Ortho-phenylene-bridged aryloxy phosphine ligands and their coordination chemistry with tantalum(V)

Christopher D. Carmichael and Michael D. Fryzuk

Abstract: The lithium complexes $RP(3,5\text{-}^{t}Bu_2C_6H_2OLi)_2(THF)_4$, where R = Ph or ^{i}Pr, $(^{R}[OPO]Li_2)_2(THF)_4$, can be converted quantitatively into the protonated forms, $^{R}[OPO]H_2$, by reaction with Et_3NHCl. Reaction of the protonated compounds with KH yields the potassium complexes $(^{Ph}[OPO]K_2)_2(THF)_6$ and $(^{iPr}[OPO]K_2)_3(THF)_3$. The reaction of $^{R}[OPO]H_2$ with $TaCl_5$ yields the sparingly soluble tantalum trichloride complexes $^{R}[OPO]TaCl_3$ via elimination of HCl. Reaction of $^{Ph}[OPO]H_2$ with $TaMe_3Cl_2$ leads to the monomethyl complex $^{Ph}[OPO]TaMeCl_2$, or the dimethyl halide complex, $^{Ph}[OPO]TaMe_2Cl$, via protonolysis, and the potassium complex $(^{Ph}[OPO]K_2)_2(THF)_6$ yields the trimethyl complex, $^{Ph}[OPO]TaMe_3$ by a metathesis process.

Key words: tantalum, phosphine, potassium, aryloxy, tridentate ligand, alkyl.

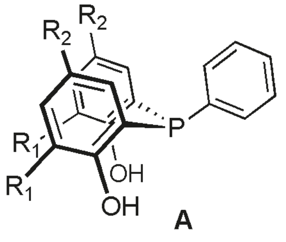
Résumé : Les complexes du lithium $RP(3,5\text{-}^{t}Bu_2C_6H_2OLi)_2(THF)_4$ dans lesquels R = Ph ou ^{i}Pr, $(^{R}[OPO]Li_2)_2(THF)_4$ peuvent être transformés quantitativement en formes protonées, $^{R}[OPO]H_2$ par réaction avec le Et_3NHCl. La réaction des composés protonés avec le KH conduit à la formation des complexes de potassium $(^{Ph}[OPO]K_2)_2(THF)_6$ et $(^{iPr}[OPO]K_2)_3(THF)_3$. La réaction du $^{R}[OPO]H_2$ avec du $TaCl_5$ conduit à la formation de complexes du trichlorure de tantale, $^{R}[OPO]TaCl_3$, qui sont très peu solubles et qui résultent d'une élimination de HCl. La réaction du $^{Ph}[OPO]H_2$ avec du $TaMe_3Cl_2$ conduit, par le biais d'une protonolyse, à la formation de complexes monométhylés, $^{Ph}[OPO]TaMeCl_2$, ou biméthylés, $^{Ph}[OPO]TaMe_2Cl$ alors que celle du complexe potassique $(^{Ph}[OPO]K_2)_2(THF)_6$ conduit, par un processus de métathèse, à la formation du complexe triméthylé, $^{Ph}[OPO]TaMe_3$.

Mots-clés : tantale, phosphine, potassium, aryloxy, ligand tridentate, alkyle.

[Traduit par la Rédaction]

Introduction

For some time, we have been interested in examining the coordination chemistry of mixed-donor multidentate ligands.[1,2] By combining hard donors, such as amido (NR_2^-), with soft phosphines (PR_3)[3–7] or arsines (AsR_3)[8,9] into chelating arrays, we have been able to prepare transition-metal complexes that can activate molecular nitrogen in certain cases.[2,10–13] We have extended this mixed-donor ligand approach to include the hard aryloxy (ArO^-) moiety with phosphines to generate OPO ligand sets with *o*-phenylene linkers.[14] The general family of OPO ligand precursors **A** is shown below with the various substitution patterns that have been examined.



A

R_1 = H, ^{t}Bu
R_2 = H, Me, ^{t}Bu

Rhenium and technetium complexes supported by the parent ligand, bis(*o*-phenoxy)phenylphosphine (**A** with $R_1 = R_2$ = H), have drawn interest for their potential use as radiopharmaceutical agents.[15,16] With group 4, the heptacyclic, tetranuclear titanium complex, $\{(^{i}PrO)_2Ti(\mu^3\text{-}O)TiCl(^{i}PrO)[(OC_6H_4)_2PPh]\}_2$, was obtained,[17] likely a result of the lack of steric bulk around the OPO donor set.

Bis(3-*tert*-butyl-5-methyl-2-phenoxy)phenylphosphine (**A**, R_1 = ^{t}Bu, R_2 = Me), which has a sterically bulky *tert*-butyl group ortho to the phenoxy group, has been complexed to titanium[18] and chromium.[19] These complexes were found to be highly active for the polymerization of ethylene.

Bis(3,5-*tert*-butyl-2-phenoxy)phenylphosphine was first reported in 2000;[20] in this report, we abbreviate it as $^{Ph}[OPO]H_2$ (**A**, $R_1 = R_2$ = ^{t}Bu), where the Ph superscript refers to the substituent at phosphorus that is not a substituted phenol. Despite the presence of two bulky *tert*-butyl substituents on the phenolic units, the donor set readily forms bis(ligand) complexes with several transition metals, including cobalt and nickel, although in these complexes one phe-

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nol arm of the ligand remains protonated.[20] Vanadium(IV) complexes supported by ^{Ph}[OPO] can be synthesized by reaction of the protonated phenol with $VCl_3(THF)_3$;[21] a short exposure to oxygen is necessary to oxidize V(III) to V(IV). Lithium and potassium salts, supported by the chelating donor solvent DME (1,2-dimethoxyethane) have been recently reported.[22]

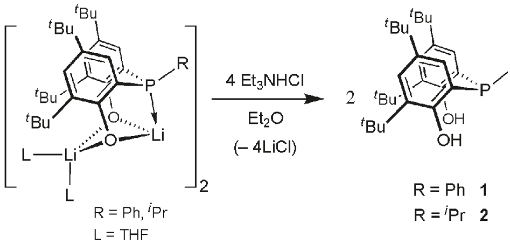
Several group-4 metal complexes have been prepared using ^{Ph}[OPO]H_2, including ^{Ph}[OPO]$TiCl_2$(THF), and the bis(ligand) derivatives ^{Ph}[OPO]$_2$M(OH_2) (M = Zr, Hf) and ^{Ph}[OPO]$_2$Ti.[23] The bis(ligand) complex is so readily formed in the titanium system that a conproportionation reaction between ^{Ph}[OPO]$_2$Ti and $TiCl_4(THF)_2$ was found to be the best method for the preparation of ^{Ph}[OPO]$TiCl_2$(THF). Similar reactions with $SnCl_4$ did not produce the bis(ligand) complex, instead leading to the clean formation of ^{Ph}[OPO]$SnCl_2$.[24]

A very recent report details the synthesis and structures of a series of bis(ligand) complexes of Ta(V) having the formula ^{Ph}[OPO]$_2$TaX, where X = Cl, H, Me, Et, and OH.[25] Of relevance to this work was the observation that the monoligand complexes ^{Ph}[OPO]TaX_3 were not accessible despite a number of different synthetic strategies attempted.

We have recently reported the structural variety of lithium aryloxide complexes based on the ^{R}[OPO] donor set[14] utilizing phenyl and *iso*-propyl substituents on phosphorus. We present herein an extension of this bis(aryloxy)phosphine chemistry by reporting an improved synthesis of the protonated compounds (^{R}[OPO]H_2) from the lithium salts, the synthesis of THF-supported potassium salts, (^{Ph}[OPO]$K_2)_2(THF)_6$ and (^{iPr}[OPO]$K_2)_3(THF)_3$, and their reactions with the tantalum precursors $TaCl_5$ and $TaMe_3Cl_2$. We also describe the preparation of the elusive monoligand complexes ^{R}[OPO]$TaCl_3$ (R = Ph, ^{i}Pr).

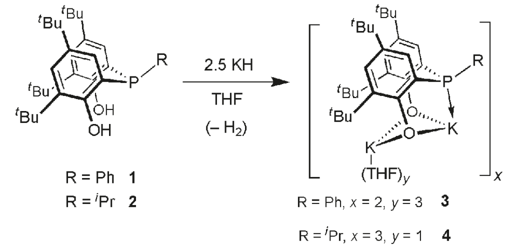
Results and discussion

Reaction of the lithium complexes, $RP(3,5\text{-}^{t}Bu_2C_6H_2OLi)_2(THF)_4$, where R = Ph or ^{i}Pr, (^{R}[OPO]$Li_2)_2(THF)_4$, with 4 equiv. of Et_3NHCl in diethyl ether, eq. [1], gives the desired products, ^{Ph}[OPO]H_2 (**1**) or ^{iPr}[OPO]H_2 (**2**), in 97% and 96% isolated yields, respectively. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **1** are consistent with literature values.[20] The $^{31}P\{^{1}H\}$ NMR spectrum of **2** displays a singlet at δ –61.6, slightly upfield from that observed for **1**, reflecting the more basic nature of the alkyl phosphine. The ^{1}H NMR spectrum of **2** contains two singlet resonances for the *tert*-butyl groups, and a characteristic doublet of septets for the methine proton of the *iso*-propyl group coupled to phosphorus and the methyl protons, which appear as a doublet of doublets.

[1] 

X-ray quality crystals of **1** containing 3 equiv. of the co-crystallized solvent were grown by slow evaporation of a saturated benzene solution. The solid-state structure is presented in Fig. 1, and selected bond distances and angles are collected in Table 1. The unit cell parameters are identical to those reported for the related phosphine oxide compound.[20] This may seem surprising at first; however, Fig. 1 shows how the oxygen of a phosphine oxide would fit easily into the molecule, while not altering the overall size of the molecule. In addition, the phenolic hydrogens, which were located in the diffraction pattern and refined isotropically, are well-positioned to engage in hydrogen bonding to a phosphine oxide. Phosphine/phosphine oxide systems with identical cell parameters are known,[26] and solid-state structures have been reported with partial oxidation of the phosphine, and thus fractional occupation in the crystal lattice.[27–29] The phenol rings in **1** are twisted with respect to each other by 23°.

The synthesis of the ^{R}[OPO] potassium derivatives is outlined in eq. [2]. Reaction of the protonated ligands **1** or **2** with an excess of KH in THF affords the products (^{Ph}[OPO]$K_2)_2(THF)_6$ (**3**) and (^{iPr}[OPO]$K_2)_3(THF)_x$ (**4**) in 92% and 71% yield, respectively. NMR studies indicate that **3** has a symmetric structure in solution as evidenced by two distinct singlet resonances in the ^{1}H NMR spectra at δ 1.64 and δ 1.33, which correspond to the two different *tert*-butyl protons on each ring; the $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet for the ^{31}P nuclei at –29.6 ppm. Mass spectral analysis indicates that the complex is dimeric in the bulk material.

[2] 

X-ray quality crystals of **3** containing three molecules of the co-crystallized solvent were grown by slow evaporation of a saturated THF solution at –40 °C. The solid-state structure is presented in Fig. 2, and selected bond distances and angles are collected in Table 2. Structurally, **3** is a symmetrical dimer, in agreement with the solution and mass spectral data, with two crystallographically related fragments. The core of the structure is virtually identical to the DME-supported complex, ^{Ph}[OPO]$K_2(DME)_2$, reported recently.[22] The only significant differences are a direct consequence of the difference in coordinating solvent. In both complexes, a single molecule of solvent is bound to K(2); however, the bidentate nature of DME results in longer bonds to the surrounding oxygen atoms than are present in **3**, where a monodentate THF is coordinated. Two solvent oxygens are coordinated to K(1) in both complexes, a single DME in ^{Ph}[OPO]$K_2(DME)_2$ and both terminal and bridging THF molecules in **3**. Although the observed K–O bond distances in the structure of **3** vary by almost 0.4 Å, they agree well with the DME structure[22] and other literature values,[30–32] as do the K–P bond distances.[33–35] With regard to the phosphine to potassium distances in the solid state, it is clear that these are weak interactions and the connectivities only indicate close interactions.

Slow diffusion of hexanes into a benzene solution of **4** af-

Fig. 1. Molecular structure (ORTEP) of ^{Ph}[OPO]H$_2$, **1**. Ellipsoids are drawn at 50% probability. Co-crystallized solvent was omitted for clarity. Modeled *t*-butyl disorder was also omitted for clarity.

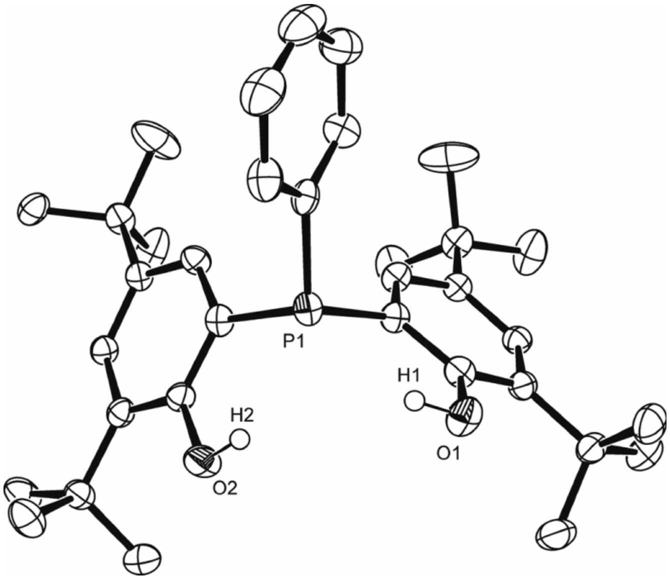


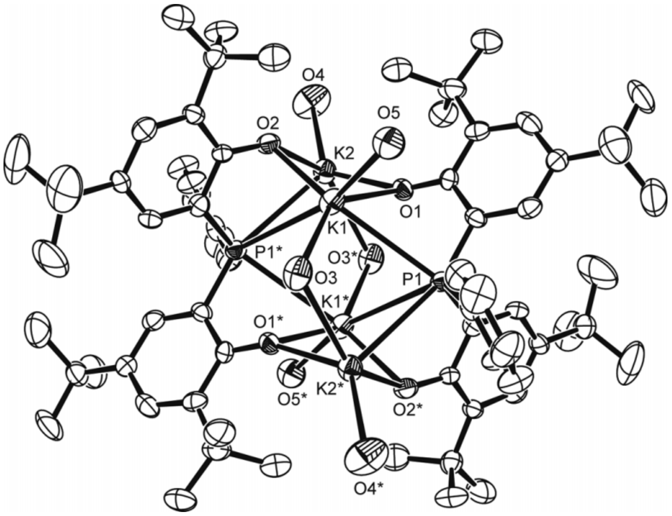
Table 1. Selected bond distances (Å), bond angles (°), and dihedral angles (°) for ^{Ph}[OPO]H$_2$, **1**.

Bond distances (Å)	
P(1)— C(1)	1.828(2)
P(1)— C(7)	1.826(2)
O(1)— H(1)	0.901(2)
O(2)— H(2)	0.950(2)
O(1)— C(2)	1.375(2)
O(2)— C(8)	1.377(2)
P(1)— C(13)	1.824(2)
Bond angles (°)	
C(1)– P(1)– C(7)	102.31(9)
C(7)– P(1)– C(13)	106.01(9)
C(1)– P(1)– C(13)	107.03(10)
C(2)– O(1)– H(1)	107.04(10)
C(8)– O(2)– H(2)	105.46(10)

forded X-ray quality crystals that have been structurally characterized as the benzene adduct (^{iPr}[OPO]K$_2$)$_3$(THF)$_3$(η^6-C$_6$H$_6$) (**4-C$_6$H$_6$**) containing four molecules of co-crystallized benzene and two molecules of co-crystallized hexane per unit cell. The solid-state structure of **4** is presented in Fig. 3. The structure is that of an asymmetric trimer, and one molecule of benzene is π-bonded in a η^6 fashion to a potassium atom, K(5), a motif that has been reported in other potassium complexes.[36–38] Unfortunately, extreme disorder in the co-crystallized and coordinated solvent results in very weak data, insufficient to support a more detailed discussion of the structure. A cif file is included in the Supplementary data.

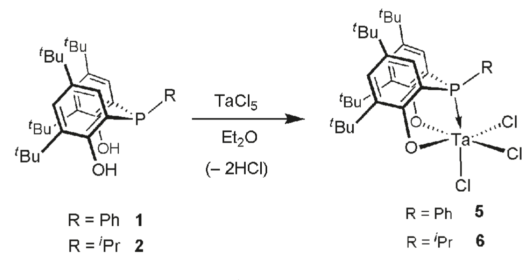
The ^{1}H and ^{31}P{^{1}H} NMR spectra of **4** show a symmetrical solution structure, which is at odds with the asymmetrical nature of the solid-state structure. A mass spectrum of **4** could not be obtained, presumably due to the high molecular weight of the trimer. One likely explanation for the symmetrical NMR spectra is that the trimer exists only in the solid state and it breaks up in solution forming monomeric species. However, the ^{1}H NMR spectrum indicates that THF exists in two different environments, with distinct multiplets attributable to one THF molecule, and broad singlets attributable to two THF molecules. The distinct multiplets indicate that one THF molecule is strongly bound and not undergoing exchange. The broad singlets indicate two THF molecules are undergoing exchange, which is unusual, given the apparent lack of donors in the system, as evidenced by the coordinated benzene in the solid-state structure.

Fig. 2. Molecular structure (ORTEP) of (^{Ph}[OPO]K$_2$)$_2$(THF)$_6$, **3**. Ellipsoids are drawn at 50% probability. Carbon atoms of the THF ligands and co-crystallized solvent were removed for clarity. Modeled *t*-butyl disorder was also omitted for clarity.



Synthesis of the tantalum chloride complexes ^{Ph}[OPO]-TaCl$_3$ (**5**) and ^{iPr}[OPO]TaCl$_3$ (**6**) is outlined in eq. [3]. Reaction of **1** with TaCl$_5$ in diethyl ether under reduced pressure affords a thick mixture of a yellow solid and a yellow solution. Filtration of the mixture and drying of the solid in vacuo affords **5** as a bright yellow powder in 92% isolated yield. The *iso*-propyl derivative is prepared in 82% yield by the analogous reaction of **2** with TaCl$_5$. The complexes were characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, mass spectrometry, and elemental analysis. Both complexes display a singlet resonance in the ^{31}P{^{1}H} NMR spectrum, **5** at δ 33.5 and **6** at δ 31.9. ^{1}H NMR spectra indicate that the complexes are C_s-symmetric, with two resonances due to the *tert*-butyl protons; **6** also displays a diagnostic doublet of septets for the *iso*-propyl methine proton and a doublet of doublets for the *iso*-propyl methyl protons.

[3]



The synthesis of **5** and **6** is strongly linked to the concentration of the reagents in the reaction mixture. For example, reaction of **1** with TaCl$_5$ in highly concentrated solution

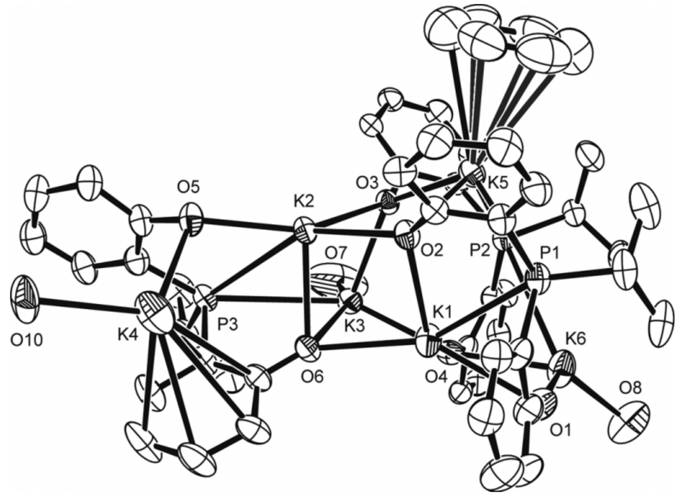
Table 2. Selected bond distances (Å) and bond angles (°) for $({}^{Ph}[OPO]K_2)_2(THF)_6$, **3**.

Bond distances (Å)	
K(1)— O(1)	2.690(6)
K(1)— O(2)	2.673(6)
K(1)— O(3)	2.913(7)
K(1)— O(5)	2.748(7)
K(1)— P(1)	3.361(3)
K(1)— P(1*)	3.507(3)
K(2)— O(1)	2.591(6)
K(2)— O(2)	2.551(6)
K(2)— O(3*)	2.909(7)
K(2)— O(4)	2.667(8)
K(2)— P(1*)	3.343(3)
Bond angles (°)	
P(1)– K(1)– O(1)	56.57(13)
P(1)– K(1)– O(2)	137.15(15)
P(1)– K(1)– O(3)	88.29(14)
P(1)– K(1)– O(5)	89.41(16)
P(1)– K(1)– P(1*)	106.25(7)
O(1)– K(1)– O(2)	84.49(18)
O(1)– K(1)– O(3)	144.73(19)
O(1)– K(1)– O(5)	98.6(2)
O(1)– K(1)– P(1*)	92.58(14)
O(2)– K(1)– O(3)	127.0(2)
O(2)– K(1)– O(5)	115.8(2)
O(2)– K(1)– P(1*)	53.88(14)
O(3)– K(1)– O(5)	82.5(2)
O(3)– K(1)– P(1*)	94.93(15)
O(1)– K(2)– O(2)	89.04(19)
O(1)– K(2)– O(3*)	77.76(19)
O(1)– K(2)– O(4)	131.4(2)
O(1)– K(2)– P(1*)	98.29(14)
O(2)– K(2)– O(3*)	141.29(19)
O(2)– K(2)– O(4)	106.4(2)
O(2)– K(2)– P(1*)	57.00(14)
O(3*)– K(2)– P(1*)	88.69(15)
K(1)– P(1)– K(1*)	73.75(7)
K(1)– P(1)– K(2*)	76.57(7)
K(1)– O(3)– K(2*)	91.02(18)
K(1)– O(1)– K(2)	88.18(18)
K(1)– O(2)– K(2)	89.38(18)
K(1)– P(1*)– K(2)	64.84(6)

leads to the formation of the known bis(OPO) complex, ${}^{Ph}[OPO]_2TaCl$ (**7**),[25] which can be easily separated from **5** by filtration, owing to its significantly increased solubility. Reaction of 2 equiv. of **1** furnishes the highest yield of **7**; however, the reaction does not go to completion.

The synthesis of **5**–**7** is somewhat unusual in that it proceeds via direct protonolysis of the Ta–Cl bond producing reactive HCl as the byproduct. Salt metathesis routes to early transition-metal coordination complexes are driven to completion by the formation of simple alkali metal salts such as lithium chloride. The formation of HCl does not offer the same driving force as the formation of an alkali metal salt. However, it is likely that the protonolysis reaction is controlled by the oxophilic nature of tantalum and the formation of strong tantalum–oxygen bonds. Alternative routes to traditional salt metathesis in tantalum halide chemistry are known, particularly in the synthesis of cyclopentadienyl derivatives containing alkyl silane or stannane functionalities that are then eliminated as silyl chlorides[39,40] or stannyl chlorides,[41,42] respectively. However, the pathway utilized in the synthesis of **5**–**7** is very rare,[43,44] presumably due to the sensitivity of Ta–O bonds to HCl.[45]

Fig. 3. Molecular structure (ORTEP) of $({}^{iPr}[OPO]K_2)_3(THF)_3(\eta^6\text{-}C_6H_6)$, **4-C₆H₆**. Ellipsoids are drawn at 50% probability. Carbon atoms of the THF ligands and *t*-butyl groups were removed for clarity.

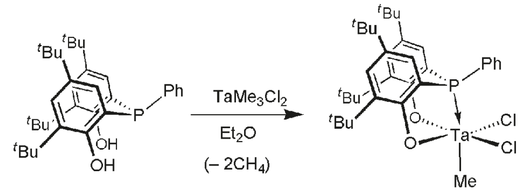


Complexes **5**–**7** are tantalum halides supported by tridentate mixed-donor ligands, something that could not be achieved with the amidophosphine ligand ^{Ph}[NPN],[3] where ${}^{Ph}[NPN] = [PhP(CH_2SiMe_2NPh)_2]$. With the tantalum-halide species reported here, it should be possible to investigate reduction of the halide in the presence of dinitrogen, a technique that has proven useful in synthesizing dinitrogen complexes of group-4 metals supported by amidophosphine ligands.[11–13] However, typical reduction protocols of complexes **5**–**7** utilizing KC_8 or Na/Hg in the presence of one or four atmospheres of dinitrogen resulted in the formation of dark brown solids that solution NMR spectral and mass spectral data indicate are composed of several different materials, none of which can be positively identified as a dinitrogen complex. It is possible that the lack of steric bulk around the metal center in these complexes opens alternative reactivity pathways for the reduced metal complex, potentially including the formation of metal–metal bonded species.[46,47]

Another route to dinitrogen complexes that has proven useful with [NPN] tantalum complexes is the hydrogenation of alkyl derivatives.[3,48] Reactions of **5** and **6** with alkylating agents such as $(PhCH_2)MgCl$ and CH_3MgCl at −40 °C and −78 °C yield only mixtures of products, from which the desired alkyl could not be cleanly isolated. However, in the absence of tantalum halide complexes supported by [NPN], work with that ligand turned to reaction of ligand precursors with tantalum alkyl halide materials, particularly $TaMe_3Cl_2$.

The synthesis of **5** has shown that phenols react with Ta–Cl bonds, so it was of interest to examine the reaction of **1** with $TaMe_3Cl_2$ where either HCl or CH_4 could be released. Addition of an ethereal solution of $TaMe_3Cl_2$ to **1** in Et_2O affords a pale yellow solid that solution NMR spectroscopy, mass spectrometry, and elemental analysis indicate is the monomethyl complex ^{Ph}[OPO]TaMeCl$_2$ (**8**), formed via elimination of two equivalents of methane, as shown in eq. [4]. In the ^{1}H NMR spectrum, the methyl ligand appears as a phosphorus-coupled doublet at δ 2.08 ($^3J_{PH}$ = 9.8 Hz) integrating to three protons; the ^{31}P{^{1}H} NMR spectrum shows a singlet at δ 38.8. A structure with a trans orientation of the Ta–Me, and the Ta–P is supported by the rather large three-bond P–H coupling constant observed in the ^{1}H NMR spectrum. For example, the bis(OPO) complex ^{Ph}[OPO]$_2$TaMe displays a singlet for the Ta–Me protons in the ^{1}H NMR spectrum, indicative of the cis disposition of phosphine groups compared to the methyl on Ta.[25]

[4]



1 **8**

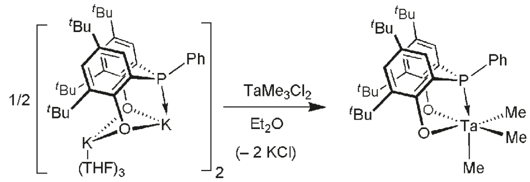
Mixed methyl chloride coordination complexes are known in tantalum chemistry, supported by various ligands, including cyclopentadienyl-based ligands,[49–51] and a biphenolate pincer ligand.[52] Although most coordination compounds of this nature are formed via salt metathesis routes, other examples of alkane elimination routes are known.[52,53]

Further reactivity of **8** has not produced results to date. Attempts to create mixed alkyl species through reaction of **8** with (PhCH$_2$)MgCl result in dark solids that are composed of several materials. A similar result is observed when **8** is reduced in the presence of dinitrogen. Much like the reduction of **7**, reductions produce dark brown materials, from which no dinitrogen complexes could be identified. Hydrogenation of **8** under 4 atm (1 atm = 101.325 kPa) of hydrogen produces a mixture of products, and no resonances attributable to tantalum hydrides can be observed in a ^{1}H NMR spectrum.

When a substoichiometric amount of **1** is reacted with TaMe$_3$Cl$_2$, an impurity is observed in solution NMR spectra that can be separated from **8** by crystallization. Slow evaporation of the reaction solution deposits bright yellow crystals of X-ray quality. These have been structurally characterized as ^{Ph}[OPO]TaMe$_2$Cl (**9**). The solid-state molecular structure is presented in Fig. 4, and selected bond distances and angles are collected in Table 3. There is a distorted octahedral geometry about the tantalum, with the chloride trans to the phosphine and the two aryloxides trans to the methyl carbons. Ta–O, Ta–P, and Ta–Cl bond distances compare well to those of similar complexes reported recently.[25] The tantalum methyl bond distances are very similar to those of ^{Ph}[NAsN]TaMe$_3$[9] and ^{Ph}[NPN]TaMe$_3$.[3] In the ^{1}H NMR spectrum, the methyl hydrogen resonances are superimposed upon one set of *t*-butyl resonances, but integrate to six protons when the *t*-butyl protons are subtracted. The ^{31}P{^{1}H} NMR spectrum shows the expected singlet at δ 40.6. The origin of **9** is likely a result of a redistribution reaction between the monomethyl ^{Ph}[OPO]TaMeCl$_2$ (**8**) and unreacted TaMe$_3$Cl$_2$.

Salt metathesis has proven productive for the synthesis of ^{Ph}[OPO]TaMe$_3$ (**10**), which is outlined in eq. [5]. Reaction of TaMe$_3$Cl$_2$ with **3** in Et$_2$O furnishes the product as an off-white solid in moderate yield (68%). The synthesis can also be carried out using the lithium salt (^{Ph}[OPO]Li$_2$)$_2$(THF)$_4$; however, the potassium salt affords a cleaner transformation. In solution, the ^{31}P{^{1}H} NMR spectrum of **10** displays a single resonance at δ 13.0, and the *t*-butyl protons appear as a pair of singlets in the ^{1}H NMR spectrum at δ 1.60 and δ 1.25, and the methyl protons appear as a phosphorus-coupled doublet ($^3J_{PH}$ = 4.4 Hz) at δ 1.53. The methyl carbons appear at δ 63.5 in the ^{13}C{^{1}H} NMR spectrum. The solid-state structure of **10** has not been determined to date; however, a mass spectrum indicates the complex is monomeric. Thus, a distorted octahedral structure similar to **9** would be expected. The observation of three equivalent Ta–Me groups by NMR spectroscopy is likely a result of a fluxional process, similar to that previously reported for ^{Ph}[NPN]TaMe$_3$.[3]

[5]



3 **10**

Reaction of **10** with 4 atm of hydrogen results in the formation of a dark orange solid. NMR spectroscopy indicates the solid is a mixture of different compounds with no resonances attributable to hydrides identifiable.

Conclusions

In this report, an improved synthesis of the bis(aryloxy)-phosphines ^{Ph}[OPO]H$_2$ and ^{iPr}[OPO]H$_2$ has been developed by reaction of precursor lithium salts with Et$_3$NHCl. Conversion of the protonated compounds to potassium salts was accomplished by reaction with KH, furnishing (^{Ph}[OPO]K$_2$)(THF)$_6$ and (^{iPr}[OPO]K$_2$)$_3$(THF)$_3$.

Tantalum complexes supported by [OPO] were synthesized by reaction of [OPO] precursors with TaCl$_5$ and TaMe$_3$Cl$_2$. Reactions with TaCl$_5$ produce the halide complexes ^{Ph}[OPO]TaCl$_3$ and ^{iPr}[OPO]TaCl$_3$, and a bis(ligand) complex, ^{Ph}[OPO]$_2$TaCl, was synthesized through manipulation of reaction concentration. Reaction with TaMe$_3$Cl$_2$ furnishing the mixed methyl chloride complexes ^{Ph}[OPO]-TaMeCl$_2$ and ^{Ph}[OPO]TaMe$_2$Cl by methane elimination, and the trimethyl complex ^{Ph}[OPO]TaMe$_3$ by salt metathesis with the potassium salt (^{Ph}[OPO]K$_2$)$_2$(THF)$_6$.

Experimental section

General procedures

Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553–2 glovebox equipped with a MO-40–2H purification system and a –40 °C freezer), unless specified. Anhydrous hexanes and toluene were purchased from Aldrich, sparged with dinitrogen, and further dried by passage through a tower of silica followed by passage through a tower of Ridox (or Q-5) catalyst prior to use.[54] Anhydrous pentane, benzene, tetrahydrofuran, and diethyl ether were purchased from Aldrich, sparged with dini-

Fig. 4. Molecular structure (ORTEP) of ^{Ph}[OPO]TaMe$_2$Cl, **9**. Ellipsoids are drawn at 50% probability.

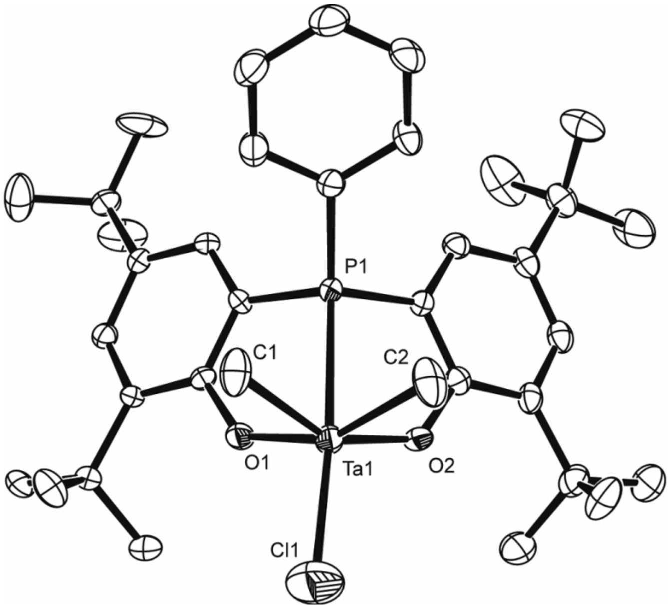


Table 3. Selected bond distances (Å), bond angles (°), and dihedral angles (°) for ^{Ph}[OPO]TaMe$_2$Cl (**9**).

Bond distances (Å)	
Ta(1)— P(1)	2.6331(13)
Ta(1)— C(1)	2.196(6)
Ta(1)— C(2)	2.179(5)
Ta(1)— O(1)	1.939(3)
Ta(1)— O(2)	1.943(4)
Ta(1)— Cl(1)	2.300(2)
Bond angles (°)	
P(1)– Ta(1)– Cl(1)	172.35(6)
P(1)– Ta(1)– C(1)	81.72(17)
P(1)– Ta(1)– C(2)	84.05(18)
P(1)– Ta(1)– O(1)	72.30(10)
P(1)– Ta(1)– O(2)	72.58(10)
C(1)– Ta(1)– C(2)	82.8(2)
C(1)– Ta(1)– O(1)	86.82(19)
C(1)– Ta(1)– O(2)	152.5(2)
C(1)– Ta(1)– Cl(1)	99.75(19)
O(1)– Ta(1)– C(2)	155.3(2)

trogen, and passed through an Innovative Technologies SPS-PureSolv-400–4 apparatus. Water was distilled and thoroughly degassed prior to use. All organic solvents were tested with addition of sodium benzophenone ketyl prior to use to ensure absence of oxygen and water. Alternatively, anhydrous diethyl ether was stored over sieves and distilled from sodium benzophenone ketyl under argon; tetrahydrofuran was refluxed over CaH$_2$ prior to distillation from sodium benzophenone ketyl under argon, and pentane was stored over sieves and distilled from sodium benzophenone ketyl solublized by tetraglyme under dry dinitrogen prior to storage over a potassium mirror. Nitrogen gas was dried and deoxygenated by passage through a column containing activated molecular sieves and MnO.

Deuterated benzene was dried by refluxing with molten sodium/potassium alloy in a sealed vessel under partial pressure, then trap-to-trap distilled, and freeze–pump–thaw-degassed three times. Deuterated tetrahydrofuran and toluene were dried by refluxing with molten potassium metal or sodium–potassium alloy in a sealed vessel under vacuum, then trap-to-trap distilled, and freeze–pump–thaw-degassed three times. ^{1}H, ^{31}P, ^{1}H{^{31}P}, ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{7}Li{^{1}H} NMR spectra were recorded on either a Bruker AMX-500 instrument operating at 500.13 MHz for ^{1}H spectra, a Bruker AVA-400 instrument operating at 400.13 MHz for ^{1}H spectra, or a Bruker AVA-300 instrument operating at 300.13 MHz for ^{1}H spectra. ^{1}H NMR spectra were referenced to residual protons in deuterated solvent as follows: C_6D_5H (δ 7.15), C_4D_7HO (δ 3.58), and C_7D_7H (δ 2.09) with respect to tetramethylsilane at δ 0.0. ^{13}C NMR spectra were referenced to 1% tetramethylsilane in CDCl$_3$ at δ 0.0. ^{31}P NMR spectra were referenced to either external or internal P(OMe)$_3$ (δ 141.0 with respect to 85% H$_3$PO$_4$ at δ 0.0). ^{7}Li NMR spectra were referenced to external LiCl (0.3 mol/L solution in MeOH at δ 0.0). Elemental analyses were performed by Mr. P. Borda and Mr. M. Lakha, and mass spectrometry (EI/MS on a Kratos MS 50 unless otherwise stated) was performed by Mr. M. Lapawa, all at the Department of Chemistry, the University of British Columbia.

Materials

The complexes (^{Ph}[OPO]Li$_2$)$_2$(THF)$_4$ and (^{iPr}[OPO]-Li$_2$)$_2$(THF)$_4$ were prepared by the literature procedure.[14] Et$_3$NHCl was prepared by the reaction of triethylamine and aqueous hydrochloric acid, and recrystallized from ethanol. Potassium hydride was purchased from Acros Chemicals and used as received; TaCl$_5$ was purchased from STREM and sublimed prior to use. TaMe$_3$Cl$_2$ was prepared according to published methods.[55]

Synthesis of ^{Ph}[OPO]H$_2$ (1)

To an intimate mixture of (^{Ph}[OPO]Li$_2$)$_2$(THF)$_4$ (5.00 g, 7.41 mmol) and Et$_3$NHCl (2.01g, 14.8 mmol) was added Et$_2$O (150 mL). The solution was stirred for 12 h, and then the solvent was removed under vacuum. The residue was extracted into toluene (50 mL), the solution filtered through Celite, and then evaporated to dryness. The colourless solid was washed with minimal pentane and dried under vacuum. Yield: 3.74 g (97%). X-ray quality crystals of **1** containing three equivalents of co-crystallized solvent were grown by slow evaporation of a saturated benzene solution. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C) δ: 7.64 (d, $^3J_{HH}$ = 2.3 Hz, 1H, *p*-PPh), 7.35 (m, 4H, *o*/*m*-PPh), 7.23 (s, 2H, Ph), 7.02 (m, 2H, Ph), 6.50 (d, $^4J_{PH}$ = 8.9 Hz, O*H*), 1.61 (s, 18H, *o*-PhC(C*H*$_3$)$_3$), 1.26 (s, 18H, *p*-PhC(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 25 °C) δ: –50.23 (s). ^{1}H NMR (300 MHz, C$_4$D$_8$O, 25 °C) δ: 7.33 (d, $^3J_{HH}$ = 2.4 Hz, 2H, Ph–*H*), 7.27 (m, 7H, Ph–*H*), 6.84 (dd, $^4J_{HH}$ = 2.4 Hz, $^4J_{PH}$ = 5.5 Hz, 2H, O*H*), 1.42 (s, 18H, *o*-PhC(C*H*$_3$)$_3$), 1.12 (s, 18H, *p*-PhC(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C$_4$D$_8$O, 25 °C) δ: –47.18 (s).

Synthesis of ^{iPr}[OPO]H$_2$ (2)

Following the procedure for **1**, Et$_2$O (150 mL) was added to an intimate mixture of Et$_3$NHCl (1.95 g, 14.18 mmol) and (^{iPr}[OPO]Li$_2$)$_2$(THF)$_4$ (4.54 g, 7.09 mmol). Yield: 3.27 g

(96%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.58 (dd, $^3J_{PH}$ = 4.5 Hz, $^4J_{HH}$ = 2.2 Hz, 2H, *o*-OPh), 7.50 (d, $^4J_{HH}$ = 2.2 Hz, 2H, *p*-OPh), 7.00 (d, $^4J_{PH}$ = 11.2 Hz, O*H*), 2.88 (ds, $^2J_{PH}$ = 12.4 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, P–C*H*(CH$_3$)$_2$), 1.50 (s, 18H, *o*-PhC(C*H*$_3$)$_3$), 1.29 (s, 18H, *p*-PhC(C*H*$_3$)$_3$), 0.92 (dd, $^3J_{PH}$ = 18.2 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, P–CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: –61.65 (s). MS (EI) *m*/*z* (%): 484 (100) [M]$^+$. Anal. calcd. for $C_{31}H_{49}O_2P$: C, 76.82; H, 10.19. Found: C, 76.62; H, 9.96.

Synthesis of (^{Ph}[OPO]K$_2$)$_2$(THF)$_6$ (3)

Potassium hydride (1.16 g, 28.9 mmol) was added in portions over 30 min to a solution of ^{Ph}[OPO]H$_2$ (5.0 g, 9.6 mmol) in THF (100 mL) with stirring. The solution was then placed under partial vacuum until the evolution of hydrogen ceased, stirred 12 h under static partial vacuum, filtered through Celite, and then evaporated to dryness. The resulting pale yellow residue was washed with minimal hexanes to give **3** as a colourless solid. Yield: 7.13 g (92%). X-ray quality crystals of **3** containing three equivalents of cocrystallized solvent were grown from a saturated THF solution at –40 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.52–6.96 (m, 18H, Ph), 3.62 (m, 24H, THF–OC*H*$_2$CH$_2$), 1.64 (s, 36H, *o*-PhC(C*H*$_3$)$_3$), 1.48 (m, 24H, THF-OCH$_2$C*H*$_2$), 1.33 (s, 36H, *p*-PhC(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: –29.59 (s). MS (EI) *m*/*z* (%): 1188 (6) [M – (THF)$_6$]$^+$, 516 (80) [OPO]$^+$. Anal. calcd. for $C_{92}H_{138}K_4O_{10}P_2 \cdot 2C_4H_8O$: C, 67.99; H, 8.79. Found: C, 68.38; H, 8.65.

Synthesis of (^{iPr}[OPO]K$_2$)$_3$(THF)$_3$ (4)

Following the procedure for **3**, KH (0.21 g, 5.19 mmol) was added to a solution of **2** (1.00 g, 2.017 mmol) in THF (25 mL). Yield: 0.93 g (71%). X-ray quality crystals of the benzene adduct **4-C$_6$H$_6$** containing one equivalent of cocrystallized benzene and half a molecule of co-crystallized hexane were grown from slow diffusion of hexanes into a benzene solution. Crystals of **4-C$_6$H$_6$** were dried and used for elemental analysis. ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.15 (d, $^3J_{HH}$ = 2.6 Hz, 6H, Ph), 6.94 (d, $^3J_{HH}$ = 2.6 Hz, 6H, Ph), 3.62 (m, 4H, THF–OC*H*$_2$CH$_2$), 3.58 (s, 8H, THF–OC*H*$_2$CH$_2$), 2.28 (m, 3H, P–C*H*(CH$_3$)$_2$), 1.78 (m, 4H, THF–OCH$_2$C*H*$_2$), 1.73 (s, 8H, THF–OCH$_2$C*H*$_2$), 1.39 (s, 54H, *o*-PhC(C*H*$_3$)$_3$), 1.21 (s, 54H, *p*-PhC(C*H*$_3$)$_3$), 1.00 (dd, $^3J_{PH}$ = 14.4 Hz, $^3J_{HH}$ = 6.6 Hz, 18H, P–C*H*(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: –37.41 (s). Anal. calcd. for $C_{105}H_{165}K_6O_9P_3 \cdot 1/3C_6H_6$: C, 67.43; H, 8.72. Found: C, 67.08; H, 8.61.

Synthesis of ^{Ph}[OPO]TaCl$_3$ (5)

To an intimate mixture of **1** (2.86 g, 3.86 mmol) and TaCl$_5$ (1.38 g, 3.86 mmol) was added diethyl ether (100 mL) with stirring. The bright yellow solution was stirred for 12 h under reduced static pressure during which time a yellow solid was deposited. The solution was filtered through Celite and evaporated to dryness. The residue was washed with hexanes and dried under vacuum to yield **5** as a bright yellow solid. Yield: 2.86 g (92%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.60 (m, 6H, Ph), 7.05 (m, 3H, Ph), 1.57 (s, 18H, *o*-PhC(C*H*$_3$)$_3$), 1.16 (s, 18H, *p*-PhC(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: 33.46 (s). MS (EI) *m*/*z* (%): 802 (100) [M]$^+$. Anal. calcd. for $C_{34}H_{45}Cl_3O_2PTa$: C, 50.79; H, 5.64. Found: C, 50.90; H, 5.76.

Synthesis of ^{iPr}[OPO]TaCl$_3$ (6)

With the same procedure described above for **5**, **2** (1.00 g, 2.07 mmol) was reacted with TaCl$_5$ (0.743 g, 2.07 mmol), giving **6** as a bright yellow solid. Yield: 1.31 g (82%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.52 (m, 2H, Ph), 7.21 (m, 2H, Ph), 3.03 (dsep, $^2J_{PH}$ = 5.8 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, P–C*H*(CH$_3$)$_2$), 1.50 (s, 18H, *o*-PhC(C*H*$_3$)$_3$), 1.35 (dd, $^3J_{PH}$ = 19.2 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, P–CH(C*H*$_3$)$_2$), 1.23 (s, 18H, *p*-PhC(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: 31.88 (s). MS (EI) *m*/*z* (%): 768 (100) [M]$^+$. Elemental analysis was not obtained.

Synthesis of ^{Ph}[OPO]$_2$TaCl (7)

A solution of **1** (2.00 g, 3.87 mmol) in toluene (10 mL) was added dropwise to a suspension of TaCl$_5$ (0.693 g, 1.93 mmol) in toluene (10 mL) with stirring. The resulting yellow solution was stirred for 24 h then evaporated to dryness. The residue was extracted into hexanes (5 mL), filtered through Celite, and the solvent was removed under vacuum, furnishing **7** as a bright yellow powder. Yield: 1.09 g (45%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.70–7.04 (m, 18H, Ph), 1.49 (s, 36H, *o*-PhC(C*H*$_3$)$_3$), 1.14 (s, 36H, *p*-PhC(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: 37.85 (s). MS (EI) *m*/*z* (%): 1249 (30) [M]$^+$. Anal. calcd. for $C_{68}H_{90}ClO_4P_2Ta$: C, 65.35; H, 7.26. Found: C, 65.56; H, 7.43.

Synthesis of ^{Ph}[OPO]TaMeCl$_2$ (8)

A solution of TaMe$_3$Cl$_2$ (0.12 g, 0.39 mmol) in Et$_2$O (10 mL) was added dropwise to a solution of **1** (0.20 g, 0.39 mmol) in Et$_2$O (50 mL) at –78 °C, and the resulting pale yellow solution was stirred at –78 °C for 1 h. Removal of the cold bath, slow warming for 40 min, followed by removal of the solvent under vacuum gave a pale yellow residue that was washed with minimal pentane and dried under vacuum to give **8** as a pale yellow solid. Yield: 0.21 g (70%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.58 (m, 6H, Ph), 7.09 (m, 3H, Ph), 2.08 (d, $^3J_{PH}$ = 9.8 Hz, 3H, Ta–C*H*$_3$), 1.56 (s, 18H, PhC(C*H*$_3$)$_3$), 1.23 (s, 6H, PhC(C*H*$_3$)$_3$), 1.19 (s, 12H, PhC(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: 38.79 (s). MS (EI) *m*/*z* (%): 782 (100) [M]$^+$. Anal. calcd. for $C_{35}H_{48}Cl_2O_2PTa$: C, 53.65; H, 6.17. Found: C, 53.87; H, 6.23.

Synthesis of ^{Ph}[OPO]TaMe$_2$Cl (9)

A solution of TaMe$_3$Cl$_2$ (0.056 g, 0.188 mmol) in Et$_2$O (5 mL) was added dropwise to a solution of **1** (0.076 g, 0.147 mmol) in Et$_2$O (5 mL) at –78 °C. After 1 h, the solution was warmed to room temperature, concentrated to about half volume, and allowed to slowly evaporate, affording **9** as yellow crystals of X-ray quality. Yield: 0.025 g (22% from **1**). ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.64 (m, 5H, Ph), 7.12 (m, 4H, Ph), 1.56 (br s, 24H, Ta–C*H*$_3$ and *o*-PhC(C*H*$_3$)$_3$), 1.22 (s, 18H, *p*-PhC(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: 40.65 (s). Elemental analysis was not recorded.

Synthesis of ^{Ph}*[OPO]TaMe*$_3$ *(10)*

A solution of $TaMe_3Cl_2$ (0.040 g, 0.135 mmol) in Et_2O (10 mL) was added dropwise to a solution of **3** (0.100 g, 0.067 mmol) in Et_2O (50 mL) at –78 °C, and the resulting pale solution was stirred at –78 °C for 1 h. Removal of the cold bath, slow warming for 40 min, followed by removal of the solvent under vacuum gave a pale yellow solid. The residue was extracted into toluene (20 mL), the solution filtered through Celite, and evaporated to dryness yielding a solid that was washed with minimal pentane and dried under vacuum to give **10** as an off-white solid. Yield: 0.068 g (68%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ: 7.82 (m, 1H, *p*-PPh), 7.65 (dd, $^3J_{HH}$ = 2.2 Hz, $^3J_{PH}$ = 6.1 Hz, 2H, *o*-PPh), 7.58 (d, $^3J_{HH}$ = 2.2 Hz, 2H, *m*-PPh), 7.11 (m, 4H, Ph), 1.60 (s, 18H, *o*-PhC(CH_3)$_3$), 1.53 (d, $^3J_{PH}$ = 4.4 Hz, 9H, Ta–CH_3), 1.25 (s, 18H, *p*-PhC(CH_3)$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 25 °C) δ: 12.98 (s). ^{13}C{^{1}H} NMR (75.4 MHz, C_7D_8, 0 °C) δ: 166.2 (s, oPh *i-C*), 145.4 (d, $^1J_{PC}$ = 4.0 Hz, PPh *i-C*), 138.3 (d, $^1J_{PC}$ = 5.7 Hz, P–PhC(CH_3)$_3$ *i-C*), 132.2 (s, PPh *o-C*), 132.0 (s, PPh *o-C*), 129.6–123.7 (Ph–*C*), 63.5 (s, Ta–(*C*H$_3$)$_3$), 35.3 (s, *o*-Ph*C*(CH$_3$)$_3$), 34.7 (s, *p*-Ph*C*(CH$_3$)$_3$), 31.5 (s, *o*-PhC(*C*H$_3$)$_3$), 29.6 (s, *p*-PhC(*C*H$_3$)$_3$). MS (EI) *m*/*z* (%): 742 (100) [M]$^+$. Anal. calcd. for $C_{37}H_{54}O_2PTa$: C, 59.83; H, 7.33. Found: C, 59.75; H, 7.45.

Crystallography

In all cases, suitable crystals were selected and mounted on a glass fibre using Paratone-N oil or an acceptable substitute and frozen to –100 °C.

Measurements for structure **1** were made on a Rigaku/ADSC CCD area detector with graphite monochromated Mo Kα radiation. The data were processed using the d*TREK[56] module, part of the CrystalClear software package, version 1.3.6 SP0,[57] and corrected for Lorentz and polarization effects and absorption. Neutral atom scattering factors for all non-hydrogen atoms were taken from Cromer and Waber.[58] Anomalous dispersion effects were included in $F_{calcd.}$.[59]

Measurements for structures **3**, **4**, and **9** were made on a Bruker X8 area detector with monochromated Mo Kα radiation. The data were processed and integrated using the Bruker SAINT software package[60] and corrected for absorption effects using the multi-scan technique (SADABS).[61]

All structures were solved by direct methods using the programs SIR97[62] or SIR2002.[63] All non-hydrogen atoms were refined anisotropically by least-squares procedures on F^2 using SHELXL-97.[64] Hydrogen atoms were included but not refined; their positional parameters were calculated with fixed C–H bond distances of 0.99 Å for sp^2 C, 0.98 Å for sp^3 C, and 0.95 Å for aromatic sp C, with U_{iso} set to 1.2 × U_{eq} of the attached sp or sp^2 C and U_{iso} set to 1.5 × U_{eq} values of the attached sp^3 C atom. Methyl hydrogen torsion angles were determined by electron density. Structure solution and refinements were conducted using the WinGX software package, version 1.64.05.[65] Structural illustrations were created using ORTEP-III for Windows.[66]

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca). CCDCs 756433–756437 contain the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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