPP)Ta(CH$_2$C$_6$H$_5$)$_3$ (13). A orange diamond shaped block of $C_{41}H_{45}O_2Ta$ was crystallized from Et_2O solution at −35 °C and was mounted on a glass fiber in a random orientation. The crystal was examined using a Bruker AXS SMART 1000 CCD detector X-ray diffractometer, and raw data were solved using the Bruker SHELXTL software package.[20] Systematic absences and intensity statistics indicate the space group to be $P2_1/c$ (No. 14), which was consistent with refinement. Hydrogen atoms were added at idealized positions, constrained to ride on the atom to which they are bonded, and given thermal parameters equal to 1.2 or 1.5 times U_{iso} of that bonded atom. Scattering factors and anomalous dispersion were taken from the *International Tables* Vol. C, Tables 4.2.6.8 and 6.1.1.4. Details of the structural determination and refinement are reported in Table 1.

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Supporting Information Available: Complete crystallographic details in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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