

Synthesis and Reactivity of Tantalum Complexes Supported by Bidentate X₂ and Tridentate LX₂ Ligands with Two Phenolates Linked to Pyridine, Thiophene, Furan, and Benzene Connectors: Mechanistic Studies of the Formation of a Tantalum Benzyldiene and Insertion Chemistry for Tantalum–Carbon Bonds

Theodor Agapie, Michael W. Day, and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received March 23, 2008

Using either alkane elimination or salt metathesis methods, tantalum complexes have been prepared with new ligand systems with tridentate bis(phenolate)donor (donor = pyridine, furan, and thiophene) or bidentate bis(phenolate)benzene arrangements. The ligand framework has two X-type phenolates connected to the flat heterocyclic L-type donor at the 2,6- or 2,5- positions or to the 2,6- positions of benzene via direct ring–ring (sp^2 – sp^2) linkages. Solid-state structures of these complexes show that in all cases the ligands bind in a *mer* fashion, but with different geometries of the LX₂ frameworks. The pyridine-linked system binds in a C_s-fashion, the furan-linked system in a C_{2v}-fashion, and the thiophene-linked system in a C₁-fashion. A bis(phenolate)pyridine tantalum tribenzyl species (**7**), upon heating in the presence of dimethylphenylphosphine, generates a stable benzyldiene complex by α -hydrogen abstraction with loss of toluene and PMe₂Ph trapping. This process was found to be independent of PMe₂Ph concentration with $\Delta H^\ddagger = 31.3 \pm 0.6 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = 3 \pm 2 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and the kinetic isotope effect $k_H/k_D = 4.9 \pm 0.4$, consistent with a mechanism involving rate determining α -hydrogen abstraction with loss of toluene, followed by fast phosphine coordination to the resulting benzyldiene species. An X-ray structure determination reveals that the benzyldiene π -bond is oriented perpendicular to the oxygen–oxygen vector, in accord with the prediction of DFT calculations. Tantalum alkyl complexes with the benzene-linked bis(phenolate) ligand (Ta(CH₃)₂[(OC₆H₂-*t*Bu₂)₂C₆H₃] (**16**), Ta(CH₂Ph)₂[(OC₆H₂-*t*Bu₂)₂C₆H₃] (**17**), and TaCl₂CH₃[(OC₆H₂-*t*Bu₂)₂C₆H₄] (**18**)) are obtained with (to afford pincer complexes) or without cyclometalation at the *ipso*-position. Deuterium labeling of the phenol hydrogens and of the linking 1,3-benzene-diyl ring reveals an unexpected mechanism for the metalation of bis(phenol)benzene with TaCl₂(CH₃)₃ to generate **18**. This process involves protonolysis of a methyl group, followed by C–H/Ta–CH₃ σ bond metathesis leading to cyclometalation of the linking ring, and finally protonation of the cyclometallated group by the pendant phenol. TaCl₂CH₃[(OC₆H₂-*t*Bu₂)₂C₆H₄] was found to undergo σ bond metathesis at temperatures over 90 °C to give the pincer complex TaCl₂[(OC₆H₂-*t*Bu₂)₂C₆H₃] (**19**) and methane ($\Delta H^\ddagger = 27.1 \pm 0.9 \text{ kcal} \cdot \text{mol}^{-1}$; $\Delta S^\ddagger = -2 \pm 2 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; $k_H/k_D = 1.6 \pm 0.2$ at 125 °C). Ta(CH₃)₂[(OC₆H₂-*t*Bu₂)₂C₆H₃] (**16**) was found to react with *t*BuNC to insert into the Ta–CH₃ bonds and generate an imino-acyl species (**23**). Reaction of **16** with Ph₂CO or PhCN leads to insertion into the Ta–Ph bond to give **21** and **22**. Complexes **6**, **7**, **10**, **11-P**, **12**, **13**, **17**, **18**, **19-OEt₂**, **21**, **22**, and **23** have been structurally characterized by single crystal X-ray diffraction, and all show a *mer* binding mode of the diphenolate ligands, but the ligand geometry varies leading to C_{2v}-, *pseudo*-C_s-, *pseudo*-C₂-, and C₁-symmetric structures.

Introduction

The organometallic chemistry of the early transition metals evolved largely with compounds having bent metallocene frameworks. More recently, some classes of early transition metal complexes based on nonmetallocene frameworks have proven to be well defined platforms for the study of elementary organometallic transformations and as catalysts for diverse reactions including olefin polymerizations, hydroaminations, hydrogenations, and olefin metathesis.^{1–13} Nonetheless, com-

pared to their metallocene counterparts, early metal systems having ligand systems other than cyclopentadienyl remain less explored and less well understood. In this context, the discovery of easily prepared and tunable ligand frameworks that could provide early transition metal complexes that are stable and well

(2) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315.

(3) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236–2257.

(4) Watson, D. A.; Chiu, M.; Bergman, R. G. *Organometallics* **2006**, *25*, 4731–4733.

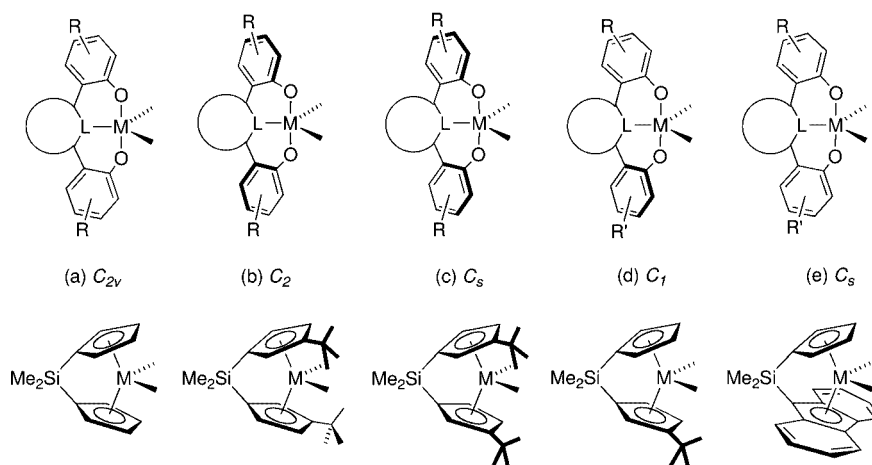
(5) Anderson, L. L.; Arnold, J.; Bergman, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 14542–14543.

(6) Ackermann, L.; Bergman, R. G.; Loy, R. N. *J. Am. Chem. Soc.* **2003**, *125*, 11956–11963.

(7) Rothwell, I. P. *Chem. Commun.* **1997**, 1331–1338.

* Corresponding author. E-mail: bercaw@caltech.edu.

(1) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428–447.

Scheme 1^a

^a R, R' = alkyl or aryl; linker = thiophene, furan, pyrrole, pyridine, NHC, or phenyl; L = C (neutral or anionic), N, O, or S.

defined, while allowing for new types of transformations with stereocontrol, is highly desirable. Phenolates are readily tunable ligands with respect to sterics and electronics.¹⁴ Multidentate phenolate ligand systems, in particular, have found applications in olefin polymerization catalysis as well as in the synthesis and study of fundamental organometallic transformations.^{15–22}

One drawback apparent for some of the multidentate ligands reported thus far is the degradation of the groups connecting the ligating atoms.^{22,26,33} For example, the tripodal tetradentate bis(phenolate) ligands described by Kol et al. have been reported to be susceptible to β -H abstraction from the position next to the metal-coordinated tertiary amine.²² We have recently reported zirconium and titanium complexes supported by tridentate LX₂ ligands with two phenolates linked to furan, thiophene, and pyridine donors.³⁴ These complexes proved to be thermally robust and effective precatalysts for propylene polymerization and oligomerization.

Herein we describe the synthesis, characterization, and investigations of the reactivity of an analogous series of tantalum complexes supported by this type of ligand (Scheme 1). The ligand frameworks have two (X-type) phenolates connected to a flat heterocyclic (L-type) donor (*N*-heterocyclic carbene, pyridine, furan, or thiophene) or a benzene ring at the 2,6- or 2,5-positions via direct ring–ring (sp^2 – sp^2) linkages. One motivation to study this ligand family stems from their resemblance to ubiquitous *ansa* metallocene frameworks that have been used to support a variety of stoichiometric and catalytic transformations (Scheme 1). Assuming that the terphenyl (or terphenyl-like) subunit enforces a *mer* binding mode, this framework could have binding geometries of C_2 , C_{2v} , C_s (two types), and C_1 symmetry, depending on the direction of twisting around the aryl–aryl linkages. This structural versatility is of interest in the context of developing stereoselective applications. Previous reports of boron and group 4 complexes supported by the bis(phenolate)pyridine ligands provide examples of C_s -symmetric structures.^{35–37} Crystallographically characterized complexes of Fe^{III}, Cu^{II}, and Al^{III} exhibit the C_2 -symmetric binding mode.³⁸

(8) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964–4977.

(9) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748–3759.

(10) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592–4633.

(11) Tsang, W. C. P.; Hultsch, K. C.; Alexander, J. B.; Bonitatebus, P. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652–2666.

(12) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145–179.

(13) Spencer, L. P.; Beddie, C.; Hall, M. B.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 12531–12543.

(14) Bradley, D. C.; Mehrotra, R. C.; Singh, A.; Rothwell, I. P. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: London, 2001.

(15) Mason, A. F.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 16326–16327.

(16) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134–5135.

(17) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706–10707.

(18) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2002**, *21*, 662–670.

(19) Tshuva, E. Y.; Groyzman, S.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2002**, *21*, 662–670.

(20) Groyzman, S.; Goldberg, I.; Kol, M.; Genizi, E.; Goldschmidt, Z. *Adv. Synth. Catal.* **2005**, *347*, 409–415.

(21) Groyzman, S.; Segal, S.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Inorg. Chem. Commun.* **2004**, *7*, 938–941.

(22) Groyzman, S.; Goldberg, I.; Kol, M.; Genizi, E.; Goldschmidt, Z. *Organometallics* **2004**, *23*, 1880–1890.

(23) Groyzman, S.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2003**, *22*, 3793–3795.

(24) Groyzman, S.; Segal, S.; Shami, M.; Goldberg, I.; Kol, M.; Goldschmidt, Z.; Hayut-Salant, E. *J. Chem. Soc., Dalton Trans.* **2002**, 3425–3426.

(25) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 2777–2783.

(26) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643–3655.

(27) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830–3831.

(28) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822–7836.

(29) Liang, L. C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797–5798.

(30) Mehrkhodavandi, P.; Bonitatebus, P. J.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841–7842.

(31) Mehrkhodavandi, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746–10747.

(32) Mehrkhodavandi, P.; Schrock, R. R.; Pryor, L. L. *Organometallics* **2003**, *22*, 4569–4583.

(33) Schrock, R. R.; Seidel, S. W.; Schrodi, Y.; Davis, W. M. *Organometallics* **1999**, *18*, 428–437.

(34) Agapie, T.; Bercaw, J. E., in press.

(35) Chan, M. C. W.; Tam, K. H.; Zhu, N. Y.; Chiu, P.; Matsui, S. *Organometallics* **2006**, *25*, 785–792.

(36) Chan, M. C. W.; Tam, K. H.; Pui, Y. L.; Zhu, N. Y. *J. Chem. Soc., Dalton Trans.* **2002**, 3085–3087.

(37) Li, Y. Q.; Liu, Y.; Bu, W. M.; Guo, J. H.; Wang, Y. *Chem. Commun.* **2000**, 1551–1552.

(38) Steinhäuser, S.; Heinz, U.; Sander, J.; Hegetschweiler, K. Z. *Anorg. Allg. Chem.* **2004**, *630*, 1829–1838.

In the context of tridentate pincer diphenolate ligands, the cyclometallated bis(phenolate)benzene (X_3 type) version bears resemblance to monoanionic LCL pincer ligand counterparts (L = phosphine, amine, thioether, or ether), an intense area of study.^{39–44} Pincer-based complexes are quite versatile and have found use in catalysis, for fundamental studies of small molecule activation, for supporting diverse organometallic structures and transformations, and for the design and development of novel materials and sensors. Most of the reported systems are based on late transition metal complexes, but early metal and lanthanide pincer complexes have been reported as well.^{43,45–57} In particular, 2,6-di(*o*-anisyl)phenyl (OCO) systems have been reported to support yttrium, samarium, and ytterbium complexes.^{45–47} Diaminophenyl (NCN) systems have been developed for supporting titanium, tantalum, lutetium, and yttrium chemistry.^{43,48–57}

The organometallic chemistry of tantalum is distinctive for the ubiquity of alkylidene and olefin complexes.^{43,48–54} In previously reported cases, the pendant ligands are based on neutral donors such as phosphines, amines, thioethers, ethers, and carbenes.^{39–44} No multiply charged cyclometallated pincer ligands appear to have been reported before part of the current work was communicated;⁵⁸ however, more recently, hafnium and molybdenum complexes supported by trianionic bis(phenolate)phenyl (OCO) and bis(amide)phenyl (NCN) ligands, respectively, have been reported.^{59,60} The use of terphenyl frameworks for pincer ligands has recently emerged as a route

to chiral, C_2 -symmetric pincer systems; systems of C_s symmetry have been reported as well.^{45–47,61,62} For early metal chemistry, in which higher oxidations states are accessible, the study of complexes supported by robust multianionic (LX_2 and X_3) ligands, which would complement the known monoanionic (L_2X) cyclometallated pincer ligands, is an underdeveloped area. We report herein new tantalum alkyl complexes with these LX_2 ligands, their preparative routes, the structures of several representative examples, mechanistic studies of the metalation of the bis(phenolate)benzene ligand as well as the thermal decomposition of a tris-benzyltantalum derivative with the bis(phenolate)pyridine ligand to a stable benzylidene complex, and the insertion of isocyanide into tantalum-methyl and benzophenone and benzonitrile into tantalum-aryl bonds.

Results and Discussion

Preparation of Tantalum Alkyl Complexes Supported by Bis(phenol)pyridine (1). Bis(phenol)pyridine ((2,6-HOC₆H₂-2,4-*t*Bu₂)₂NC₅H₃, **1**), thiophene ((2,5-HOC₆H₂-2,4-*t*Bu₂)₂SC₄H₂, **2**), furan ((2,5-HOC₆H₂-2,4-*t*Bu₂)₂OC₄H₂, **3**), and benzene linkers ((2,6-HOC₆H₂-2,4-*t*Bu₂)₂C₆H₄, **4**) are prepared using palladium-catalyzed aryl–aryl coupling chemistry, as described previously.⁵⁸ Tantalum metalation has been performed using either salt metathesis or alkane eliminations routes. Common tantalum alkyl starting materials such as Ta(CH₂Ph)₅, TaCl₂(CH₂Ph)₃, TaCl₃(CH₂Ph)₂, TaCl₂Me₃, or TaCl₃Me₂ are used as precursors to phenoxide supported complexes (Scheme 1).^{63,64} Deprotonation of **1** has been performed in situ with KCH₂Ph. The tantalum precursors are added to a slurry of potassium bis(phenoxide)pyridine in benzene or diethyl ether (Scheme 2). The ¹H NMR spectra of the crude reaction mixtures show nearly quantitative formation of the desired products. Filtration to remove the KCl byproduct, followed by recrystallization, provides analytically pure samples of the tantalum complexes. The ¹H NMR spectroscopic features of these compounds are revealing. Complex **5** displays one singlet integrating for 4 H corresponding to the benzyl CH₂ resonances, suggesting that the two benzyl groups are related by a mirror plane (Scheme 1). Another possible explanation involves a fast interchange process. Complex **6** shows a sharp singlet integrating to 9 H corresponding to the three tantalum coordinated methyl groups, in a variety of deuterated solvents. A variable temperature ¹H NMR study was undertaken, and at –90 °C, the Ta–CH₃ signals give rise to two broad singlets in a two to one ratio. There is no geometry available to complex **6** that could lead to three chemically equivalent methyl groups, if the bis(phenolate)pyridine ligand is meridionally coordinated. In that case, a fluxional process that allows for methyl exchange, consistent with the variable temperature behavior, must be invoked (*vide infra*). The low temperature spectrum indicates a favored structure with two equivalent methyls. This can be accomplished by the presence of a mirror plane such as in a C_{2v} structure (Scheme 1). However, a C_s structure, with a facial binding of the tridentate ligand is consistent with the low temperature NMR data as well.

(39) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020–1024.

(40) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759–1792.

(41) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750–3781.

(42) Crabtree, R. H. *Pure Appl. Chem.* **2003**, *75*, 435–443.

(43) Rietveld, M. H. P.; Grove, D. M.; vanKoten, G. *New J. Chem.* **1997**, *21*, 751–771.

(44) Slagt, M. Q.; van Zwieten, D. A. P.; Moerkerk, A.; Gebbink, R.; van Koten, G. *Coord. Chem. Rev.* **2004**, *248*, 2275–2282.

(45) Rabe, G. W.; Berube, C. D.; Yap, G. P. A. *Inorg. Chem.* **2001**, *40*, 4780–4784.

(46) Rabe, G. W.; Zhang-Presse, M.; Riederer, F. A.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L. *Inorg. Chem.* **2003**, *42*, 7587–7592.

(47) Rabe, G. W.; Zhang-Presse, M.; Riederer, F. A.; Yap, G. P. A. *Inorg. Chem.* **2003**, *42*, 3527–3533.

(48) Rietveld, M. H. P.; Klumpers, E. G.; Jastrzebski, J.; Grove, D. M.; Veldman, N.; Spek, A. L.; vanKoten, G. *Organometallics* **1997**, *16*, 4260–4267.

(49) Rietveld, M. H. P.; Lohner, P.; Nijkamp, M. G.; Grove, D. M.; Veldman, N.; Spek, A. L.; Pfeffer, M.; vanKoten, G. *Chem.—Eur. J.* **1997**, *3*, 817–822.

(50) Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J.; Kooijman, H.; Vandersluijs, P.; Smeets, W. J. J.; Spek, A. L.; Vankoten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773–9781.

(51) Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Kooijman, H.; Spek, A. L.; Vankoten, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 996–998.

(52) Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Spek, A. L.; Pfeffer, M.; Vankoten, G. *Organometallics* **1993**, *12*, 2227–2235.

(53) Abbenhuis, H. C. L.; Grove, D. M.; Vandersluijs, P.; Spek, A. L.; Vankoten, G. *Recl. Trav. Chim. Pays-Bas-J. Roy. Neth. Chem. Soc.* **1990**, *109*, 446–448.

(54) Abbenhuis, H. C. L.; Rietveld, M. H. P.; Haarman, H. F.; Hogerheide, M. P.; Spek, A. L.; Vankoten, G. *Organometallics* **1994**, *13*, 3259–3268.

(55) Hogerheide, M. P.; Boersma, J.; Spek, A. L.; vanKoten, G. *Organometallics* **1996**, *15*, 1505–1507.

(56) Hogerheide, M. P.; Grove, D. M.; Boersma, J.; Jastrzebski, J.; Kooijman, H.; Spek, A. L.; Vankoten, G. *Chem.—Eur. J.* **1995**, *1*, 343–350.

(57) Donkervoort, J. G.; Jastrzebski, J.; Deelman, B. J.; Kooijman, H.; Veldman, N.; Spek, A. L.; vanKoten, G. *Organometallics* **1997**, *16*, 4174–4184.

(58) Agapie, T.; Bercaw, J. E. *Organometallics* **2007**, *26*, 2957–2959.

(59) Sarkar, S.; Carlson, A. R.; Veige, M. K.; Falkowski, J. M.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 1116–1117.

(60) Koller, J.; Sarkar, S.; Abboud, K. A.; Veige, A. S. *Organometallics* **2007**, *26*, 5438–5441.

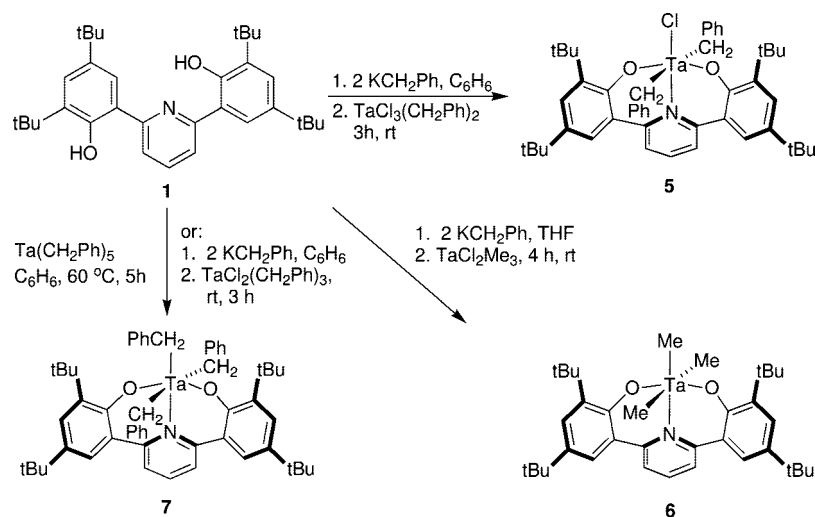
(61) Ma, L. Q.; Woloszynek, R. A.; Chen, W. Z.; Ren, T.; Protasiewicz, J. D. *Organometallics* **2006**, *25*, 3301–3304.

(62) Smith, R. C.; Protasiewicz, J. D. *Organometallics* **2004**, *23*, 4215–4222.

(63) Schrock, R. R.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5288–5290.

(64) Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209–225.

Scheme 2



The solid-state structure of compound **6** shows *mer* coordination of the tridentate ligand (Figure 1). The Ta–N bond length is in the long range compared to other reported Ta–pyridine complexes, but the most unusual and unexpected feature is the bending of the pyridine ring away from the Ta–N axis (Ta–N–C9 angle = 146.6 °). This distortion is likely a consequence of the inherent rigidity in the terphenyl framework that prevents all of the rings from adopting their preferred conformations while maintaining optimal metal–ligand bond distances and angles. The [Ta–CH₃] groups are clearly different, with one trans to the pyridine nitrogen and two roughly trans

to each other. The Ta–CH₃ bond lengths are typical for tantalum methyl complexes, and C35–Ta–C34 and C35–Ta–C36 angles are 108.42(7)° and 104.62(8)°, respectively, with atoms C34 and C36 leaning toward the pyridine donor. With this distortion and the long Ta–N bond, the structure could be viewed as trigonal bipyramidal with an additional weak interaction with the pyridine. It is worth noting that the two methyl groups cis to the nitrogen donor are chemically different in the solid state because of the tilting of the pyridine plane. The low temperature spectrum observed for **6** could be accounted for by fast flipping of the pyridine ring between the two sides of

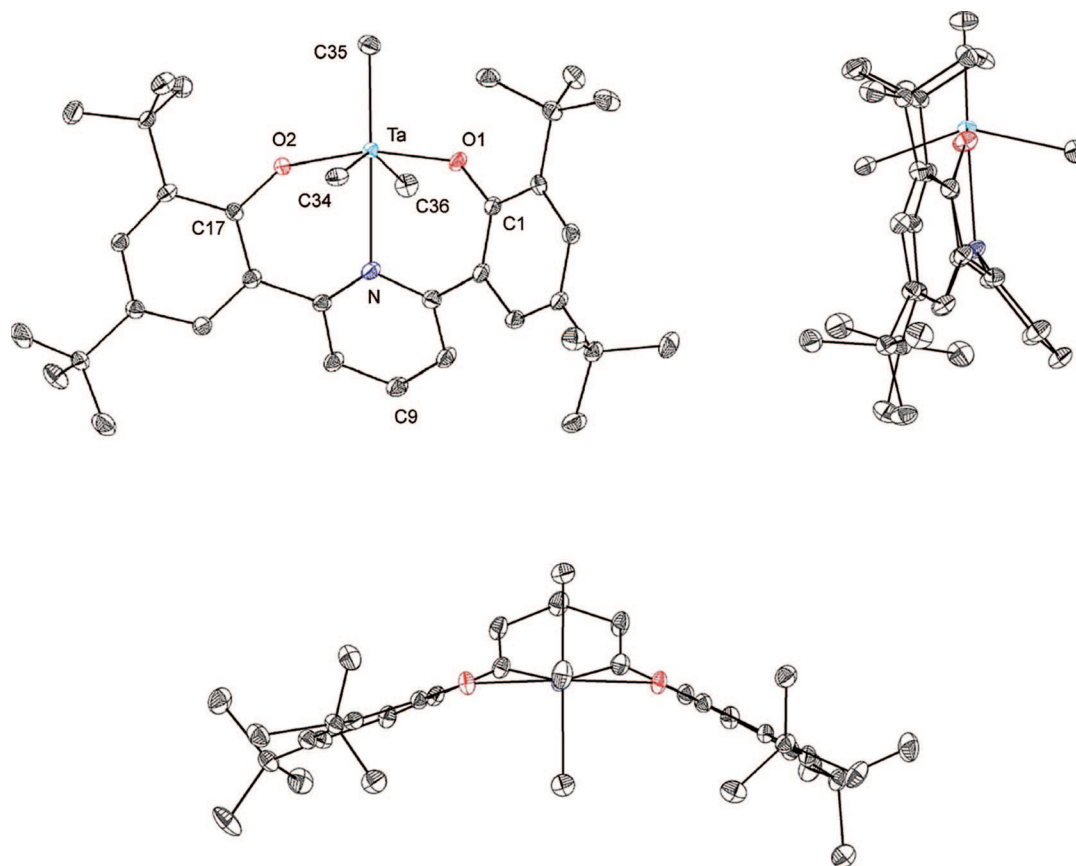
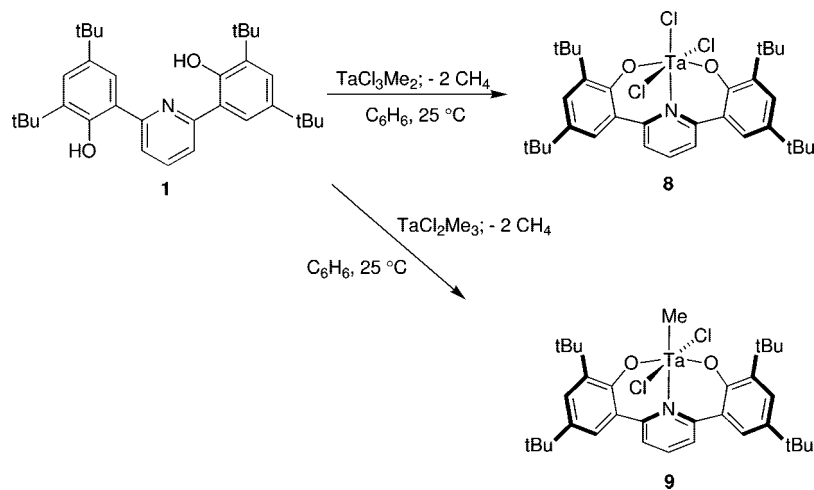


Figure 1. Drawings of the structure of **6**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.9113(13); Ta–O2 1.9020(13); Ta–C35 2.1573(18); Ta–C34 2.1931(18); Ta–C36 2.2032(19); Ta–N 2.4428(14); Ta–N–C9 146.6; O1–Ta–O2 163.45(5); C35–Ta–C34 108.42(7); C35–Ta–C36 104.62(8); Ta–O1–C1 138.09(11); Ta–O2–C17 141.66(11).

Scheme 3



the ONO plane. Given that this cannot be frozen even at -90°C , the energy of the C_{2v} transition state structure is likely not too different from that for the ground state.

Preliminary experiments have been conducted to examine the olefin polymerization activity using **6**. An NMR scale experiment was performed: $\text{Ta}(\text{CH}_3)_3[(\text{OC}_6\text{H}_2-t\text{Bu}_2)\text{NC}_5\text{H}_3]$ (**6**) was treated with $\text{B}(\text{C}_6\text{F}_5)_3$ to generate a major new species based on ^1H NMR spectroscopy. Treatment with ethylene of this in situ generated species led to no reaction at room temperature (^1H NMR spectroscopy). Heating the mixture to 80°C led to the formation of ethylene oligomers as indicated by peaks in the olefinic region of the ^1H NMR spectrum.

Alkane elimination routes were found to be facile for methyl tantalum starting materials. In those cases, reaction with bis(phenol)pyridine is complete within hours at room temperature to give $\text{TaCl}_3[(\text{OC}_6\text{H}_2-t\text{Bu}_2)\text{NC}_5\text{H}_3]$ (**8**) or $\text{TaCl}_2(\text{CH}_3)[(\text{OC}_6\text{H}_2-t\text{Bu}_2)\text{NC}_5\text{H}_3]$ (**9**), when starting with TaCl_3Me_2 or TaCl_2Me_3 , respectively (Scheme 3). Tantalum pentabenzyl requires heating at 60°C for five hours for complete conversion to $\text{Ta}(\text{CH}_2\text{Ph})_3[(\text{OC}_6\text{H}_2-t\text{Bu}_2)\text{NC}_5\text{H}_3]$ (**7**) (Scheme 2); at room temperature, this reaction is only 60% completed after 35 h. The lower reactivity for the benzyl precursor could be due to the decreased basicity of benzyl versus methyl, as well as to a more hindered metal center in the tantalum benzyl versus tantalum methyl species. The ^1H NMR spectrum of **7** shows two singlets for the benzylic protons ($\text{Ta}-\text{CH}_2\text{Ph}$) in a two to one ratio, consistent with a *mer* binding mode. For a *fac* binding mode, the methylene protons trans to oxygen donors would be diastereotopic and thus should display two distinct signals (not observed). A single crystal X-ray diffraction study of **7** (Figure 2) confirmed the meridional binding mode indicated by the ^1H NMR spectroscopic data. Compared to the trimethyl compound **5**, the tantalum tribenzyl species shows a notable difference with respect to the binding of the alkyl groups: the $\text{C}41-\text{Ta}-\text{C}34$ and $\text{C}41-\text{Ta}-\text{C}48$ angles are about 30° smaller ($75.14(7)^{\circ}$ and $76.32(7)^{\circ}$, respectively). It is not clear if this orientation is adopted to avoid some steric interactions between the pyridine ring the bulkier benzyl groups or to facilitate some bonding interaction between the metal center and the π system of the benzyl group: one of the $\text{Ta}-\text{C}-\text{C}(\text{phenyl})$ angles is more acute than the others, at 97° versus 119° and 120° , and the $\text{Ta}-\text{C}(\text{ipso})$ bond length is $2.81 \text{ \AA}$. Furthermore, this geometry allows one of the benzyl phenyls

to be in close proximity to the pyridine ring indicating the possibility of some $\pi-\pi$ stacking interactions.^{65,66}

Attempts to Prepare a Tantalum Benzylidene Complex: Formation of $\text{TaF}_2(\text{CH}_2\text{Ph})[(\text{OC}_6\text{H}_2-t\text{Bu}_2)\text{NC}_5\text{H}_3]$. Given the number of stable alkylidene complexes of tantalum, we have pursued a commonly used route to tantalum alkylidenes that involves deprotonation of cationic alkyl species with bases such as Me_3PCH_2 or $\text{KN}(\text{SiMe}_3)_2$.⁶⁷ This strategy was attempted starting with $\text{Ta}(\text{CH}_2\text{Ph})_3[(\text{OC}_6\text{H}_2-t\text{Bu}_2)\text{NC}_5\text{H}_3]$ (**7**). Reaction with $[\text{Ph}_3\text{C}][\text{BF}_4]$, in toluene, leads cleanly to one species according to NMR spectroscopy. The ^1H NMR spectrum of the isolated product displays a triplet corresponding to a benzyl group, which integrates to only 2 H (instead of expected 4 H) relative to the phenoxide ligand *t*Bu groups. This species also displays a broad peak in the ^{19}F NMR spectrum. A single-crystal X-ray diffraction study allowed the identification of the product, a tantalum monobenzyl difluoride **10** (Figure 3). In the solid-state, the benzyl binds trans to the pyridine ligand, consistent with the solution ^1H and ^{19}F NMR spectroscopic data. This species is possibly formed by fluoride abstraction by the electrophilic, cationic tantalum species, followed by a fluoride–benzyl interchange. The target benzylidene species has been prepared by a different route (see below), and alternative procedures involving the cationic alkyl strategy have not been further explored.

Preparation of a Tantalum Benzylidene by Toluene Elimination: Formation and Characterization of $\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})(\text{PMe}_2\text{Ph})[(\text{OC}_6\text{H}_2-t\text{Bu}_2)\text{NC}_5\text{H}_3]$ (11-P**).** Another common route to alkylidene complexes involves intramolecular α -H abstraction, often carried out in the presence of an additional ligand such as a phosphine.^{68–74} Accordingly,

(65) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.

(66) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

(67) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577–6578.

(68) Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964–5966.

(69) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962–5964.

(70) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370.

(71) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793–3800.

(72) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

(73) Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746.

(74) Morton, L. A.; Chen, S. J.; Qiu, H.; Xue, Z. L. *J. Am. Chem. Soc.* **2007**, *129*, 7277–7283.

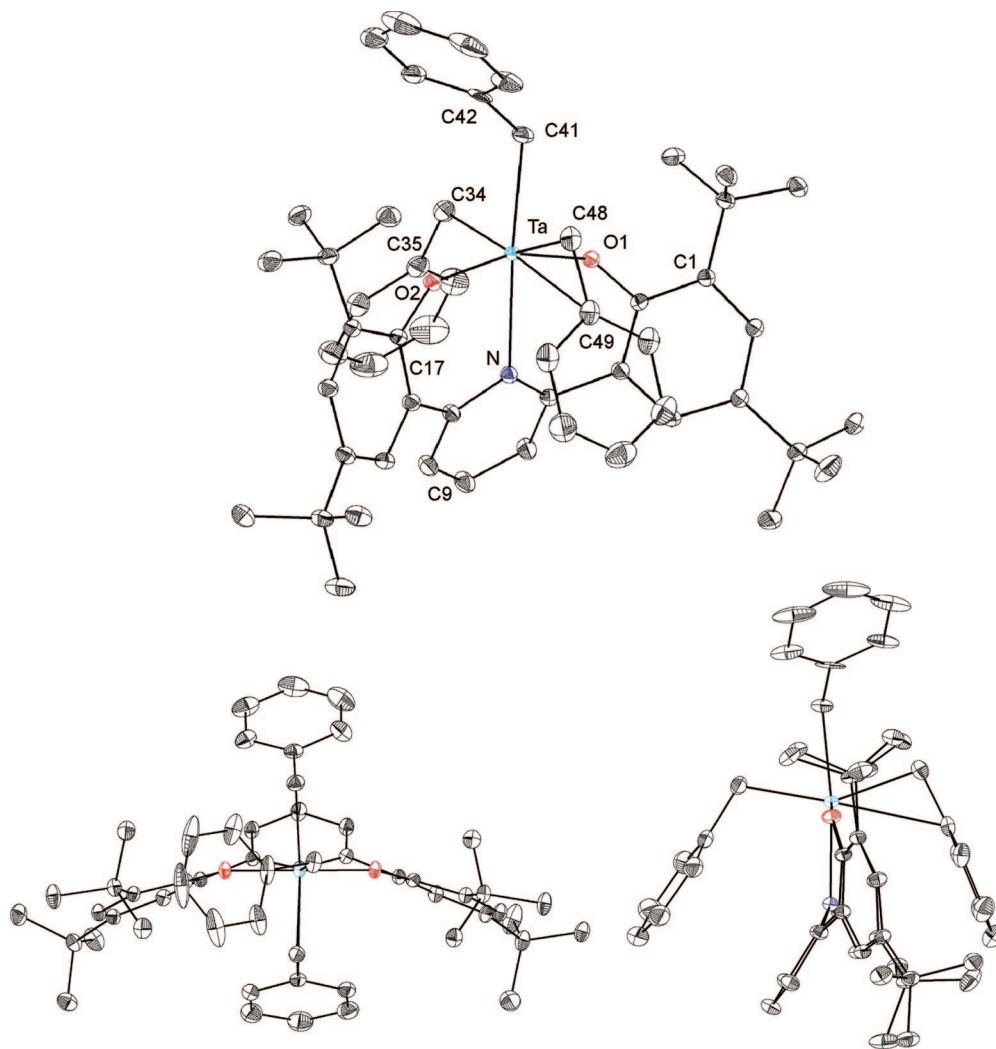
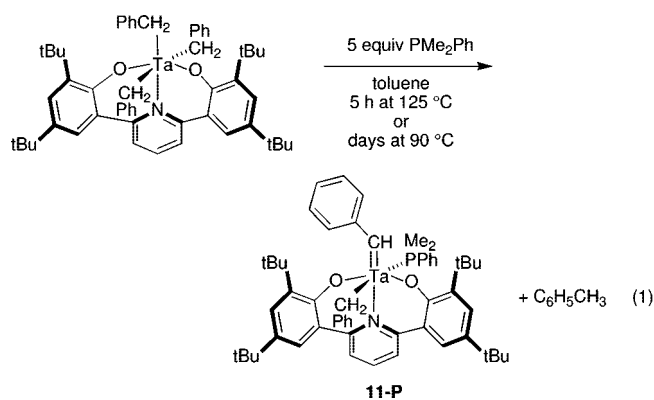


Figure 2. Drawings of the structure of **7**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.8961(11); Ta–O2 1.8972(11); Ta–C41 2.3088(16); Ta–C34 2.2243(18); Ta–C48 2.2269(18); Ta–N 2.4299(13); Ta–N–C9 150.5; O1–Ta–O2 158.89(5); C41–Ta–C34 75.14(7); C41–Ta–C48 76.32(7); Ta–O1–C1 145.20(11); Ta–O2–C17 145.45(10).

compound **7** was heated to temperatures over 90 °C in benzene- d_6 or toluene- d_8 in the presence of excess PMe_2Ph . Clean formation of a new species (**11-P**) was observed by ^1H NMR spectroscopy (eq 1). The singlet at 9.03 ppm is particularly diagnostic for a benzylidene species. The reaction proceeds quite slowly at 90 °C, reaching completion after more than three days. At 125 °C, however, the reaction is complete within hours. In the absence of phosphine, benzylidene formation still appears to occur, judging by the appearance of a peak at 9.20 ppm (^1H NMR spectroscopy); however, the reaction is not as clean. The use of other bases such as quinuclidine or PMe_3 has been explored. The reaction occurs cleanly in the presence of PMe_3 , presumably to the analogue of **11-P**, but decomposition is observed in the presence of quinuclidine. Even for the phosphines that afford clean formation of the benzylidene, prolonged subsequent heating leads to decomposition. Preliminary studies with **11-P** indicate that it reacts with ethylene and diphenylacetylene suggesting promise for further exploration. Notably, the observed clean formation of **11-P** from **7** and PMe_2Ph at such high temperatures emphasizes the chemical robustness of this ligand framework. Even under milder conditions, other reported multidentate biphenoxides undergo reaction with the supporting ligands.²²

The structure and tantalum-benzylidene bonding for **11-P** was investigated using single-crystal X-ray diffraction, NMR spec-



troscopy, and DFT calculations. The solid-state structure of **11-P** (Figure 4) displays hexacoordination at tantalum, with meridionally coordinated pyridine bisphenoxide, benzylidene trans to pyridine, and phosphine and benzyl groups trans to each other. Interestingly, the benzylidene is oriented such that the π -bond roughly bisects the O_2N plane. This orientation is sterically unfavorable, pointing the phenyl group toward a phenoxide *t*-butyl. The ^1H coupled ^{13}C NMR spectrum of **11-P** shows a coupling constant $^1J_{\text{CH}} = 103$ Hz for the alkylidene carbon. Both the TaCC angle and the alkylidene $^1J_{\text{CH}}$ coupling constants have been used as indicators of the degree of α -agostic interaction.

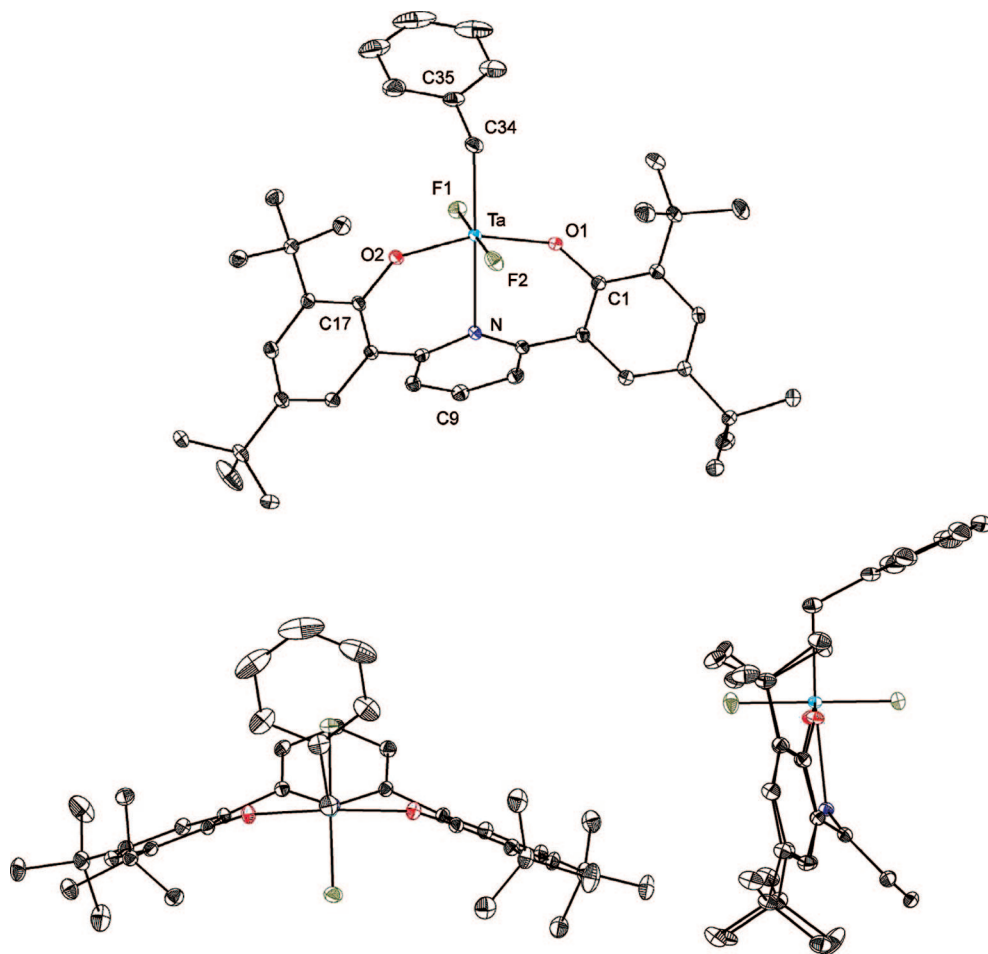


Figure 3. Drawings of the structure of **10**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.8906(13); Ta–O2 1.8908(13); Ta–F1 1.8927(10); Ta–C34 2.1872(19); Ta–F2 1.9110(11); Ta–N 2.4486(14); Ta–N–C9 142.8; O1–Ta–O2 158.28(5); F1–Ta–C34 90.74(6); F2–Ta–C34 89.21(6); Ta–O1–C1 143.78(12); Ta–O2–C17 144.38(11).

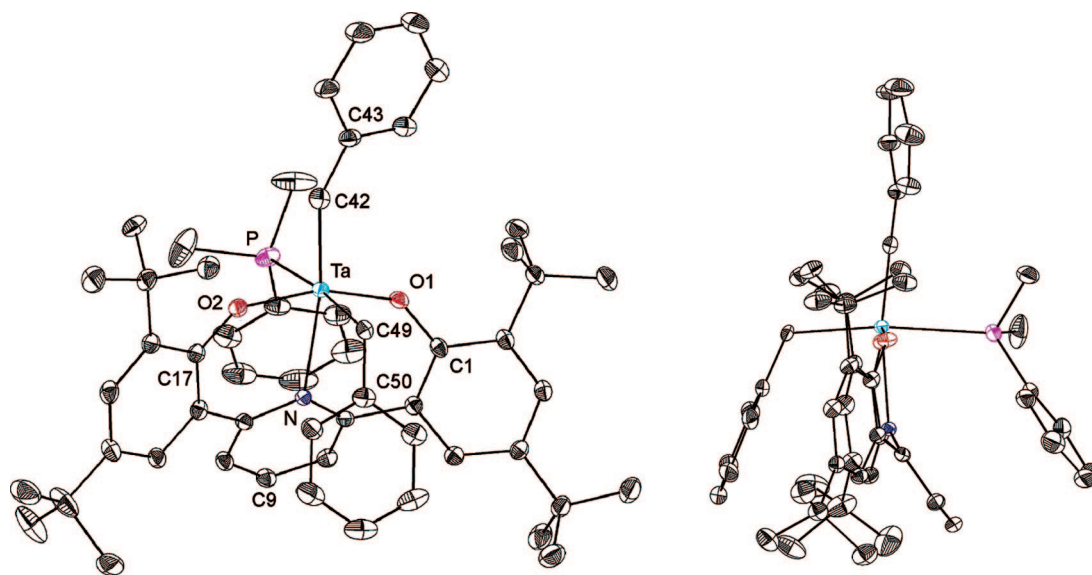


Figure 4. Drawings of the structure of **11-P**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.9355(18); Ta–O2 1.9095(18); Ta–C42 1.996(2); Ta–C49 2.279(2); Ta–P 2.7058(7); Ta–N 2.4827(17); O1–Ta–O2 159.17(6); Ta–C42–C43 149.7(2); Ta–O1–C1 137.10(15); Ta–O2–C17 145.33(15); Ta–N–C9 150.0.

A large TaCC angle correlates with a small C–H coupling constant (due to increased p-character in the CH bond) and is indicative of an increased degree of α -agostic interaction.^{12,75} For example, complex $\text{Cp}_2\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})$, which does not

present a low-energy orbital of appropriate symmetry for an α -agostic interaction, shows a coupling constant $^1J_{\text{CH}} = 127$ Hz and a TaCC angle of 135.2° .⁷¹ At the other end of the spectrum lies $\text{Cp}^*\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})$, which has a coupling

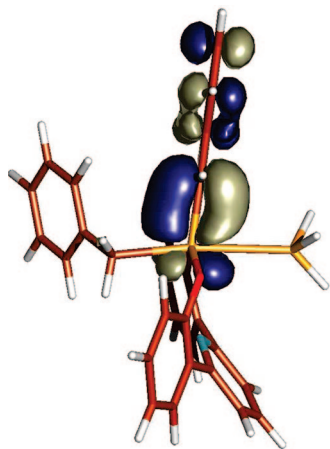


Figure 5. Depiction of HOMO of the optimized gas-phase structure of complex **11-P**.

constant of $^1J_{\text{CH}} = 82$ Hz with a TaCC angle of 166° .⁷⁶ The value of $^1J_{\text{CH}} = 103$ Hz for **11-P** is indicative of a modest amount of α -agostic interaction. This correlates well with the Ta–C42–C43 angle of 149.7° . Interestingly, the benzylidenes prepared by Kol et al. supported by bisamino-diphenolate ligands display significantly more acute alkylidene TaCC angles (140° and 142°).²² However, for all those cases, the phenolates display either chloride or hydrogen in the ortho-position to the phenolate oxygen. Hence, the observed larger alkylidene TaCC angle in the pyridine-diphenolate case could be due, at least in part, to a steric interaction between the phenyl group and the bulky *ortho-t*-butyl group of the phenolate. This possibility was explored computationally.

DFT calculations were performed on a model of **11-P** displaying hydrogens in the positions ortho to the phenolate oxygens (B3LYP, basis set LACVP**, model **11-Pm**, Figure 1 in the Supporting Information). The unrestricted optimized geometry of **11-Pm** displays an alkylidene Ta–C–C angle of 141° , more acute than the one observed in the solid state for the *t*-Bu substituted species and similar to the ones observed for the Kol systems bearing smaller substituents. This indicates that the intrinsic preference for α -agostic interaction is small on the basis of the DFT calculation, almost as small as in the metallocene systems. For the ortho substituted system of **11-P**, the *t*-butyl group probably pushes the phenyl group away from the tantalum center by steric repulsion, increasing the Ta–C–C angle and enforcing more p-character to the alkylidene CH bond. The Ta–C π -interaction for the alkylidene moiety, the calculated HOMO, is shown in Figure 5. This interaction is roughly perpendicular to the Ta–O vectors and correlates with the predicted interactions between the frontier orbitals of the tantalum fragment and of those of the carbene (Figure 2, Supporting Information). Thus, meridonal [TaO₂N] and [TaCp₂] fragments are related electronically due to a structural asymmetry (2-fold, rather than higher) that differentiates the nature of the orthogonal orbitals used to interact with additional ligands. The d-orbitals that have a contribution toward the Cp or O ligands are involved in π -bonding with ancillary ligands and are destabilized with respect to interaction with additional ligands. The remaining d-orbitals, found perpendicular to the O–O or Cp–Cp vector, are available for bonding with an

incoming ligand. Given that the carbene has a similar asymmetry, only a p-orbital energetically accessible perpendicular to the plane of the fragment, the expected geometry is the one allowing for maximal overlap and formation of a Ta=C π -bond.

Mechanistic Study of the Generation of Tantalum Benzylidene Complex Ta(CHPh)(CH₂Ph)(PMe₂Ph)[(OC₆H₂-*t*Bu₂)₂NC₅H₃] (11-P**) by α -Abstraction.** Several mechanisms may be envisioned for the formation of benzylidene **11-P**. One pathway, based on literature precedents,^{71,76,77} involves initial coordination of the phosphine to give rise to a crowded species, **7-P**, that brings an α -H and a neighboring benzyl group into close proximity facilitating α -H abstraction and leads to alkylidene formation with toluene loss. Formation of **7-P** could occur via a fast pre-equilibrium, followed by a rate determining α -H abstraction (Scheme 4, mechanism 1). Because the major tantalum species observed during the reaction are **7** and **11-P**, with no buildup of detectable concentrations of intermediates such as **7-P**, the observed rate constant according to mechanism 1 is expected to be first-order in the phosphine concentration. Alternatively, **7-P** could be generated in a slow step followed by a fast α -H abstraction (Scheme 4, mechanism 2). For this pathway, the observed rate constant again is expected to have a first-order dependence on phosphine concentration. For mechanism 3, α -H abstraction would occur in a rate-determining step directly from **7**, followed by fast phosphine trapping of the alkylidene. For this pathway, the rate would be independent of phosphine concentration.

A series of kinetics experiments was performed with varying phosphine concentrations under pseudo-first-order conditions (more than 20-fold excess vs **7**). As can be seen in Figure 6, the reaction rate at 115°C was found to be cleanly first order in **7**. Provided that the rate of the reaction is predicted to be first order in the phosphine concentration for two of the three proposed mechanisms, kinetic measurements were performed at 115°C at various concentrations of phosphine. Over a phosphine concentration range varied 15-fold, the reaction rate was found to remain essentially constant (Figure 7) consistent only with mechanism 3. Moreover, comparison of the rates at 115°C for Ta(CH₂Ph)₃[(OC₆H₂-*t*Bu₂)₂NC₅H₃] (**7**) and Ta(CD₂Ph)₃[(OC₆H₂-*t*Bu₂)₂NC₅H₃] (**7-d₆**) reveals a kinetic deuterium isotope effect $k_{\text{H}}/k_{\text{D}} = 4.9 \pm 0.4$ (Figure 8) indicating that the rate determining step involves C–H bond cleavage. This value is thus inconsistent with mechanism 2. Rate measurements performed over a temperature range of 37°C (Figure 9) provides Eyring activation parameters of $\Delta H^\ddagger = 31.3 \pm 0.6$ kcal·mol^{−1} and $\Delta S^\ddagger = 3 \pm 2$ cal·mol^{−1}·K^{−1} for **7** (for **7-d₆**, $\Delta H^\ddagger = 34.4 \pm 0.6$ kcal·mol^{−1} and $\Delta S^\ddagger = 8 \pm 2$ cal·mol^{−1}·K^{−1}). The small activation entropy is most consistent with a unimolecular rate determining step (mechanisms 1 and 3). Thus, of the proposed pathways, only mechanism 3 is consistent with all of the above experimental results.

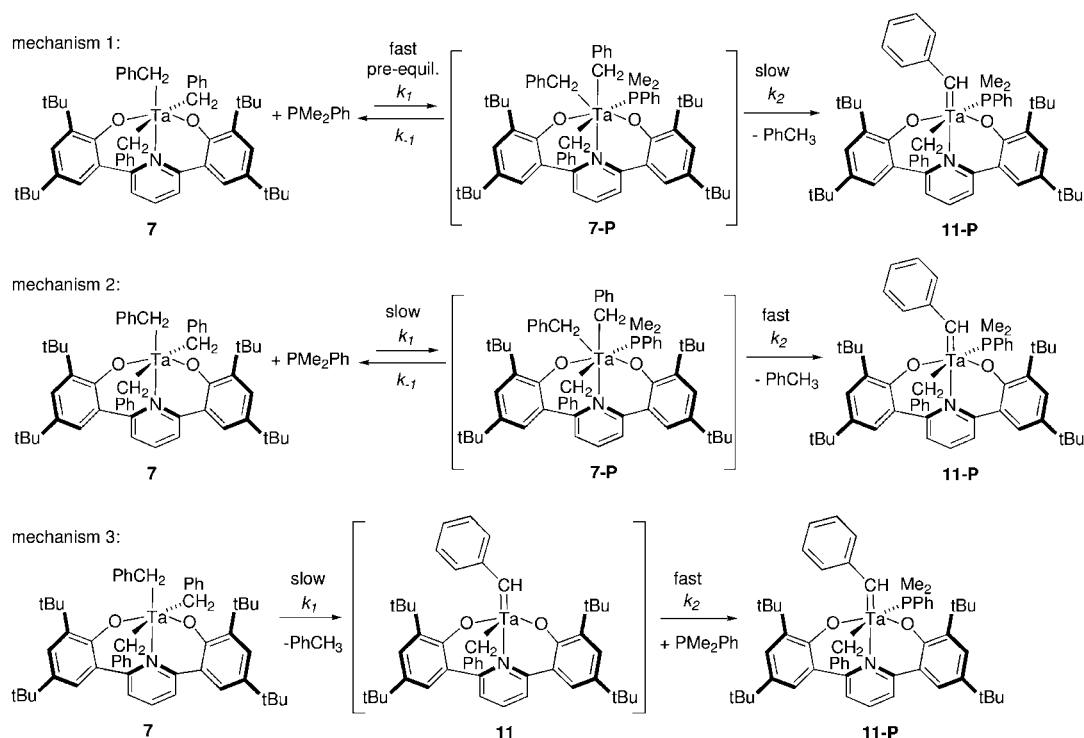
To explore the relevant electronic features of the α -abstraction reaction, the synthesis of compounds with mixed benzyl ligand sets was targeted. Ta(CH₂Ph)₂Cl[(OC₆H₂-*t*Bu₂)₂NC₅H₃] (**5**) was treated with Grignard reagents substituted with OMe and CF₃ in the para position. Mixtures of products were obtained in both cases. The reaction of **5** with deuterium labeled benzyl Grignard reagent PhCD₂MgBr leads to the tribenzyl species with label incorporation at all positions, and treatment of **7** with PhCD₂MgBr also leads to [PhCH₂-]/[PhCD₂-] exchange. These results suggest that exchange occurs between the benzyl Grignard reagent and the benzyl groups of **7**, precluding clean

(75) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(76) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. J. *Am. Chem. Soc.* **1980**, *102*, 6744–6752.

(77) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236–6244.

Scheme 4



preparation of the desired mixed benzyl complexes to probe the electronic effects of the α -abstraction process.

Synthesis and Characterization of a Trimethyltantalum Complex Supported by a Bis(phenolate)thiophene $\text{Ta}(\text{CH}_3)_3\text{-(OC}_6\text{H}_2\text{-}t\text{Bu}_2\text{)}_2\text{SC}_4\text{H}_2$ (12**).** Following the success of metallating the bis(phenolate)pyridine ligand, five-member ring linkers have been investigated. A solution of thiophene-2,5-diphenol (**2**) and $\text{TaCl}_2(\text{CH}_3)_3$ was allowed to stir at room temperature overnight. Only unreacted diphenol is observed by ^1H NMR spectroscopy. The increased steric bulk of the larger sulfur substituent is possibly the reason behind the reduced reactivity of the free phenol. The salt metathesis route proved successful, however. Phenol deprotonation with KBn or $\text{KN}(\text{SiMe}_3)_2$, followed by reaction with $\text{TaCl}_2(\text{CH}_3)_3$, leads to the clean formation of one species assigned as $\text{Ta}(\text{CH}_3)_3[(\text{OC}_6\text{H}_2\text{-}t\text{Bu}_2)_2\text{SC}_4\text{H}_2]$ (**12**, eq 2) based on ^1H NMR spectroscopy. Surprisingly, the ^1H NMR

spectrum of **12** at room temperature shows only a broad peak corresponding to the TaCH_3 groups. A variable temperature ^1H NMR study revealed that at low temperatures (below -20°C) the broad peak decoalesces into three singlets. This behavior is consistent with an exchange process for the methyl groups. The low temperature static structure displays three chemically different methyl groups.

Complex **12** was characterized crystallographically (Figure 9) and represents the first structurally characterized example of a thiophene tantalum complex. The Ta-S bond length ($2.773(2) \text{ \AA}$) is among the longest reported in the Cambridge Structural Database. Mononuclear tantalum(V) complexes displaying Ta-S bond lengths longer than $2.7 \text{ \AA}$ involve SET_2 and $(\text{PhSCH}_2)_2$ adducts positioned trans to multiple bound ligands

Rate dependence on the equivalents of added dimethylphenylphosphine

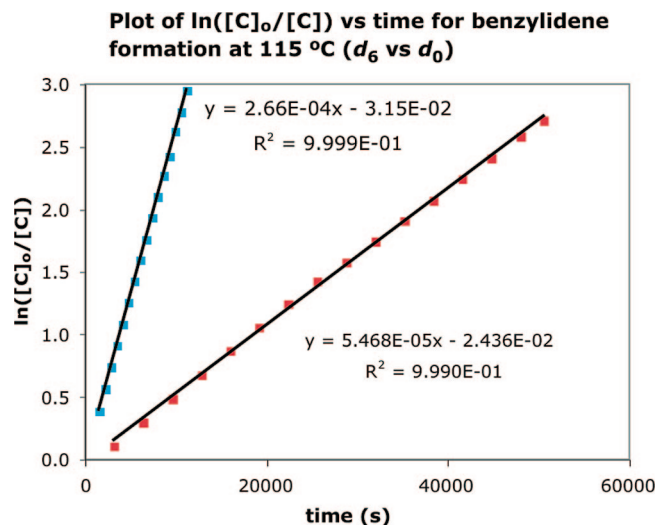


Figure 6. Kinetic plots for the conversion of **7** (blue) and **7- d_6** (red) with dimethylphenylphosphine to **11-P**.

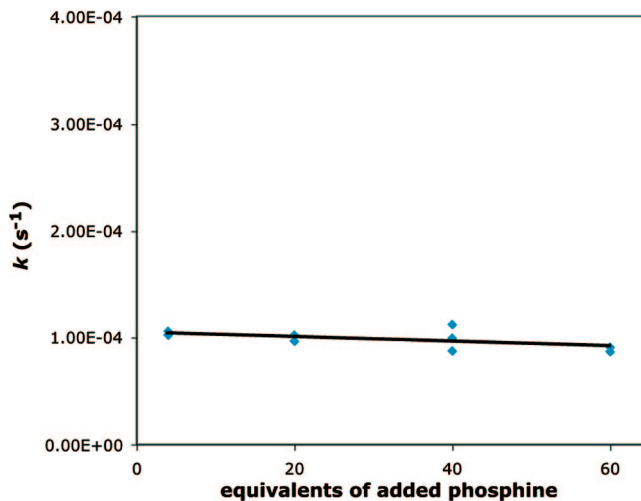


Figure 7. Plot of the dependence of the observed rate constant on the concentration of dimethylphenylphosphine for the conversion of **7** to **11-P**.

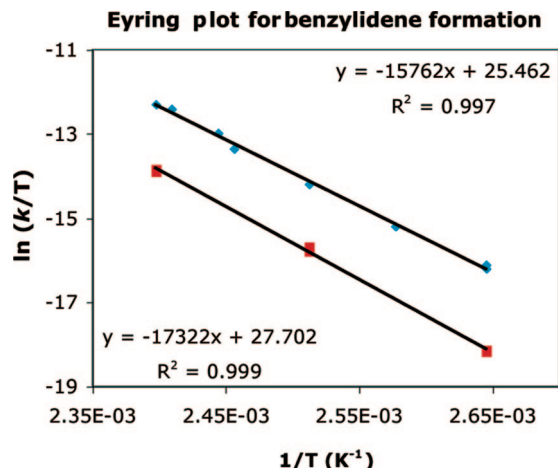
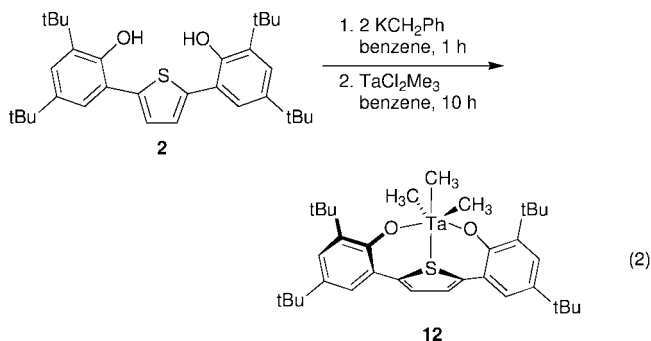


Figure 8. Eyring plots for the conversion of **7** (blue) and **7-d₆** (red) to **11-P**.

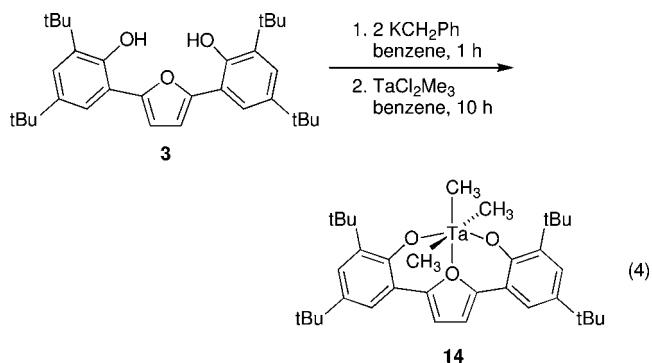
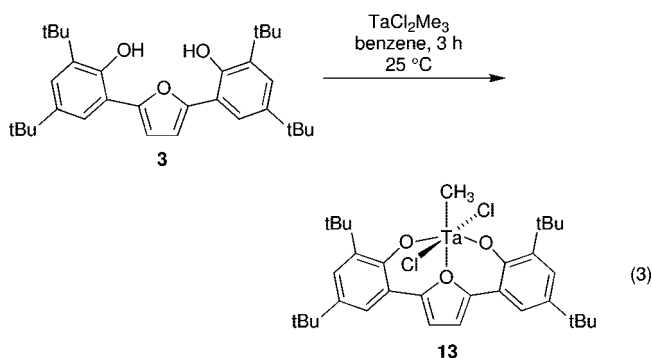


with strong trans influence (alkylidene and sulfide, respectively).^{78,79} Complex **12** displays a meridional coordination mode of the thiophene-diphenolate moiety with a few additional notable features. The angle between the thiophene plane and the Ta–S vector is 104°, significantly more acute than in the pyridine linked system, possibly due to the bigger sulfur atom leading to a longer Ta–S distance which, in turn, rotates the thiophene ring away from tantalum. Alternatively, the involvement of the sulfur lone pair in aromatic delocalization is diminished such that the degree of sp² hybridization of sulfur is smaller compared to that of nitrogen. Consequently, the thiophene sulfur is more likely to coordinate to tantalum more perpendicular to the ring rather than parallel. Another difference consists in the orientation of the tantalum methyl groups. Unlike in the bis(phenolate)pyridine system, the two methyl groups cis to the thiophene donor move closer to the methyl trans to sulfur (C34–Ta–C33 and C34–Ta–C35 are 76.2(2)° and 76.5(2)°, respectively). This could be due to the larger size of the sulfur compared to nitrogen, which may force the methyl groups away from the thiophene donor. Interestingly, the three methyl groups and tantalum are not found in the same plane, and the overall symmetry is reduced C₁. Thus, the solid-state structure is consistent with the low temperature ¹H NMR data, with all the tantalum methyl groups chemically different. In order to equivalence the two methyls cis to sulfur, the thiophene ring must pivot roughly 180° about its 2,5-phenolate linkages, forcing the sulfur closer to tantalum, a process that has a substantial barrier of ca. 15 kcal·mol^{−1}.

(78) Wallace, K. C.; Davis, W. M.; Schrock, R. R. *Inorg. Chem.* **1990**, 29, 1104–1106.

(79) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1984**, 845–848.

Synthesis and Characterization of Tantalum Complexes Supported by a Bis(phenolate)furan Ligand. The bis(phenolate)furan ligand (**3**) was found to metalate well via both alkane elimination and salt metathesis routes. A colorless benzene solution of TaCl₂(CH₃)₃ turns slightly orange upon addition of furan-2,5-diphenol, and the color darkens upon stirring at room temperature for a few hours (eq 3). The desired product, TaCl₂(CH₃)[(OC₆H₂-*t*Bu₂)₂OC₄H₂] (**13**), was isolated as an orange powder upon precipitation from cold petroleum ether. The rapid methane elimination with the furan-linked ligand stands in contrast to the behavior of the thiophene linked system, lending support to the steric argument for the lower reactivity of the latter. For the salt metathesis route, potassium diphenolate was used in the reaction with TaCl₂(CH₃)₃, leading to the isolation of Ta(CH₃)₃[(OC₆H₂-*t*Bu₂)₂OC₄H₂] (**14**) as an off-white powder (eq 4). Similar to the trimethyl compounds supported by the pyridine- and thiophene-linked diphenolates, compound **14** displays an unexpected ¹H NMR spectrum; the three tantalum methyl groups display only one singlet at room temperature. A variable temperature ¹H NMR study revealed that lowering the temperature leads to a broadening of the Ta–CH₃ peak eventually leading to decoalescence around −55 °C. At −90 °C, the methyl groups display two sharp singlets in a two to one ratio. This behavior reflects a fluxional process as described above, which exchanges the methyl groups. The lowest energy structure is likely that depicted in eq 4, with two equivalent methyls and one different.



Complex **13** was examined by single crystal X-ray diffraction (Figure 10) and confirms it as the first structurally characterized example of a furan tantalum complex. The Ta–O bond length (2.405(2) Å) is longer than a typical tantalum–ether bond. Complex **13** displays a meridional coordination mode of the furan-diphenolate moiety. As the molecule is found on a C₂ crystallographic axis, the TaO vector lies in the plane of the furan ring. Given that the twist of the two phenolate rings is small (6° from the plane of the furan), this molecule is almost C_{2v} symmetric.

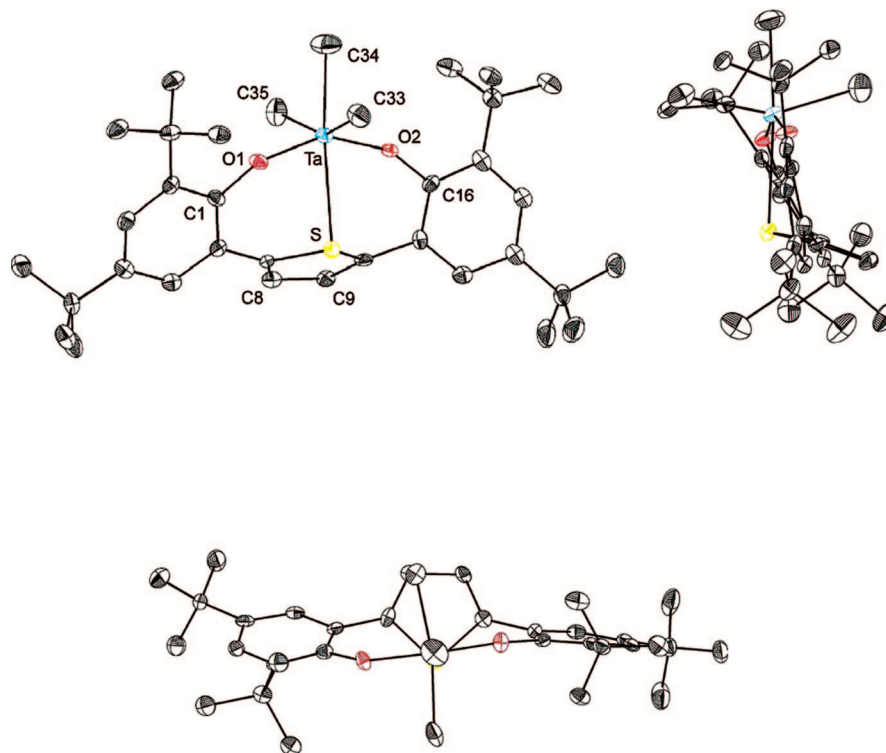


Figure 9. Drawings of the structure of **12**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.9119(38); Ta–O2 1.9136(34); Ta–C33 2.1676(66); Ta–C34 2.2164(65); Ta–C35 2.2179(62); Ta–S 2.7730(16); O2–Ta–O3 149.23(16); C34–Ta–C33 76.2(2); C34–Ta–C35 76.5(2); C16–O2–Ta 152.4(3); C1–O1–Ta 155.2(3); Ta–S–C8 103.6; Ta–S–C9 102.5.

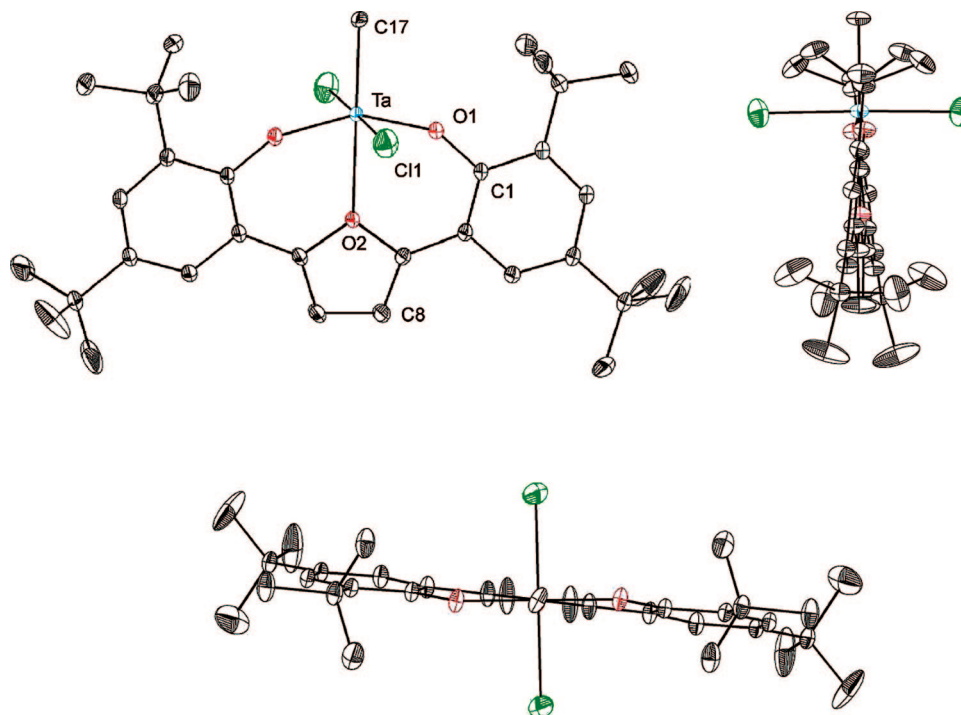


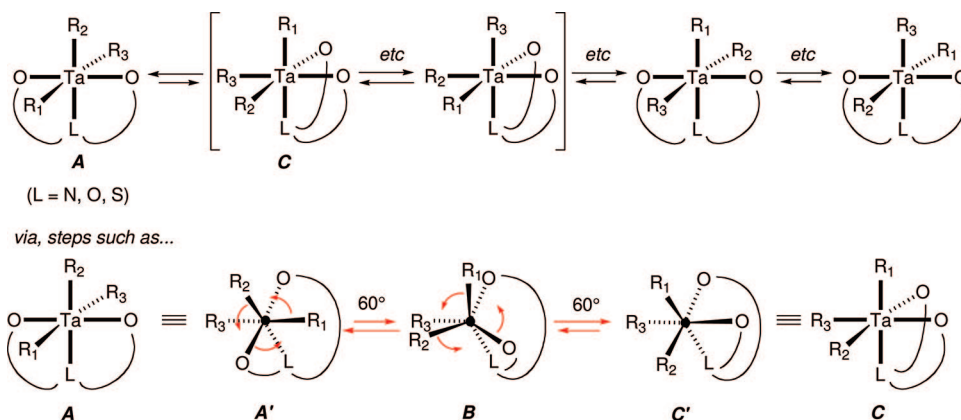
Figure 10. Drawings of the structure of **13**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.8692(14); Ta–C17 2.154(2); Ta–O3 2.4052(18); O1–Ta–O1A 152.34(9); C1–O1–Ta 150.10(12).

Methyl Exchange Processes in the Tantalum Trimethyl Species 6, 12, and 14. High temperature ^1H NMR spectra of compounds **6**, **12**, and **14** display only one signal at high temperature, indicative of a fast methyl exchange process. While the precise nature of this process is not well understood, it is probable that a significant distortion of the bis(phenolate)donor ligand framework is required to interchange methyls. The solid

state structures display *mer* binding of the tridentate ligand and, accordingly, *mer* binding of the three methyl groups. One possible pathway would involve twists of the trigonal faces of the octahedral structure (Scheme 5).^{80,81} An alternative pathway

(80) Marinescu, S. C.; Agapie, T.; Day, M. W.; Bercaw, J. E. *Organometallics* **2007**, 26, 1178–1190.

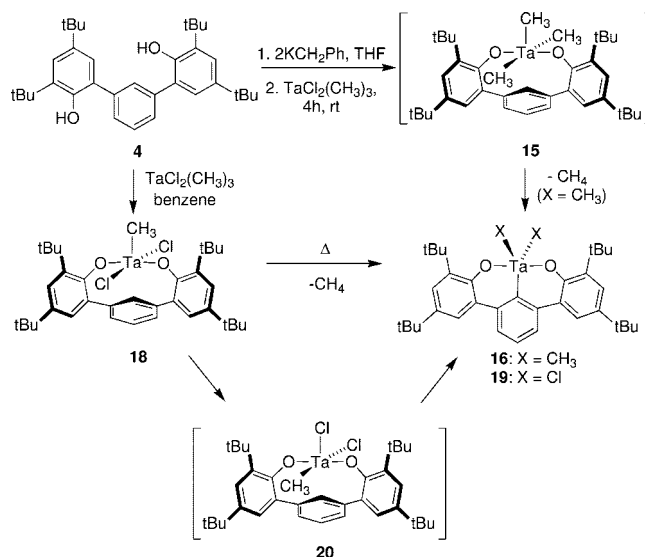
Scheme 5



could involve decooordination of the donor on the linker to generate a five-coordinated species, which could undergo Berry pseudorotations. In order for the alkyl groups to exchange by either mechanism, they need to access a trigonal face of an octahedral (or trigonal bipyramidal) structure. In this context, the two oxygens would have to be *cis*, a geometry that has not been documented in these tantalum systems. Given the presence of aryl–aryl linkages in the multitentate framework, facial binding modes are expected to be strained and higher in energy than meridional binding modes. The observed sharp singlets at room temperature for **6** and **14** indicate, however, that these LX_2 ligands are quite flexible, being able to easily attain transient facial geometries.

Preparation of Tantalum Complexes Supported by a Benzene-Linked Bis(phenolate) Ligand. Two strategies have been used for the metalation of the benzene-linked diphenol **4**: salt metathesis and alkane elimination.⁵⁸ For the salt metathesis route, diphenol **4** was deprotonated in situ with KCH_2Ph and then treated with $TaCl_2(CH_3)_3$. Within hours, the reaction was complete with the generation of one major species **16** (1H NMR). Recrystallization from petroleum ether afforded analytically clean material. The 1H NMR spectrum shows a singlet corresponding to the $Ta-CH_3$ groups integrating to 6H, and only two peaks (a doublet and a triplet) for the linking benzene group integrating to 3H. The ^{13}C NMR spectrum of the product presents two diagnostic peaks, at 60.6 and 198.5 ppm. A survey of some previously reported tantalum(V) methyls with at least two phenolate ligands indicates that the ^{13}C NMR chemical shift range for the methyl group is between 43 and 64 ppm.^{82,83} The ^{13}C NMR chemical shift for $Ta-C(ipso)$ is 190–210 ppm.^{50,84–88} These data support the structural assignment of **16** as $Ta(CH_3)_2(OC_6H_2-tBu)_2(C_6H_3)$ (Scheme 6) Formation of **16** presumably occurs

Scheme 6



via intermediate generation of a simple salt metathesis product, complex **15**, bound through the oxygens (Scheme 6). This species then cyclometallates, with loss of methane. Utilization of $TaCl_2(CH_2Ph)_3$ instead of $TaCl_2(CH_3)_3$ as a metal precursor in this reaction leads to the formation of analogous bis(alkyl) $Ta(CH_2Ph)_2[(OC_6H_2-tBu)_2C_6H_3]$ (**17**). Previous reports of cyclometallated pincer ligand complexes of early metals rely on using starting materials in which the hydrogen connected to the metallated carbon had been already replaced with a transmetalating agent (Grignard reagents or lithium aryls). The CH (or CC) activation route for accessing the cyclometallated pincer frameworks is, however, common for late transition metal systems.⁸⁹ The preparations described here rely on a CH activation at the desired position upon coordination of the ligand to the metal center. These reactions are reminiscent of cyclometalations via σ -bond metathesis observed for tantalum systems with phenolate ligands ortho-substituted with *t*-butyl, *i*-propyl, or phenyl groups.^{82,85,90–95} An interesting comparison is

(81) Fay, R. C.; Lindmark, A. F. *J. Am. Chem. Soc.* **1983**, *105*, 2118–2127.

(82) Chesnut, R. W.; Yu, J. S.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1990**, *9*, 1051–1058.

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

(84) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963–968.

(85) Chesnut, R. W.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1988**, *7*, 753–756.

(86) Bonanno, J. B.; Henry, T. P.; Neithamer, D. R.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1996**, *118*, 5132–5133.

(87) Rietveld, M. H. P.; Hagen, H.; vandeWater, L.; Grove, D. M.; Kooijman, H.; Veldman, N.; Spek, A. L.; vanKoten, G. *Organometallics* **1997**, *16*, 168–177.

(88) Rietveld, M. H. P.; Teunissen, W.; Hagen, H.; vandeWater, L.; Grove, D. M.; vanderSchaaf, P. A.; Muhlebach, A.; Kooijman, H.; Smeets, W. J. J.; Veldman, N.; Spek, A. L.; vanKoten, G. *Organometallics* **1997**, *16*, 1674–1684.

(89) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798–807.

(90) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153–159.

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

(92) Baley, A. S.; Chauvin, Y.; Commereuc, D.; Hitchcock, P. B. *New J. Chem.* **1991**, *15*, 609–610.

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

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

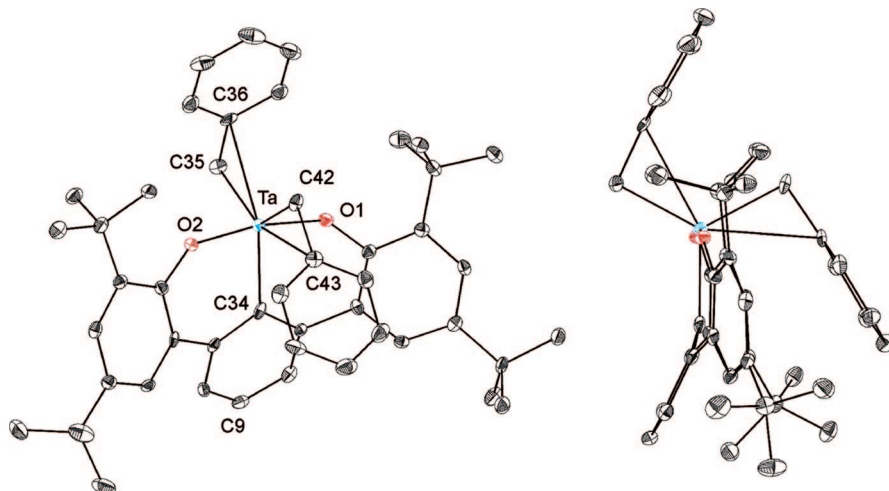


Figure 11. Drawings of the structure of **17**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.904(2); Ta–O2 1.903(2); Ta–C34 2.176(3); Ta–C35 2.190(4); Ta–C42 2.203(4); O1–Ta–O2 169.17(9); Ta–C35–C36 93.2(2); Ta–C42–C43 96.4(2); C17–O2–Ta 142.9(2); C1–O1–Ta 141.6(2); C34–Ta–C35 117.86(13); C34–Ta–C42 118.24(14); Ta–C34–C9 156.5.

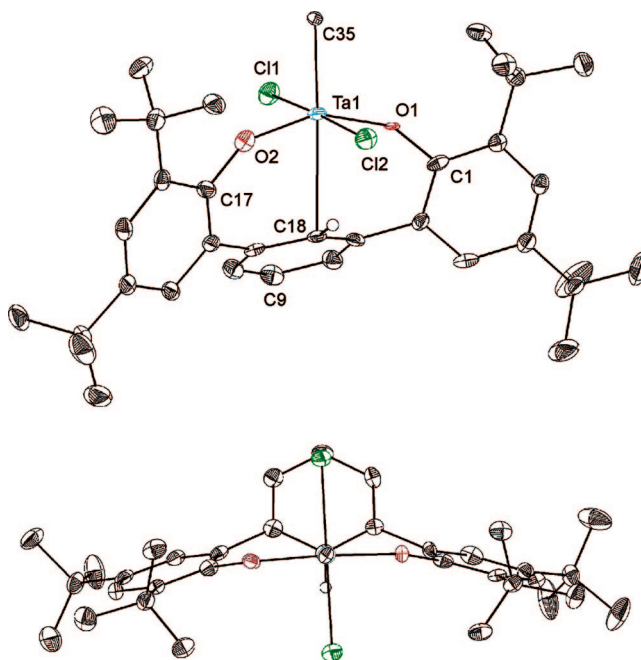


Figure 12. Drawings of the structure of **18**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.876(4); Ta–O2 1.859(4); Ta–C35 2.147(4); Ta–C18 2.7913(47); Ta–C18–C9 120°; O1–Ta–O2 152.45(15); Ta–O1–C1 151.7(3); Ta–O2–C17 149.1(4).

provided by the previously characterized $\text{Ta}(\text{CH}_3)_3(\text{OC}_6\text{H}_3\text{-2,6-Ph}_2)_2$ and $\text{Ta}(\text{CH}_2\text{Ph})_3(\text{OC}_6\text{H}_3\text{-2,6-Ph}_2)_2$ that lose CH_4 only above 200 °C and toluene above 175 °C, respectively.⁸⁵ By contrast, the related proposed tantalum trialkyl species **15** is only a transient in the formation of the cyclometallated product **16** at room temperature. This suggests that the pincer nature of the ligand, with initial chelation of the two phenolates facilitates the cyclometallation, possibly by locking the aryl group into the necessary orientation for σ -bond metathesis.

The structure of complex **17** was investigated by single-crystal X-ray diffraction (Figure 11). Similarly to the pyridine-linked systems, this molecule displays *pseudo-C_s* symmetry. The angle between the Ta–C(phenyl) vector and the plane of the bridging benzene group is, however, about 10° larger than that in the pyridine case, and the Ta–C(benzene) distance is shorter

compared to the Ta–N(pyridine) distance, likely a consequence of the greater strength of the normal covalent Ta–C bond *vis-à-vis* the dative Ta–N bond of the latter.

An alkane elimination route was explored for the metalation of **4** with $\text{TaCl}_2(\text{CH}_3)_3$ leading at room temperature to a species that still displays signals for a TaCH₃ group and the C(*ipso*)-H in the ¹H and ¹³C NMR spectra (compound **18**, Scheme 6). A single crystal X-ray diffraction study supports the spectroscopic assignment of **18** (Figure 12). The tantalum center is six-coordinate, taking into account the weak interaction with the arene *ipso*-carbon (Ta–C bond length of 2.791(5) Å). The methyl group is located trans to site of the arene linker, the position with the smallest trans influence. The other bond lengths to tantalum are typical. The Ta–C18–C8 angle of 120° indicates a significant twist of the arene, probably to avoid a steric interaction between tantalum and the ring as well as to

(95) Chamberlain, L.; Keddington, J.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1982**, *1*, 1538–1540.

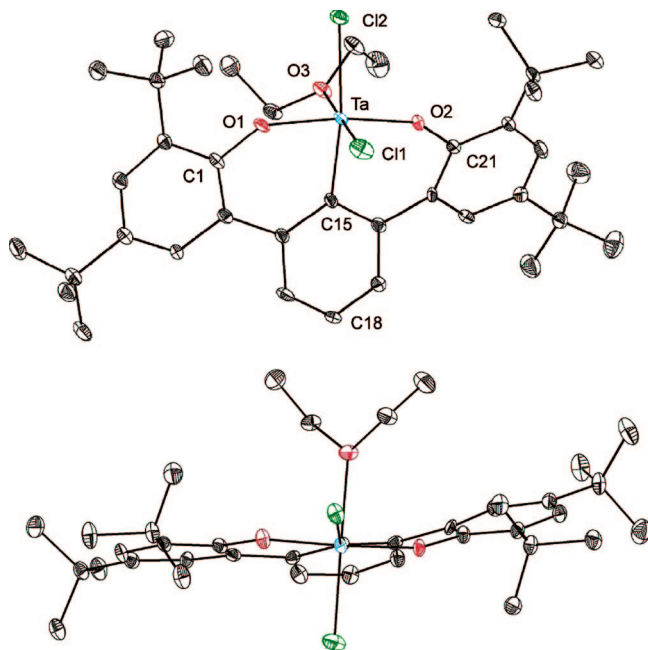


Figure 13. Drawings of the structure of **19-OEt₂**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.8828(13); Ta–O2 1.8755(13); Ta–O3 2.2446(14); Ta–C15 2.1870(19); Ta–C15–C18 164.2; O1–Ta–O2 168.75(6); C21–O2–Ta 145.34(13); C1–O1–Ta 142.51(13).

increase a bonding interaction between the metal center and the π -system.

The isolation of compound **18** provides support for the proposed route for the formation of **16** (Scheme 6) by affording isolation of the diphenolate species without C–H activation. In this case, the cyclometallation reaction is not as facile as for the putative Ta(CH₃)₃[(OC₆H₂-*t*Bu₂)₂C₆H₃] (**15**). Access to **18** also provides an opportunity to perform kinetic studies of the cyclometallation reaction. To that end, the synthesis of isotopically labeled compounds was undertaken. In this context, an unexpected mechanism for metalation of the benzene-linked bis(phenol) with TaCl₂(CH₃)₃ to generate **4** was uncovered.⁵⁸ As reported earlier, this process involves protonolysis of a methyl group, followed by C–H/Ta–CH₃ σ bond metathesis leading to cyclometallation of the linking benzene, and finally protonation of the cyclometallated group by the pendant phenol.

Compound **18** does indeed undergo σ -bond metathesis at elevated temperatures, leading to the cyclometallated product **19** (Scheme 6) along with CH₄. Crystals of the cyclometallated product, suitable for an X-ray diffraction study, were obtained from a diethyl ether solution (Figure 13). An ether molecule coordinates to the metal center to satisfy six-coordination. In contrast with the structure of **18**, the Ta–C(*ipso*) vector almost lies in the cyclometallated benzene plane (Ta–C15–C18 angle is 164°) maximizing the interaction of the metal with carbon σ -orbital.

Unimolecular conversion of **18** to **19** almost certainly requires an isomerization to place the reactive (incipient *ipso*) C–H bond and the Ta–CH₃ cis as in **20** (Scheme 6). To examine the molecularity of the process, a kinetic study was undertaken. The reaction was performed in C₆D₅Br over a range of 34 °C (91–125 °C) and found to obey kinetics first order in **18** (Figure 14) supporting the proposal of a unimolecular σ -bond metathesis. The Eyring analysis yielded $\Delta H^\ddagger = 27.1 \pm 0.9$ kcal·mol^{–1}; $\Delta S^\ddagger = -2 \pm 2$ cal·mol^{–1}·K^{–1} (Figure 15). The activation enthalpy and entropy values are similar to those observed for

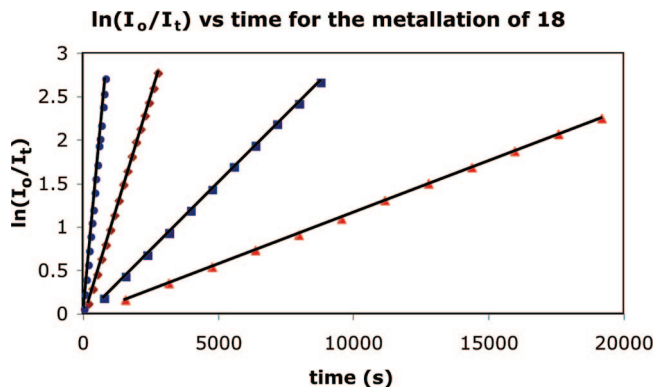


Figure 14. Kinetic plots for the cyclometallation of **18** at different temperatures (91 °C, red triangles; 101 °C, blue squares; 111 °C, red diamonds; 125 °C, blue circles).

Eyring plot for the cyclometallation of **18** and **18-d₁**

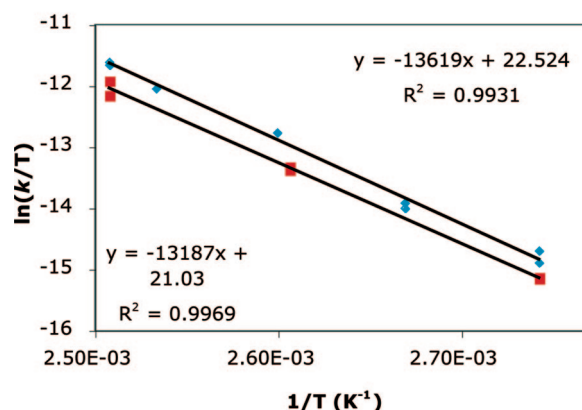


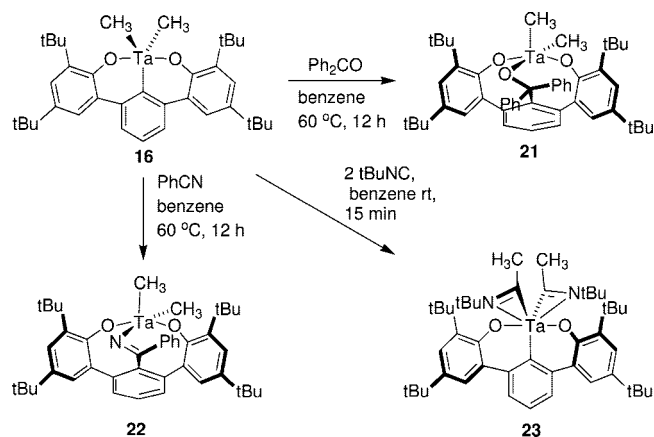
Figure 15. Eyring plots for the cyclometallation of **18** (blue) and **18-d₁** (red).

cyclometallations with methane elimination for tantalum supported by monodentate phenolates.⁹⁰ Isomerization (**18** to **20**) is expected to involve some degree of reorganization, possibly via a process analogous to that shown in Scheme 5, leading to a somewhat negative entropy of activation, especially for a semirigid terphenyl system.^{80,81}

To investigate further the possibility that the isomerization from **18** to **20** is the rate determining step in this transformation, the (incipient *ipso*) C–H bond was deuterated (**18-d₁**). Kinetic data were obtained over the same temperature range, allowing the derivation of the activation parameters. The experimental error does not allow a distinction between the slopes of the cyclometallation reactions from **18** and **18-d₁** (Figure 15). Thus, the isotope effect is essentially the same ($k_H/k_D = 1.6 \pm 0.2$) over a range of 34 °C (91–125 °C). These isotope effects are (marginally) smaller than the one observed for the intermolecular σ -bond metathesis reactions of Cp^{*}₂Sc–CH₃ and the C–H bond of benzene ($k_H/k_D = 2.8(2)$ at 80 °C),⁹⁶ and than those observed in cyclometallations of *t*-butyl groups ortho to tantalum phenolates ($k_H/k_D = 5.2(4)$ at 180 °C, $k_H/k_D = 2.3(5)$ at 118 °C, and $k_H/k_D = 1.9(5)$ at 135 °C for different ligand sets.^{90,94} The observation of an isotope effect for the present system, even though relatively small, suggests that the rate determining step does involve σ -bond metathesis (**20** to **19**).

(96) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219.

Scheme 7



Insertion Chemistry of $\text{Ta}(\text{CH}_3)_2[(\text{OC}_6\text{H}_2-t\text{Bu}_2)_2\text{C}_6\text{H}_3]$ (16**): Reactions with Benzophenone, Benzonitrile, and *t*-Butylisocyanide.** Compound **16**, with two types of Ta–C single bonds provides an interesting case for the study of insertion chemistry with various substrates. The reaction with excess (1.5 equiv) benzophenone was performed in benzene- d_6 at 60 °C. Clean formation of a single product is observed after 12 h. The nature of the insertion product is suggested by ^{13}C and ^1H NMR spectroscopic data. In the ^{13}C NMR spectrum, the peak corresponding to the [Ta–CH $_3$] groups of the starting material appears at 60.6 ppm; this was replaced in the product by two peaks with a similar chemical shift (60.8 and 62.7 ppm). If one of these methyl groups is carbon-bound, it should shift significantly upfield. Hence, this suggests a loss of symmetry of the molecule, but no insertion into the Ta–CH $_3$ bonds, consistent with structure **21** (Scheme 7). Furthermore, the Ta–C(*ipso*) peak, which has a chemical shift of 198.5 ppm in the starting material, is absent from this region in the product. Finally, a single crystal X-ray diffraction study confirmed the structural assignment (Figure 4, Supporting Information), but the quality of the data set precluded reliable determination of structural parameters. The clean formation of only one product suggests a significant preference for the insertion into the Ta–aryl bond. The reasons behind this selectivity are currently not well understood. It is also noteworthy that the excess substrate does not insert into the Ta–CH $_3$ bonds still available after the first insertion into Ta–aryl.

Reaction of **16** with benzonitrile was performed under conditions similar to the ones with benzophenone. The ^{13}C NMR spectrum of the reaction product shows that the two [Ta–CH $_3$] groups become inequivalent, but their chemical shifts (57.0 and 59.1 ppm) remain in the expected region for metal-bound alkyls. No signal is observed in the [Ta–C(phenyl)] region. The ketimide carbon resonance appears at 169.9 ppm. These data are consistent with insertion into the Ta–phenyl bond to generate compound **22** (Scheme 7). Interestingly, if less than one equivalent of PhCN is used, the reaction proceeds with the formation of an additional product. It may be possible that the imide functionality further reacts with another equivalent of tantalum starting material to give a species as yet unidentified. The solid structure of **22** was determined by a single crystal X-ray diffraction study (Figure 16). The tantalum center is five coordinate, with a distorted trigonal bipyramid geometry. The Ta–N–C19 angle is very acute because of the geometric constraints of this unusual chelating ligand. The angle between the Ta–C19 vector and the bridging benzene ring is acute as well, probably to accommodate the two atom bridge (CN) between Ta and C19 resulting from the insertion of PhCN.

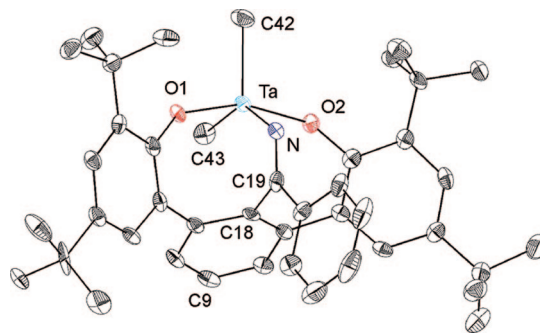


Figure 16. Drawing of the structure of **22**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.912(3); Ta–O2 1.919(4); Ta–N 2.037(4); Ta–C42 2.148(6); Ta–C43 2.163(6); O1–Ta–O2 156.34(15); Ta–N–C19 114.2(4); C17–O2–Ta 142.1(3); C1–O1–Ta 143.6(3); N–Ta–C42 114.7(2); N–Ta–C43 140.9(2); Ta–C18–C9 110.2.

To investigate the scope of insertion chemistry with complex **16**, the reaction with $t\text{BuN}\equiv\text{C}$ was also explored. It was found that the reaction with two equivalents of isocyanide occurs fast, reaching completion within 15 min at room temperature, to cleanly generate one species. The ^1H NMR spectrum of the product shows only one singlet corresponding to the [Ta–CH $_3$] groups from the starting material. The ^{13}C NMR spectrum displays a peak at 179.6 ppm corresponding to Ta–C(phenyl). Furthermore, no peaks are observed in the [Ta–CH $_3$] region (~55–65 ppm). Instead, one new peak is observed in the aliphatic region at 22.2 ppm. A new downfield peak (226.0 ppm) indicates the formation of the iminoacyl moiety. These data are consistent with 1,1-insertion of isocyanide into the Ta–CH $_3$ bonds selectively, without any observable insertion into the Ta–phenyl bond. This assignment was confirmed by a single crystal X-ray diffraction study (Figure 17). The solid-state structure is essentially C_2 -symmetric with the phenolate aryl rings significantly twisting away from each other. The O1–Ta–O2 angle is 166°, similar to the cyclometallated species **19-OEt $_2$** . The iminoacyl groups are both κ^2 , with the nitrogen coordinated next to the aryl ligand. The structural parameters of the tantalum-iminoacyl units are similar to previously reported ones.^{97–99}

On the basis of the findings for the substrates examined thus far, we may conclude that 1,2-inserting substrates prefer insertion into the Ta–phenyl bond, while 1,1-inserting substrates prefer insertion into the Ta–Me bond. While currently not understood, the complete switch in selectivity observed for the two types of substrates may result from the geometrical requirements of the transition state for the insertion into the Ta–aryl bond. The Ta–phenyl bond, rather constrained in the chelate, may be able to better accommodate a two-atom rather than a one-atom insertion.

Conclusions

A series of diphenols connected at the ortho positions via semirigid, ring–ring linkages to a flat ring (pyridine, furan, or thiophene) that presents another ligand was efficiently prepared, and their ability to support tantalum chemistry has been investigated. Metalations were performed using salt metathesis

(97) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390–402.

(98) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079.

(99) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203–1205.

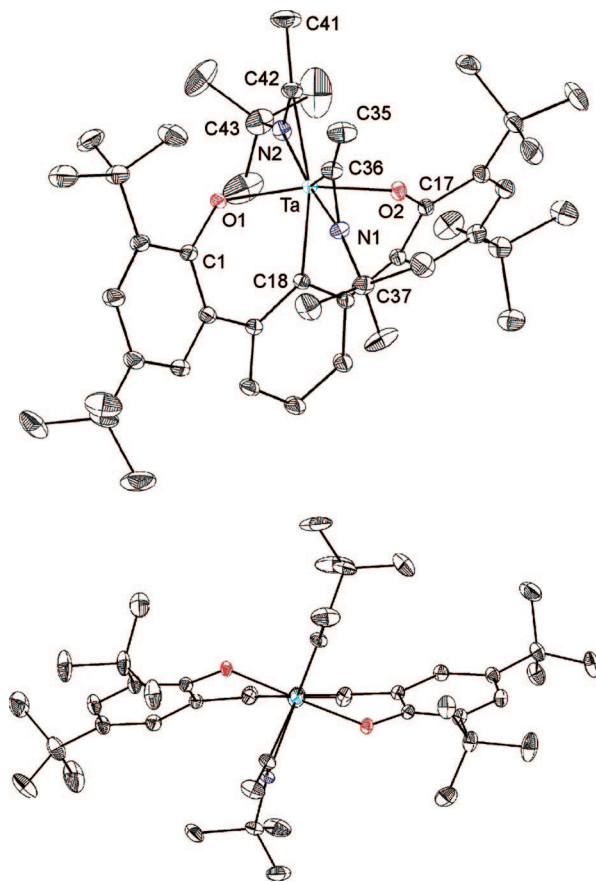


Figure 17. Drawings of the structure of **23**. Selected bond lengths (Å) and angles (deg): Ta–O1 1.9517(11); Ta–O2 1.9415(11); Ta–N1 2.1414(12); Ta–N2 2.1494(13); Ta–C36 2.1574(15); Ta–C42 2.1576(15); Ta–C18 2.2256(14); N1–C36 1.275(2); N2–C42 1.278(2); C(36)–Ta(1)–C(42) 103.50(6); Ta–C36–N1 72.06(9); Ta–C42–N2 72.39(9); O1–Ta–O2 166.30(5); C17–O2–Ta 133.22(10); C1–O1–Ta 129.80(10).

and alkane elimination routes. Variable temperature ^1H NMR studies of tantalum trimethyl species indicate that, in solution, these complexes are fluxional, leading to exchange of the methyl groups. A tantalum tribenzyl species supported by the bis(phenolate)pyridine framework undergoes α -H abstraction upon heating to 90 °C in the presence of Lewis bases. This process exhibiting first order rate for the disappearance of the trialkyl species was found to be independent of phosphine concentration and $k_{\text{H}}/k_{\text{D}} = 4.9 \pm 0.4$ (125 °C), consistent with a mechanism involving rate determining α -H abstraction in the six-coordinate species to give a five-coordinate benzylidene, which is trapped by the phosphine in a fast, subsequent step.

A diphenol connected in the ortho-position via a 1,3-benzenediyl group, related conceptually to the diphenols above, was prepared, and its ability to support tantalum chemistry has been investigated as well. An alkane elimination route with $\text{Ta}(\text{CH}_3)_3\text{Cl}_2$ leads to the isolation of $\text{Ta}(\text{CH}_3)_2\text{Cl}_2[(\text{OC}_6\text{H}_2-t\text{Bu}_2)_2\text{C}_6\text{H}_4]$ by a mechanism implicating that the C–H/Ta–CH $_3$ σ -bond metathesis is faster than the O–H/M–CH $_3$ protonolysis. High temperature kinetics and labeling studies of the cyclometalation of $\text{Ta}(\text{CH}_3)_2\text{Cl}_2[(\text{OC}_6\text{H}_2-t\text{Bu}_2)_2\text{C}_6\text{H}_4]$ to give $\text{TaCl}_2[(\text{OC}_6\text{H}_2-t\text{Bu}_2)_2\text{C}_6\text{H}_4]$ suggest that σ -bond metathesis is the rate determining step, rather than isomerization to place the methyl group cis to the C–H bond to be activated. Salt metathesis routes into tantalum chemistry afforded access to cyclometallated species $\text{Ta}(\text{CH}_3)_2[(\text{OC}_6\text{H}_2-t\text{Bu}_2)_2\text{C}_6\text{H}_3]$ and $\text{Ta}(\text{CH}_2\text{Ph})_2[(\text{OC}_6\text{H}_2-t\text{Bu}_2)_2\text{C}_6\text{H}_3]$ at room temperature. $\text{Ta}(\text{CH}_3)_2[(\text{OC}_6\text{H}_2-t\text{Bu}_2)_2\text{C}_6\text{H}_3]$

was found to undergo 1,2-insertions with benzophenone and benzonitrile into the Ta-(*ipso*)C bond and 1,1-insertion of *t*-butylisocyanide into the Ta–CH $_3$ bonds.

In the solid state, these pincer ligands were found to bind in a meridional fashion exclusively, to generate C_1 , C_{2v} , C_2 , and C_s ligand geometries. The observed geometries were mostly dependent on the size of the ring linking the two phenolates and the nature of the donor in the ring. While with a furan linker the three rings can accommodate an almost planar geometry upon binding tantalum (C_{2v}), with thiophene, having a larger sulfur donor, the ring system twists to give a C_1 structure. Switching from a five- to a six-member ring linker, the ligand generally assumes C_s geometries (with one exception, C_2 in **23**). This trend is probably due to a smaller angle between the two ring–ring linkages in the case of 6-membered pyridine and benzene versus 5-membered furan and thiophene. Overall, the present ligand frameworks have been found to be thermally robust and to support tantalum alkyl and alkylidene motifs lending promise to diverse, potentially useful reactions based on these architectures.

Experimental Section

General Considerations and Instrumentation. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques, or in a drybox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or by the method of Grubbs.¹⁰⁰ Benzene- d_6 was purchased from Cambridge Isotopes and distilled from sodium benzophenone ketyl. Chloroform- d_1 and dichloromethane- d_2 were purchased from Cambridge Isotopes and distilled from calcium hydride. Compounds **1**,³⁴ **2**,³⁴ **3**,³⁴ and **4**,⁵⁸ $\text{TaCl}_2(\text{CH}_2\text{Ph})_3$,⁶⁴ $\text{TaCl}_3(\text{CH}_2\text{Ph})_2$,⁷⁶ $\text{Ta}(\text{CH}_2\text{Ph})_5$,^{23,64} $\text{TaCl}_3(\text{CH}_3)_2$,¹⁰¹ and $\text{TaCl}_2(\text{CH}_3)_3$,^{102,103} were prepared according to literature procedures. Other materials were used as received. ^1H and ^{13}C NMR spectra were recorded on Varian Mercury 300 or Varian INOVA-500 spectrometers at room temperature unless otherwise indicated. Chemical shifts are reported with respect to internal solvent: 7.16 and 128.38 (t) ppm (C_6D_6); 7.27 and 77.23 (t) ppm (CDCl_3); 5.32 and 54.00 (q) ppm (CD_2Cl_2); for ^1H and ^{13}C data.

Synthesis of 5. KBn (139 mg, 1.07 mmol, 2 equiv) was added with the aid of C_6H_6 (5 mL) to a solution of **1** (260 mg, 0.534 mmol, 1 equiv) in C_6H_6 (10 mL). This mixture was allowed to stir at room temperature for 2 h during which the orange KBn dissolved and discolored to lead to the formation of a colorless emulsion of phenolate. A C_6H_6 solution of $\text{TaCl}_3(\text{CH}_2\text{Ph})_2$ (250 mg, 0.534 mmol, 1 equiv) was added, and the reaction mixture was allowed to stir at room temperature for 5 h. Salts were removed by filtration through a bed of Celite, and volatile materials were removed under vacuum. The resulting residue was suspended in petroleum ether, and the mixture was cooled to –35 °C. The desired product was collected by filtration as an orange solid and was washed with cold petroleum ether. This procedure affords 0.460 g (97% yield) of **5**. ^1H NMR (500 MHz, CD_2Cl_2) δ : 1.40 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.60 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.39 (s, 4H, $\text{Ta}(\text{CH}_2)_2$), 6.26 (d, 4H, *o*- C_6H_3 -H $_2$), 6.60–6.67 (m, 6H, *m*- and *p*- C_6H_3 -H $_3$), 7.23 (d, 2H, aryl-H), 7.60 (d, 2H, aryl-H), 7.74 (d, 2H, 3,5-NC $_5$ H-H $_2$), 7.84 (t, 1H, NC $_5$ H $_2$ -H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ : 30.6 ($\text{C}(\text{CH}_3)_3$), 31.9 ($\text{C}(\text{CH}_3)_3$), 35.2 ($\text{C}(\text{CH}_3)_3$), 35.7 ($\text{C}(\text{CH}_3)_3$), 75.2 (TaCH_2), 125.3,

(100) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

(101) Fowles, G. W. A.; Rice, D. A.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1973**, 961–965.

(102) Juvinal, G. L. *J. Am. Chem. Soc.* **1964**, *86*, 4202–4203.

(103) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389–2399.

Table 1. Crystal and Refinement Data for Complexes 6, 7, 10, and 11-P

	6	7	10	11-P
empirical formula	C ₃₆ H ₅₂ NO ₂ Ta	C ₅₄ H ₆₄ NO ₂ Ta · 1/2C ₆ H ₁₄	C ₄₀ H ₅₀ NO ₂ F ₂ Ta · C ₆ H ₆	C ₅₅ H ₆₈ NO ₂ PTa · 2.5(C ₆ H ₆)
formula weight	711.74	983.10	873.87	1182.29
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)
<i>a</i> (Å)	11.1983(3)	11.6884(3)	13.6879(4)	29.1034(6)
<i>b</i> (Å)	11.4259(3)	18.9587(4)	28.6266(7)	43.7491(9)
<i>c</i> (Å)	14.4511(4)	21.6301(5)	11.3658(3)	19.1359(4)
α (deg)	88.7580(10)			
β (deg)	75.2440(10)	95.3950(10)	113.9359(10)	
γ (deg)	70.9590(10)			
volume (Å ³)	1686.39(8)	4771.93(19)	4070.57(19)	24364.7(9)
<i>Z</i>	2	4	4	16
crystal system	triclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Fdd</i> 2
<i>d</i> _{calc} (g/cm ³)	1.402	1.368	1.426	1.289
θ range (deg)	1.89 to 47.50	1.89 to 42.95	1.63 to 40.73	1.68 to 41.03
μ (mm ⁻¹)	3.289	2.346	2.747	1.875
abs. correction	SADABS	SADABS	SADABS	none
GOF	1.206	1.216	1.229	1.095
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0392, 0.0703	0.0389, 0.0626	0.0398, 0.0580	0.0415, 0.0665

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Table 2. Crystal and Refinement Data for Complexes 12, 13, 17, and 18

	12	13	17	18
empirical formula	C ₃₅ H ₅₁ O ₂ STa	C ₃₃ H ₄₅ O ₃ Cl ₂ Ta	C ₄₈ H ₅₇ O ₂ Ta · CH ₂ Cl ₂	2(C ₃₅ H ₄₇ O ₂ Cl ₂ Ta) · C ₆ H ₆
formula weight	716.77	809.65	931.81	1581.26
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)
<i>a</i> (Å)	9.8813(16)	15.0003(3)	10.7524(5)	11.2683(7)
<i>b</i> (Å)	11.3580(18)	15.1231(3)	11.2822(5)	17.5151(11)
<i>c</i> (Å)	15.332(2)	16.5600(4)	18.5744(8)	18.2677(12)
α (deg)	86.956(3)	95.7320(10)	88.9940(10)	88.7480(10)
β (deg)	76.513(3)	97.0480(10)	82.324(2)	88.5720(10)
γ (deg)	80.423(3)	91.9980(10)	74.9580(10)	89.2020(10)
volume (Å ³)	1649.7(5)	3705.40(14)	1649.7(5)	3603.1(4)
<i>Z</i>	2	4	2	2
crystal system	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>d</i> _{calc} (g/cm ³)	1.443	1.451	1.435	1.457
θ range (deg)	1.82 to 28.41	1.35 to 50.18	1.87 to 27.50	1.59 to 33.65
μ (mm ⁻¹)	3.423	3.144	2.710	3.229
abs. correction	semiempirical from equiv.	none	semiempirical from equiv.	none
GOF	1.276	1.000	1.818	1.622
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0421, 0.0665	0.0390, 0.0748	0.0410, 0.0908	0.0605, 0.1014

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Table 3. Crystal and Refinement Data for Complexes 19-OEt₂, 22, and 23

	19-OEt ₂	22	23
empirical formula	C ₃₈ H ₅₃ O ₃ Cl ₂ Ta	C ₄₃ H ₄₈ NO ₂ Ta · C ₅ H ₁₂	C ₄₆ H ₆₇ N ₂ O ₂ Ta
formula weight	809.65	863.92	860.97
<i>T</i> (K)	100(2)	100(2)	100(2)
<i>a</i> (Å)	15.0003(3)	12.4786(8)	10.1483(3)
<i>b</i> (Å)	15.1231(3)	28.9867(18)	14.5504(4)
<i>c</i> (Å)	16.5600(4)	12.6931(8)	15.6639(4)
α (deg)	95.7320(10)°		88.0490(10)
β (deg)	97.0480(10)	102.621(3)	86.7020(10)
γ (deg)	91.9980(10)°		73.7530(10)
volume (Å ³)	3705.40(14)	4480.3(5)	2216.53(11)
<i>Z</i>	4	4	2
crystal system	triclinic	monoclinic	triclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>d</i> _{calc} (g/cm ³)	1.451	1.281	1.290
θ range (deg)	1.35 to 50.18	1.40 to 29.03	1.94 to 45.15
μ (mm ⁻¹)	3.144	2.489	2.515
abs. correction	none	Gaussian	none
GOF	1.000	1.439	1.155
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0390, 0.0748	0.0556, 0.1045	0.0349, 0.0749

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

125.6, 127.2, 127.66, 127.68, 129.0, 131.2, 138.6, 139.0, 141.6, 145.1, 152.1, 156.1 (aryl). Anal. Calcd. for C₄₇H₅₇ClNO₂Ta (%): C, 63.83; H, 6.50; N, 1.58. Found: C, 63.53; H, 6.55; N, 1.58.

Synthesis of 6. KBN (85.2 mg, 0.66 mmol, 2 equiv) was added with the aid of C₆H₆ (4 mL) to a solution of **1** (159.6 mg, 0.33

mmol, 1 equiv) in C₆H₆ (4 mL). This mixture was allowed to stir at room temperature for 0.5 h, which afforded a pale gray mixture of deprotonated phenol. A C₆H₆ solution of TaCl₂(CH₃)₃ (97.3 mg, 0.33 mmol, 1 equiv) was added, and the reaction mixture was allowed to stir at room temperature for 4 h. Salts were removed by filtration through a bed of Celite. Volatile materials were removed under vacuum to give the desired product as a white powder. ¹H NMR (500 MHz, CD₂Cl₂) δ: 0.40 (s, 9H, Ta(CH₃)₃), 1.37 (s, 18H, C(CH₃)₃), 1.61 (s, 18H, C(CH₃)₃), 7.37 (d, 2H, aryl-*H*), 7.56 (d, 2H, aryl-*H*), 7.70 (d, 2H, NC₅H-*H*), 7.92 (t, 1H, NC₅H-*H*). ¹H NMR (500 MHz, CD₂Cl₂, -90 °C) δ: -0.01 (s, 6H, TaCH₃), 0.79 (s, 3H, TaCH₃). ¹H NMR (500 MHz, C₆D₆) δ: 0.90 (s, 9H, Ta(CH₃)₃), 1.33 (s, 18H, C(CH₃)₃), 1.73 (s, 18H, C(CH₃)₃), 7.03 (t, 1H, NC₅H-*H*), 7.24 (d, 2H, NC₅H-*H*), 7.34 (d, 2H, aryl-*H*), 7.73 (d, 2H, aryl-*H*). ¹³C NMR (125 MHz, CD₂Cl₂) δ: 30.2 (C(CH₃)₃), 31.9 (C(CH₃)₃), 35.0 (C(CH₃)₃), 35.9 (C(CH₃)₃), 56.1 (TaCH₃), 124.8, 126.3, 127.4, 128.7, 138.9, 139.2, 144.2, 153.5, 156.9 (aryl). Anal. Calcd. for C₃₆H₅₂NO₂Ta (%): C, 60.75; H, 7.36; N, 1.97. Found: C, 60.77; H, 7.35; N, 1.97.

Synthesis of 7 from TaCl₂(CH₂Ph)₃. KBN (78.5 mg, 0.604 mmol, 2 equiv) was added with the aid of C₆H₆ (4 mL) to a solution of **1** (147 mg, 0.302 mmol, 1 equiv) in C₆H₆ (4 mL). This mixture was allowed to stir at room temperature for 1.5 h, which afforded a colorless mixture of deprotonated phenol. A C₆H₆ solution of TaCl₂(CH₂Ph)₃ (158.5 mg, 0.302 mmol, 1 equiv) was added, and

the reaction mixture was allowed to stir at room temperature for 10 h. Salts were removed by filtration through a bed of Celite, and volatile materials were removed under vacuum. The resulting residue was suspended in petroleum ether, and the mixture was cooled to $-35\text{ }^{\circ}\text{C}$. The desired product was collected by filtration and washed with cold petroleum ether. This procedure affords 168 mg (59% yield) of **7** as an orange powder.

Synthesis of 7 from Ta(CH₂Ph)₅. A C₆H₆ solution of **1** (314.6 mg, 0.646 mmol, 1 equiv) was added to a Schlenk bomb charged with a solution of Ta(CH₂Ph)₅ (411 mg, 0.646 mmol, 1 equiv) in C₆H₆ (20 mL total volume). The flask was sealed, immersed in an oil bath at $60\text{ }^{\circ}\text{C}$, and stirred for 5 h. Volatile materials were removed under vacuum, and petroleum ether was added, and the mixture was stored at $-35\text{ }^{\circ}\text{C}$. Compound **7** was collected by filtration and washed with cold petroleum ether (484 mg, 79% yield). ¹H NMR (500 MHz, C₆D₆) δ : 1.35 (s, 18H, C(CH₃)₃), 1.78 (s, 18H, C(CH₃)₃), 3.08 (s, 4H, TaCH₂), 3.88 (s, 2H, TaCH₂), 6.25 (t, 2H, aryl-*H*), 6.36 (t, 4H, aryl-*H*), 6.45 (d, 4H, aryl-*H*), 6.69 (t, 1H, aryl-*H*), 7.04–7.06 (m, 3H, aryl-*H* overlap), 7.18 (d, 2H, aryl-*H*), 7.52 (t, 2H, aryl-*H*), 7.72 (t, 2H, aryl-*H*), 7.78 (t, 2H, aryl-*H*). ¹³C NMR (125 MHz, C₆D₆) δ : 31.1 (C(CH₃)₃), 32.1 (C(CH₃)₃), 35.0 (C(CH₃)₃), 36.0 (C(CH₃)₃), 73.5 (TaCH₂), 81.6 (TaCH₂), 122.9, 124.7, 125.2, 126.6, 127.2, 127.8, 128.0, 128.3, 129.2, 132.1, 138.1, 139.3, 143.1, 144.8, 152.3, 154.8, 156.9 (aryl). Anal. Calcd. for C₅₄H₆₄NO₂Ta (%): C, 68.99; H, 6.86; N, 1.49. Found: C, 69.10; H, 7.38; N, 1.49.

Synthesis of 8. A solution of phenol **1** (100 mg, 0.205 mmol, 1 equiv) in C₆H₆ (3 mL) was added to a solution of TaCl₃(CH₃)₂ (31.2 mg, 0.205 mmol, 1 equiv) in C₆H₆ (3 mL). The reaction mixture was allowed to stir for 10 h at room temperature. Volatile materials were removed under vacuum, and the desired product was recrystallized from petroleum ether at $-35\text{ }^{\circ}\text{C}$. Compound **8** was obtained as an orange powder (153 mg, 97% yield) upon collection by filtration. ¹H NMR (500 MHz, CD₂Cl₂) δ : 1.39 (s, 18H, C(CH₃)₃), 1.63 (s, 18H, C(CH₃)₃), 7.51 (d, 2H, aryl-*H*), 7.70 (d, 2H, aryl-*H*), 8.05 (d, 2H, NC₅H₂-*H*), 8.22 (t, 1H, NC₅H₂-*H*). ¹³C NMR (125 MHz, CD₂Cl₂) δ : 30.4 (C(CH₃)₃), 31.9 (C(CH₃)₃), 35.3 (C(CH₃)₃), 35.7 (C(CH₃)₃), 126.0, 126.5, 127.7, 128.9, 138.7, 142.1, 147.4, 151.3, 157.3 (aryl).

Synthesis of 9. A solution of phenol **1** (101 mg, 0.207 mmol, 1 equiv) in C₆H₆ (3 mL) was added to a solution of TaCl₂(CH₃)₃ (61.6 mg, 0.207 mmol, 1 equiv) in C₆H₆ (3 mL). The reaction mixture was allowed to stir at room temperature for 3 h. Volatile materials were removed under vacuum to give the desired product as a yellow powder. ¹H NMR (500 MHz, CD₂Cl₂) δ : 1.39 (s, 18H, C(CH₃)₃), 1.70 (s, 18H, C(CH₃)₃), 1.82 (s, 3H, TaCH₃), 7.45 (d, 2H, aryl-*H*), 7.68 (d, 2H, aryl-*H*), 7.86 (d, 2H, NC₅H₂-*H*), 8.10 (t, 1H, NC₅H₂-*H*). ¹³C NMR (125 MHz, CD₂Cl₂) δ : 30.7 (C(CH₃)₃), 31.9 (C(CH₃)₃), 35.2 (C(CH₃)₃), 35.9 (C(CH₃)₃), 68.3 (TaCH₃), 125.4, 126.7, 127.0, 128.2, 138.3, 141.3, 146.7, 151.8, 157.7 (aryl).

Reaction of 7 with [Ph₃C][BF₄]. A toluene solution of **7** (50.8 mg, 54 μmol , 1 equiv) was added to a slurry of [Ph₃C][BF₄] (17.8 mg, 54 μmol , 1 equiv) in toluene. The reaction mixture, initially cloudy and orange, changes to yellow within 2 h, as the insoluble [Ph₃C][BF₄] reacts and dissolves. Volatile materials were removed under vacuum, and the residue was suspended in petroleum ether and cooled to $-35\text{ }^{\circ}\text{C}$. A precipitate was collected by filtration, washed with cold petroleum ether, and dried under vacuum to give **10** as an off-white powder. ¹⁹F NMR (282 MHz, toluene) δ : 148.7. ¹H NMR (300 MHz, C₆D₆) δ : 1.30 (s, 18H, C(CH₃)₃), 1.61 (s, 18H, C(CH₃)₃), 3.81 (br t, *J*_{HF} = 5.3 Hz, 2H, TaCH₂), 6.86–6.96 (app t, 2H, aryl-*H*), 7.08 (d, 2H, aryl-*H*), 7.28 (t, 2H, aryl-*H*), 7.51 (d, 2H, aryl-*H*), 7.68 (d, 2H, aryl-*H*).

Synthesis of 11-P. A toluene (5 mL) solution of **7** (115 mg, 0.122 mmol, 1 equiv) and PMe₂Ph (84.5 mg, 0.612 mmol, 5 equiv) was placed in a Schlenk flask fitted with a screw-in Teflon stopper. The flask was sealed and immersed in an oil bath at $125\text{ }^{\circ}\text{C}$. Upon

stirring for 5 h, the mixture was allowed to cool to room temperature, and volatile materials were removed under vacuum. Petroleum ether was added, and the desired product was recrystallized at $-35\text{ }^{\circ}\text{C}$. Collection by filtration affords 55.4 mg (46% yield) of **11-P**. ¹H NMR (500 MHz, CD₂Cl₂) δ : 1.10 (br s, 6H, P(CH₃)₂), 1.41 (s, 18H, C(CH₃)₃), 1.60 (s, 18H, C(CH₃)₃), 2.20 (s, 2H, TaCH₂), 5.96 (d, 2H, aryl-*H*), 6.23 (t, 1H, aryl-*H*), 6.40 (t, 2H, aryl-*H*), 6.79 (t, 1H, aryl-*H*), 6.9–7.2 (br s and sharp d and t, 9H, aryl-*H*), 7.31 (t, 2H, aryl-*H*), 7.46 (d, 2H, aryl-*H*), 7.55 (d, 2H, aryl-*H*), 7.68 (t, 1H, aryl-*H*), 8.59 (s, 1H, TaCHPh). ¹³C NMR (125 MHz, CD₂Cl₂) δ : 13.8 (br P(CH₃)₂), 30.6 (C(CH₃)₃), 32.0 (C(CH₃)₃), 35.0 (C(CH₃)₃), 35.9 (C(CH₃)₃), 60.6 (br TaCH₂), 119.7, 124.3, 124.6, 126.3, 126.6, 126.9, 127.1, 128.0, 128.4, 128.5, 129.1 (br), 130.8, 130.9, 131.0, 137.7, 139.0, 143.6, 148.3, 153.1, 153.7, 158.7 (aryl), 243.0 (TaCHPh).

Kinetic Measurements for the Conversion of 7 to 11-P. Stock solutions containing **6** ($1.22 \cdot 10^{-2}\text{ M}$) and PMe₂Ph ($4.88 \cdot 10^{-2}$ to $73.2 \cdot 10^{-2}\text{ M}$) were prepared in xylene-*d*₁₀ and stored at $-35\text{ }^{\circ}\text{C}$. The NMR probe was brought to the desired temperature and calibrated with an ethylene glycol standard. A J-Young tube charged with the solution of **6** was utilized in these experiments. The decay of the Ta–CH₂Ph peak was integrated against residual CD₂H in the deuterated solvent. The data were plotted using Microsoft Excel. Typical NMR spectroscopic data for the kinetic runs are presented in Figure 16.

Synthesis of 12. KBn (52.8 mg, 0.406 mmol, 2 equiv) was added with the aid of C₆H₆ (2 mL) to a solution of **2** (100 mg, 0.203 mmol, 1 equiv) in C₆H₆ (5 mL). This mixture was allowed to stir at room temperature for 5 h. The orange KBn discolored to give a phosphorescent pale green mixture. TaCl₂(CH₃)₃ (60.4 mg, 0.203 mmol, 1 equiv) in C₆H₆ (5 mL) was added and the reaction mixture stirred at room temperature to give a pale yellow solution. Salts were removed by filtration through a bed of Celite. Volatile materials were removed under vacuum, and petroleum ether was added to the residue. Upon cooling to $-35\text{ }^{\circ}\text{C}$, the desired product was collected as a very pale yellow powder (43.2 mg, 28% yield). ¹H NMR (500 MHz, CD₂Cl₂) δ : 1.01 (v br s, 9H, TaCH₃), 1.37 (s, 18H, C(CH₃)₃), 1.46 (s, 18H, C(CH₃)₃), 7.14 (s, 2H, SC₄H₂), 7.50 (d, 2H, aryl-*H*), 7.52 (d, 2H, aryl-*H*). ¹H NMR (500 MHz, CD₂Cl₂, $-55\text{ }^{\circ}\text{C}$) δ : 0.40 (s, 3H, TaCH₃), 1.06 (s, 3H, TaCH₃), 1.25 (s, 3H, TaCH₃). ¹³C NMR (125 MHz, CD₂Cl₂) δ : 30.4 (C(CH₃)₃), 31.8 (C(CH₃)₃), 35.1 (C(CH₃)₃), 35.8 (C(CH₃)₃), 123.3, 124.7, 126.1, 130.7, 139.2, 141.1, 145.4, 158.1 (aryl). Anal. Calcd. for C₃₅H₅₁O₂StA (%): C, 59.00; H, 6.91. Found: C, 58.65; H, 7.17.

Synthesis of 13. A solution of phenol **3** (50.2 mg, 0.105 mmol, 1 equiv) in C₆H₆ (5 mL) was added to a solution of TaCl₂(CH₃)₃ (31.2 mg, 0.105 mmol, 1 equiv) in C₆H₆ (5 mL). The reaction mixture was allowed to stir at room temperature. Volatile materials were removed under vacuum, and the desired product was crystallized as an orange solid (53 mg, 68% yield) from petroleum ether at $-35\text{ }^{\circ}\text{C}$. ¹H NMR (500 MHz, CD₂Cl₂) δ : 1.42 (s, 18H, C(CH₃)₃), 1.75 (s, 18H, C(CH₃)₃), 2.11 (s, 3H, TaCH₃), 7.28 (s, 2H, OC₄H₂), 7.64 (d, 2H, aryl-*H*), 7.75 (d, 2H, aryl-*H*). ¹H NMR (500 MHz, CD₂Cl₂, $-55\text{ }^{\circ}\text{C}$) δ : -0.16 (s, 6H, TaCH₃), 0.89 (s, 3H, TaCH₃). ¹³C NMR (125 MHz, CD₂Cl₂) δ : 30.7 (C(CH₃)₃), 31.8 (C(CH₃)₃), 35.3 (C(CH₃)₃), 36.0 (C(CH₃)₃), 70.1 (TaCH₃), 110.9, 121.1, 122.2, 125.2, 139.4, 147.2, 150.8, 152.6 (aryl). Anal. Calcd. for C₃₃H₄₅Cl₂O₃Ta (%): C, 53.45; H, 6.12. Found: C, 53.50; H, 5.92.

Synthesis of 14. KBn (53.1 mg, 0.408 mmol, 2 equiv) was added with the aid of C₆H₆ (4 mL) to a solution of **3** (97.3 mg, 0.204 mmol, 1 equiv) in C₆H₆ (4 mL). This mixture was allowed to stir at room temperature for 0.5 h, which afforded a pale gray mixture of deprotonated phenol. A C₆H₆ solution of TaCl₂(CH₃)₃ (60.7 mg, 0.204 mmol, 1 equiv) was added, and the reaction mixture was allowed to stir at room temperature for 1 h. Salts were removed by filtration through a bed of Celite. Volatile materials were removed under vacuum to give the desired product as a white powder. ¹H

NMR (500 MHz, CD_2Cl_2) δ : 0.32 (s, 9H, $\text{Ta}(\text{CH}_3)_3$), 1.40 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.65 (s, 18H, $\text{C}(\text{CH}_3)_3$), 6.95 (s, 2H, OC_4H_2), 7.54 (d, 2H, aryl-*H*), 7.61 (d, 2H, aryl-*H*). ^{13}C NMR (125 MHz, CD_2Cl_2) δ : 30.3 ($\text{C}(\text{CH}_3)_3$), 31.8 ($\text{C}(\text{CH}_3)_3$), 35.1 ($\text{C}(\text{CH}_3)_3$), 36.0 ($\text{C}(\text{CH}_3)_3$), 58.2 (TaCH_3), 110.8, 121.1, 123.6, 124.9, 139.9, 144.5, 151.8, 152.2 (aryl). Anal. Calcd. for $\text{C}_{35}\text{H}_{51}\text{O}_3\text{Ta}$ (%): C, 59.99; H, 7.34. Found: C, 60.32; H, 7.53.

Preparation of $\text{Ta}(\text{CH}_3)_2[(\text{OC}_6\text{H}_2-t\text{Bu})_2\text{C}_6\text{H}_3]$ (16**).** KBn (234 mg, 1.8 mmol, 2 equiv) was added as a solid to an $\text{Et}_2\text{O}/\text{THF}$ (17/1 mL respectively) solution of diphenol **4** (437 mg, 0.90 mmol, 1 equiv). Orange solid KBn dissolves and discolors over less than an hour. The reaction mixture was allowed to react for 2 h, then TaCl_2Me_3 (267 mg, 0.90 mmol, 1 equiv) was added. Within minutes, the color of the reaction mixture turns brown. The mixture was stirred for 4 h, then filtered through a bed of Celite. Volatile materials were removed under vacuum. Petroleum ether was added to the brown residue, and the mixture was stirred for ~10 min. This mixture was filtered through Celite to remove dark solids. The pale brown filtrate was concentrated and cooled to -35°C . The resulting white precipitate was collected by filtration, washed with cold petroleum ether, and dried under vacuum. This procedure affords 339 mg (0.49 mmol, 54% yield) of **16** as a white powder. ^1H NMR (500 MHz, C_6D_6) δ : 0.81 (s, 6H, $\text{Ta}(\text{CH}_3)_2$), 1.40 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.73 (s, 18H, $\text{C}(\text{CH}_3)_3$), 7.48 (t, 1H, $\text{C}_6\text{H}_2\text{-H}$), 7.69 (d, 2H, aryl-*H*), 8.04 (d, 2H, aryl-*H*), 8.23 (d, 2H, $\text{C}_6\text{H}_2\text{-H}$). ^{13}C NMR (125 MHz, C_6D_6) δ : 31.3 ($\text{C}(\text{CH}_3)_3$), 32.3 ($\text{C}(\text{CH}_3)_3$), 35.3 ($\text{C}(\text{CH}_3)_3$), 35.8 ($\text{C}(\text{CH}_3)_3$), 60.6 (TaCH_3), 123.8, 125.1, 131.2, 135.4, 137.4, 144.1, 144.8, 153.6 (aryl), 198.5 (aryl-CTa). Anal. Calcd. for $\text{C}_{36}\text{H}_{49}\text{O}_2\text{Ta}$ (%): C, 62.24; H, 7.11. Found: C, 60.88; H, 7.24.

Synthesis of $\text{Ta}(\text{CH}_2\text{Ph})_2[(\text{OC}_6\text{H}_2-t\text{Bu})_2\text{C}_6\text{H}_3]$ (17**).** KBn (35.6 mg, 0.27 mmol, 2 equiv) was added as a solid to a slurry of **4** (66.5 mg, 0.136 mmol, 1 equiv) in benzene (10 mL). The reaction mixture was stirred for 1 h at room temperature during which the orange color of KBn disappears. A benzene (5 mL) solution of $\text{TaCl}_2(\text{CH}_2\text{Ph})_3$ (71.8 mg, 0.136 mmol, 1 equiv) was added to the reaction mixture containing the deprotonated phenol. The reaction mixture was stirred for 10 h at room temperatures, then filtered through a bed of Celite. Volatile materials were removed under vacuum. The residue was recrystallized from petroleum ether at -35°C . The desired product was collected by filtrations as a white powder, washed with cold petroleum ether, and dried under vacuum (62.1 mg, 73.4 μmol , 54% yield). ^1H NMR (500 MHz, CD_2Cl_2) δ : 1.41 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.72 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.82 (s, 4H, TaCH_2), 6.70–6.83 (m, 10H, C_6H_5), 7.38 (t, 1H, 4- $\text{C}_6\text{H}_2\text{-H}$), 7.45 (d, 2H, aryl-*H*), 7.48 (d, 2H, aryl-*H*). ^{13}C NMR (125 MHz, CD_2Cl_2) δ : 31.5 ($\text{C}(\text{CH}_3)_3$), 32.0 ($\text{C}(\text{CH}_3)_3$), 35.1 ($\text{C}(\text{CH}_3)_3$), 35.8 ($\text{C}(\text{CH}_3)_3$), 71.7 (TaCH_2), 123.2, 125.6, 126.2, 127.1, 129.1, 129.3, 131.1, 131.6, 135.6, 135.9, 142.0, 144.4, 153.3 (aryl), 197.3 (aryl-CTa). Anal. Calcd. for $\text{C}_{48}\text{H}_{57}\text{O}_2\text{Ta}$ (%): C, 68.07; H, 6.78. Found: C, 67.96; H, 6.72.

Preparation of $\text{TaCl}_2(\text{CH}_3)[(\text{OC}_6\text{H}_2-t\text{Bu})_2\text{C}_6\text{H}_4]$ (18**).** An Et_2O (5 mL) solution of diphenol **4** (152 mg, 0.31 mmol, 1 equiv) was added to an Et_2O (5 mL) solution of $\text{TaCl}_2(\text{CH}_3)_3$. The reaction mixture changes gradually from colorless to yellow. The mixture was stirred for 16 h, and then volatile materials were removed under vacuum. The residue was suspended in petroleum ether and cooled to -35°C . A yellow precipitate was collected by filtration and washed with cold petroleum ether. Drying under vacuum gives 131 mg (0.17 mmol, 56% yield) of **18** as a bright yellow powder. ^1H NMR (300 MHz, C_6D_6) δ : 1.31 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.74 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.27 (s, 3H, TaCH_3), 7.02 (dd, 2H, $\text{C}_6\text{H}_2\text{-H}$), 7.17 (t, overlap with $\text{C}_6\text{D}_5\text{H}$, 1H, $\text{C}_6\text{H}_3\text{-H}$), 7.38 (d, 2H, aryl-*H*), 7.52 (t, 1H, $\text{C}_6\text{H}_3\text{-H}$), 7.69 (d, 2H, aryl-*H*). ^{13}C NMR (125 MHz, CD_2Cl_2) δ : 31.2 ($\text{C}(\text{CH}_3)_3$), 31.9 ($\text{C}(\text{CH}_3)_3$), 35.2 ($\text{C}(\text{CH}_3)_3$), 36.0 ($\text{C}(\text{CH}_3)_3$), 69.3 (TaCH_3), 112.6, 124.7, 125.0, 130.9, 133.4, 134.9, 138.4,

145.3, 147.7, 157.5 (aryl). Anal. Calcd. for $\text{C}_{35}\text{H}_{47}\text{Cl}_2\text{O}_2\text{Ta}$ (%): C, 55.93; H, 6.30. Found: C, 54.81; H, 6.06.

Preparation of **19.** A C_6D_6 (0.6 mL) solution of **18** (15 mg) was placed in a J-Young tube, sealed, and immersed almost completely in an oil bath at 110°C , behind a blast shield. After 10 h, the sample was cooled to room temperature. ^1H and ^{13}C spectroscopic analyses show the clean formation of the species assigned to **18**. ^1H NMR (500 MHz, C_6D_6) δ : 1.35 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.74 (s, 18H, $\text{C}(\text{CH}_3)_3$), 7.31 (t, 1H, $\text{C}_6\text{H}_2\text{-H}$), 7.66 (d, 2H, aryl-*H*), 7.85 (d, 2H, aryl-*H*), 8.04 (d, 2H, $\text{C}_6\text{H}_2\text{-H}$). ^{13}C NMR (125 MHz, C_6D_6) δ : 31.4 ($\text{C}(\text{CH}_3)_3$), 32.2 ($\text{C}(\text{CH}_3)_3$), 35.3 ($\text{C}(\text{CH}_3)_3$), 35.9 ($\text{C}(\text{CH}_3)_3$), 124.4, 124.5, 128.3, 133.9, 135.2, 138.2, 144.2, 146.5, 154.0 (aryl), 205.4 (aryl-CTa).

Kinetic Measurements for the Conversion of **17 to **18**.** Stock solutions containing **17** and Ph_2CH_2 as a standard were prepared in $\text{C}_6\text{D}_5\text{Br}$ and stored at -35°C . The NMR probe was brought to the desired temperature and calibrated with an ethylene glycol standard. After the NMR run was complete, the temperature was checked again. Deflections less than a degree were found indicating temperature stability during the experiment. A J-Young tube charged with the solution of **17** was utilized in these experiments. The decay of the $\text{Ta}-\text{CH}_3$ peak was integrated against the methylene hydrogens of the standard Ph_2CH_2 . Data were acquired for at least three half-lives. The data were plotted using Microsoft Excel. The standard error for each rate constant measurement was found to be less than 1% using the regression function in Excel.

Compound **21 (Ph_2CO Insertion).** A toluene (5 mL) solution containing Ph_2CO (26 mg, 1.4 μmol , 1 equiv) and **16** (100 mg, 1.4 μmol , 1 equiv) was placed in a Schlenk flask with a screw-in Teflon stopper. Upon sealing, the flask was immersed in an oil bath at 60°C and stirred for 12 h. Volatile materials were removed under vacuum, and the residue was triturated with petroleum ether. Recrystallization from petroleum ether at -35°C allows the isolation of **21** (62.8 mg, 50%) by filtration, as a white powder. ^1H NMR (500 MHz, CD_2Cl_2) δ : 0.23 (s, 3H, TaCH_3), 1.22 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.31 (s, 3H, TaCH_3), 1.54 (s, 18H, $\text{C}(\text{CH}_3)_3$), 6.68 (app t, 2H, 2- $\text{p}-\text{C}_6\text{H}_4\text{-H}$), 6.72 (app td, 2H, 2- $\text{m}-\text{C}_6\text{H}_4\text{-H}$), 6.76 (d, 2H, aryl-*H*), 6.86 (app td, 2H, 2- $\text{m}-\text{C}_6\text{H}_4\text{-H}$), 6.95 (app d, 2H, 2- $\text{o}-\text{C}_6\text{H}_4\text{-H}$), 7.03 (d, 2H, aryl-*H*), 7.26 (app dt, 2H, 2- $\text{o}-\text{C}_6\text{H}_4\text{-H}$), 7.28 (d, 2H, $\text{C}_6\text{H}_2\text{-H}$), 7.53 (d, 1H, $\text{C}_6\text{H}_2\text{-H}$). ^{13}C NMR (125 MHz, CD_2Cl_2) δ : 30.1 ($\text{C}(\text{CH}_3)_3$), 31.7 ($\text{C}(\text{CH}_3)_3$), 34.6 ($\text{C}(\text{CH}_3)_3$), 35.6 ($\text{C}(\text{CH}_3)_3$), 60.9 (TaCH_3), 62.0 (TaCH_3), 84.0 (OC), 123.2, 125.3, 126.1, 126.2, 126.4, 127.6, 127.9, 130.7, 133.7, 135.3, 135.7, 136.0, 142.6, 145.6, 151.0, 157.5 (aryl). Anal. Calcd. for $\text{C}_{49}\text{H}_{59}\text{O}_3\text{Ta}$ (%): C, 67.11; H, 6.78. Found: C, 68.03; H, 6.95.

Compound **22 (PhCN Insertion).** A toluene (5 mL) solution containing PhCN (30 mg, 2.9 μmol , 2 equiv) and **16** (100 mg, 1.4 μmol , 1 equiv) was placed in a Schlenk flask with a screw-in Teflon stopper. Upon sealing, the flask was immersed in an oil bath at 60°C and stirred for 12 h. Volatile materials were removed under vacuum, and the residue was triturated with petroleum ether. Recrystallization from petroleum ether at -35°C allows the isolation of **22** (53.3 mg, 46%) by filtration, as a white powder. ^1H NMR (500 MHz, CD_2Cl_2) δ : 0.23 (s, 3H, $\text{Ta}(\text{CH}_3)_2$), 1.20 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.22 (s, 3H, $\text{Ta}(\text{CH}_3)_2$), 1.52 (s, 18H, $\text{C}(\text{CH}_3)_3$), 6.98 (d, 2H, aryl-*H*), 7.06 (t, 2H, $\text{C}_6\text{H}_2\text{-H}$), 7.12–7.16 (d and t overlapped, 3H, aryl-*H*), 7.16 (d, 2H, aryl-*H*), 7.35 (d, 2H, aryl-*H*), 7.68 (t, 1H, aryl-*H*). ^{13}C NMR (125 MHz, CD_2Cl_2) δ : 30.1 ($\text{C}(\text{CH}_3)_3$), 31.7 ($\text{C}(\text{CH}_3)_3$), 34.8 ($\text{C}(\text{CH}_3)_3$), 35.6 ($\text{C}(\text{CH}_3)_3$), 56.4 (TaCH_3), 59.2 (TaCH_3), 123.9, 125.0, 126.2, 126.3, 128.3, 130.5, 131.8, 132.2, 133.1, 138.2, 139.8, 141.5, 144.7, 158.5 (aryl), 169.8 (NC). Anal. Calcd. for $\text{C}_{43}\text{H}_{54}\text{NO}_2\text{Ta}$ (%): C, 64.73; H, 6.82; N, 1.76. Found: C, 63.20; H, 6.84; N, 1.73.

Compound **23 ($t\text{BuNC}$ Insertion).** A mixture of $t\text{BuNC}$ (25 mg, 3.0 μmol , 2.7 equiv) and C_6H_6 (~1 mL) was added to a solution of **16** (72 mg, 1.1 μmol , 1 equiv) in C_6H_6 (5 mL) in a 20 mL vial. Upon addition, the colorless mixture turned yellow. The reaction

mixture was stirred for 1.5 h, and volatile materials were removed under vacuum. ^1H NMR spectroscopic analysis shows the clean formation of **23**. Recrystallization from petroleum ether at $-35\text{ }^\circ\text{C}$ followed by collection by filtration leads to the isolation of 28.5 mg (31%) of **23** as a yellow powder. ^1H NMR (300 MHz, C_6D_6) δ : 0.84 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.29 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.41 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.91 (s, 6H, TaCCH_3), 7.37 (d, 2H, aryl-*H*), 7.58 (t, 1H, C_6H_2 -*H*), 8.05 (d, 2H, aryl-*H*), 8.23 (d, 2H, C_6H -*H*). ^{13}C NMR (75 MHz, C_6D_6) δ : 22.2 (TaCCH_3), 29.5 ($\text{C}(\text{CH}_3)_3$), 30.7 ($\text{C}(\text{CH}_3)_3$), 32.4 ($\text{C}(\text{CH}_3)_3$), 35.0 (aryl- $\text{C}(\text{CH}_3)_3$), 35.4 (aryl- $\text{C}(\text{CH}_3)_3$), 62.7 ($\text{NC}(\text{CH}_3)_3$), 121.5, 125.1, 125.6, 127.7, 134.9, 135.1, 141.9, 145.6, 153.2 (aryl), 198.5 (aryl-CTa), 226.0 (TaCCH_3). Anal. Calcd. for $\text{C}_{46}\text{H}_{67}\text{N}_2\text{O}_2\text{Ta}$ (%): C, 64.17; H, 7.84; N, 3.25. Found: C, 63.87; H, 7.92; N, 3.21.

X-ray Crystal Data: General Procedure. Crystals were removed quickly from a scintillation vial to a microscope slide coated with Paratone N oil. Samples were selected and mounted on a glass fiber with Paratone N oil. Data collection was carried out on a Bruker Smart 1000 CCD diffractometer. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotro-

pically. Some details regarding refined data and cell parameters are available in Tables 1, 2, and 3. Selected bond distances and angles are supplied in the corresponding figures.

Acknowledgment. We thank Lawrence M. Henling (Caltech) for assistance with single crystal X-ray crystallographic studies. This work has been supported by USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER13431).

Supporting Information Available: Tables of bond lengths, angles, and anisotropic displacement parameters for the presented solid-state structures. Computed structure of **11-Pm**. Frontier orbitals of tantalocene, tantalum pyridine-bisphenolate, and carbene. ^1H NMR spectra for the conversion of **7** to **11-P**. Structural drawing of **21**. X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM8002653