Preparation, Characterization, and Reactivity of Tantalum Complexes Containing Tridentate Bis(phenolato) [OSO]-Type Ligands

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A series of new tantalum-tbcp [tbcp = 2,2′-thiobis(4,6-dichlorophenolato)] and tantalum-tbop [tbop = 2,2′-thiobis(6-*tert*-octylphenolato)] complexes [TaCp*Cl_2(κ^3-tbop)] (**1**), [TaCp*Cl_2(κ^3-tbcp)] (**2**), [TaCp*Me_2(κ^3-tbop)] (**3**), [TaCp*Me_2(κ^3-tbcp)] (**4**), [TaCp*Me(κ^3-tbop)(OTf)] (OTf = triflate) (**5**), [TaCp*Me(κ^3-tbcp)(OTf)] (**6**), [TaCp*(κ^3-tbop)$(OTf)_2$] (**7**), and [TaCp*(κ^3-tbcp)$(OTf)_2$] (**8**) have been synthesized. Insertion processes into the methyl groups of complex **3** were not observed upon reaction with CO or isocyanides. In contrast, complex **4** reacted slowly with 1 equiv of xylyl isocyanide (xylyl = 2,6-dimethylphenyl) or *tert*-butyl isocyanide to yield complexes [TaCp*(κ^2-Me_2CNxylyl)(κ^3-tbcp)] (**9**) and [TaCp*Me(κ^2- MeCN^{t}Bu)(κ^3-tbcp)] (**10**), respectively. All products were characterized by NMR spectroscopy and elemental analysis. The single-crystal structures of **2**, **3**, **6**, and **9** were also determined.

Introduction

Organometallic oxides[1] and alkoxides[2] play an important role in numerous stoichiometric and catalytic processes[3] and also serve as molecular models for catalyst−substrate surface interactions.[4] It is equally significant that some of the earliest and best known organic−inorganic systems, with extraordinary implications in the development of multifunctional materials, are certainly derived from these kinds of complexes.[5]

All of these interesting properties derive from the extreme versatility of alkoxide ligands, since appropriate substitution patterns allow for significant modification of the steric and electronic requirements.[6] In addition, chelating alkoxide ligands have become the focus of a great deal of attention as ancillary ligand frameworks for group 4 and 5 metal centers.[7] In this field, in recent years we have developed studies based on the synthesis of several families of early transition metal cyclopentadienyl complexes with different types of assisted ligands, namely, tantalum complexes with [ONO]-type[8] and [OOO]-type[9] alkoxides.

We are currently interested in the preparation of monocyclopentadienyltantalum derivatives with [OSO]-type ligands and the study of their reactivity patterns. Research into this class of complexes that incorporate sulfur donor alkoxide ligands is of interest for two reasons, namely, to compare the potential isolated tantalum complexes with some analogous group 4 metal complexes reported previously[10] and to explore if the nature of the substituents on the aromatic rings of the ligands affects the reactivity of the metal center in this kind of complex.

In this article we report the synthesis, characterization, and reactivity of some monocyclopentadienyltantalum complexes containing tridentate [OSO]-type ligands with different groups on the aromatic rings, namely, tbopH_2 {tbop: 2,2′-thiobis(6-*tert*-octylphenolato)} and tbcpH_2 {tbcp: 2,2′-thiobis(4,6-dichlorophenolato)} (Scheme 1).

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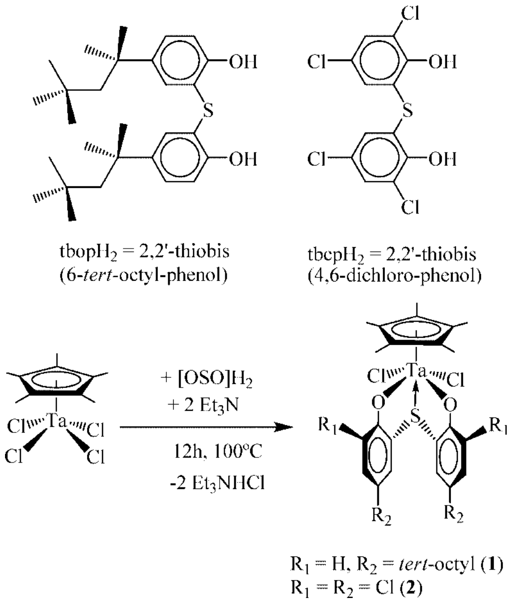
10.1021/om8004838 CCC: $40.75

Scheme 1



Results and Discussion

A general way to achieve the synthesis of alkoxide derivatives of early transition metals is by reaction of the corresponding metal halide precursors with alcohols, normally in the presence of an amine, which facilitates the elimination of XH by formation of the corresponding adduct R_3NHX. In fact, when [TaCp*Cl_4] was reacted with tbopH_2 or tbcpH_2 and Et_3N in a 1:1:2 molar ratio during 12 h at 100 °C, the corresponding alkoxide-containing complexes [TaCp*Cl_2(κ^3-tbop)] (**1**) and [TaCp*Cl_2(κ^3-tbcp)] (**2**) were isolated after the appropriate workup as air- and moisture-sensitive yellow solids (Scheme 1).

With regard to the solubilities of the compounds, complex **1** proved to be very soluble in toluene, THF, acetonitrile, and dichloromethane and quite soluble in pentane and diethyl ether, while complex **2** was insoluble in pentane and only partially soluble in THF, acetonitrile, dichloromethane, and toluene at room temperature. It seems that the presence of the *tert*-octyl chain in the tbop in **1** provides a complex with greater solubility than **2**, and this behavior is reproduced in the rest of the compounds reported (see below), with the κ^3-tbop derivatives being more soluble than the κ^3-tbcp ones in all cases.

These complexes were characterized by commonly used spectroscopic and analytical techniques. In the ^{1}H NMR spectrum of **1** in C_6D_6 the resonance for the Cp* ligand appears at 2.23 ppm. The *tert*-octyl moiety gives rise to one singlet at 0.66 ppm for the three terminal methyl groups and at 1.53 ppm for the methylene fragments. Additionally, the most remarkable feature of the resonances in the ^{1}H NMR spectrum of complex **1** is the presence of two singlet signals at 1.16 and 1.19 ppm, which correspond to the inequivalent methyl groups of the *tert*-octyl moiety and indicates a *fac* coordination mode of the κ^3-tbop ligand to the metal center.[9,11]

The ^{1}H NMR spectrum of complex **2** is very simple, showing a singlet at 2.31 ppm for the Cp* protons and two doublets at 6.78 ($^4J_{H-H}$ = 2.44 Hz) and 6.80 ($^4J_{H-H}$ = 2.44 Hz) for the aromatic protons of the tbcp rings. Unfortunately, this spectrum does not provide information about the *fac* or *mer* coordination of the ligand. Nevertheless, crystals of complex **2** suitable for X-ray diffraction were obtained by crystallization from toluene. The molecular structure of this compound was established by X-ray diffraction, and it was confirmed that the coordination mode of the κ^3-[OSO] ligand is *fac*. Some selected bond distances and angles for complex **2** are listed in Tables 1−4, and the ORTEP views are shown in Figure 1.

Table 1. Bond Lengths and Angles for 2

bond distances [Å]		bond angles [deg]	
Ta(1)−Cl(1)	2.408(2)	Cl(1)−Ta(1)−Cl(2)	87.9(1)
Ta(1)−Cl(2)	2.403(2)	O(1)−Ta(1)−O(2)	86.0(2)
Ta(1)−O(1)	2.009(4)	Cl(1)−Ta(1)−O(1)	151.2(1)
Ta(1)−O(2)	2.009(4)	Cl(1)−Ta(1)−O(2)	86.3(1)
Ta(1)−S(1)	2.641(2)	Cl(1)−Ta(1)−S(1)	75.2(1)
Ta(1)−C(14)	2.402(6)	Cl(2)−Ta(1)−O(1)	85.3(1)
Ta(1)−C(15)	2.445(6)	Cl(2)−Ta(1)−O(2)	150.6(1)
Ta(1)−C(16)	2.487(6)	Cl(2)−Ta(1)−S(1)	74.6(1)
Ta(1)−C(17)	2.495(6)	O(1)−Ta(1)−S(1)	76.0(1)
Ta(1)−C(18)	2.429(6)	O(2)−Ta(1)−S(1)	76.1(1)

The crystal of **2** consists of discrete molecules separated by van der Waals distances. The tantalum atom is bonded to the cyclopentadienyl ring in a η^5-mode. In addition, the tbcp ligand is bonded to the metal center in a bent mode through the oxygen atoms, which are located in the equatorial plane and are *cis* to each other, and the central sulfur atom is occupying the position *trans* to the Cp* group. The coordination around the metal is best described as a pseudo-octahedral geometry, with the tantalum atom 0.549(2) Å out of the plane defined by the atoms Cl(1), Cl(2), O(1), and O(2). The Ta(1)−O(1) and Ta(1)−O(2) bond distances are equal to 2.009(4) Å, and these are within the normal range for tantalum alkoxide complexes.[9,12] The Ta(1)−S(1) bond length [2.641(2) Å] is comparable to that found previously by our group for similar ligands [2.641(7) Å].[13] As a result of its *cis* coordination mode, the [OSO] ligand is bent and the angles O(1)−Ta(1)−O(2) and C(1)−S(1)−C(7) are 86.0(2)° and 100.0(3)°, respectively.

Another well-documented general way to achieve the synthesis of alkoxide derivatives of early transition metals corresponds to the reaction of metal alkyl complexes with alcohols to yield the corresponding alkanes and the alkoxide complexes. A likely mechanism for the protonolysis of the carbon−metal bond requires initial donation of an oxygen lone pair to the metal

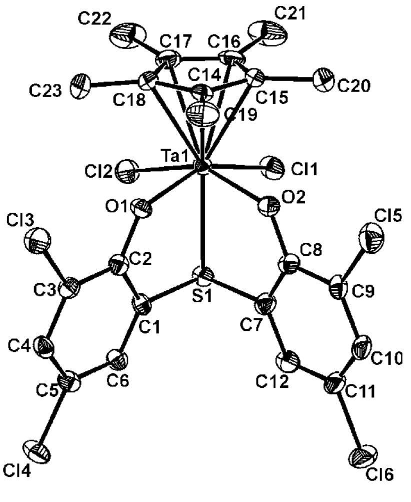


Figure 1. ORTEP drawing of complex **2** with the atomic labeling scheme. Hydrogen atoms are omitted for clarity; thermal ellipsoids are at the 30% level of probability.

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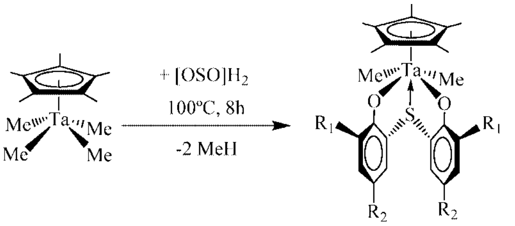
Scheme 2



$R_1 = H$, $R_2 =$ *tert*-octyl (**3**)
$R_1 = R_2 = Cl$ (**4**)

center.[14] This methodology has proven to be useful in the synthesis of alkyl/alkoxide tantalum complexes. This synthetic methodology was investigated and the tantalum complex $[TaCp^*Me_4]$ reacted with tbopH_2 and tbcpH_2 in a 1:1 ratio at 100 °C during 8 h to render the complexes $[TaCp^*Me_2(\kappa^3\text{-tbop})]$ (**3**) and $[TaCp^*Me_2(\kappa^3\text{-tbcp})]$ (**4**), respectively, as air- and moisture-sensitive yellow solids (see Scheme 2). In agreement with the behavior previously described for **1** and **2**, complex **3** is soluble in common organic solvents, while complex **4** is soluble only in hot toluene and partially soluble in THF, acetonitrile, dichloromethane, and toluene at room temperature.

The spectroscopic and analytical data for **3** and **4** are consistent with the proposed structure (see Scheme 2). For example, the ^1H NMR spectrum of **3** shows singlet signals at 0.07 and 1.99 ppm, and these are attributed to the methyl groups bonded to the metal center and to the Cp* ligand, respectively. The κ^3-tbop ligand gives rise to several multiplets centered at 6.63, 7.05, and 7.73 ppm corresponding to the aromatic protons. The signal due to the terminal methyl groups of the *tert*-octyl chain appears at 0.71 ppm and the methylene fragments at 1.61 ppm, while the two methyl groups are inequivalent and their signals appear at 1.25 and 1.28 ppm; this points to a *fac* disposition of the κ^3-tbop ligand. This proposal was confirmed by X-ray diffraction studies. The X-ray crystal structure of **3** is depicted in Figure 2. In the structure, the pentamethylcyclopentadienyl ring is bound to the Ta atom in an almost symmetric η^5-fashion, and the κ^3-tbop ligand is coordinated in a *fac*-fashion.

This complex can be described as pseudo-octahedral with the Ta atom displaced by 0.552(1) Å from the equatorial plane containing the atoms O(1), O(2), C(1), and C(2). The distance between the metal and the centroid of the ring is 2.129(2) Å. The Ta atom is also bound to two oxygen atoms, Ta−O(1) 2.025(4) Å and Ta−O(2) 2.003(4) Å, with the Ta coordination sphere completed by the carbon atoms of the methyl groups [Ta−C(1) 2.249(6) Å, Ta−C(2) 2.242(7) Å] and the sulfur donor atom of the *fac*-κ^3-tbop ligand occupying the position *trans* to the Cp* group. The Ta−S distance of 2.677(1) Å is similar to those found in complexes **1** and **2** and similar to those found in the literature for similar complexes.[13]

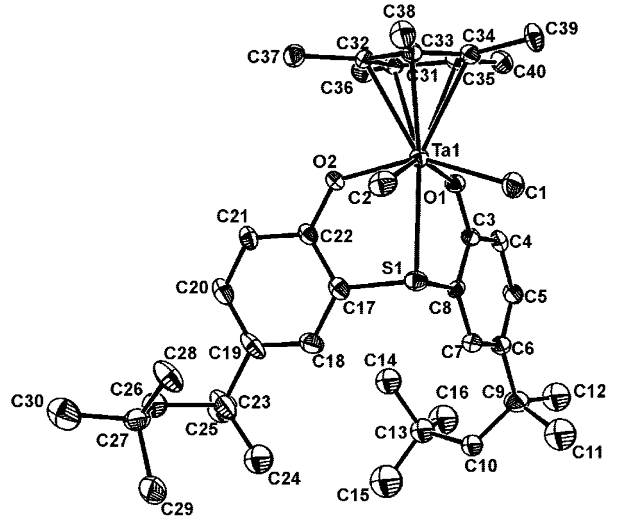
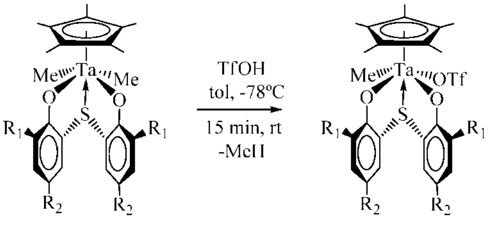


Figure 2. ORTEP drawing of complex **3** with the atomic labeling scheme. Hydrogen atoms are omitted for clarity; thermal ellipsoids are at the 30% level of probability.

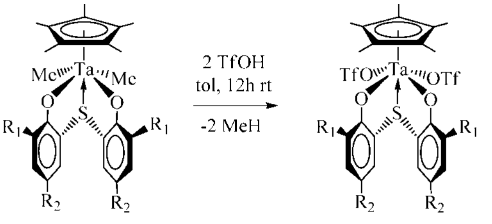
Scheme 3



$R_1 = H$, $R_2 =$ *tert*-octyl (**3**)
$R_1 = R_2 = Cl$ (**4**)

$R_1 = H$, $R_2 =$ *tert*-octyl (**5**)
$R_1 = R_2 = Cl$ (**6**)

Scheme 4



$R_1 = H$, $R_2 =$ *tert*-octyl (**3**)
$R_1 = R_2 = Cl$ (**4**)

$R_1 = H$, $R_2 =$ *tert*-octyl (**7**)
$R_1 = R_2 = Cl$ (**8**)

The reactivity of the dimethyl complexes **3** and **4** with protonating reagents and unsaturated molecules was also studied. Reaction with 1 equiv of triflic acid occurs in a rather selective way to yield, through protonolysis of only one tantalum−methyl bond, the corresponding mono-triflate complexes **5** and **6** (Scheme 3). When 2 equiv of triflic acid are used, the bis-triflate complexes **7** and **8** are also formed by protonolysis of both Me−Ta bonds (Scheme 4). The most remarkable aspect of these reactions is that while mono-triflate complex generation is complete in 15 min, the bis-triflate formation requires 12 h at room temperature (see Experimental Section for details).

The solubility pattern of these triflate complexes is consistent with the behavior described above, namely, that the κ^3-tbop mono- and bis-triflate derivatives **5** and **7** are soluble in common organic solvents, while the κ^3-tbcp mono- and bis-triflate complexes **6** and **8** are markedly less soluble at room temperature but quite soluble in hot solvents such as toluene. This behavior points to a covalent nature for the triflate−tantalum bonds.

All of these triflate-containing complexes (**5**−**8**) were characterized by spectroscopic and analytical methods, and their data are in agreement with the proposed structures (see Schemes 3 and 4). For example, the ^1H NMR spectrum of **5** shows two singlet signals, one at 1.99 ppm corresponding to the Cp* protons and the other at 0.74 ppm corresponding to the Ta-Me group protons. The most remarkable feature in this spectrum is

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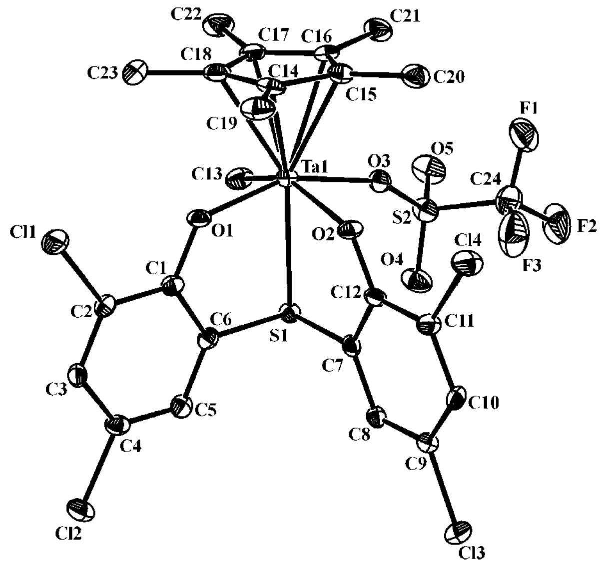

Figure 3. ORTEP drawing of complex **6** with the atomic labeling scheme. Hydrogen atoms are omitted for clarity; thermal ellipsoids are at the 30% level of probability.

that the tbop ligand gives rise to two sets of signals due to the asymmetry of the molecule. As an example, two singlet signals are observed at 0.61 and 0.72 ppm, integrating for 9H each, corresponding to the terminal CMe_3 groups of the inequivalent *tert*-octyl chains. This lack of equivalence between the rings is also evidenced in the spectra of complex **6**; for example, in the ^{1}H NMR spectrum four doublet signals are observed at 6.73, 6.80, 6.89, and 6.99 ppm, corresponding to the aromatic ring protons. In this spectrum the Cp* signal appears at 2.08 ppm and the methyl group bonded to the tantalum center gives rise to a singlet at 0.62 ppm.

In contrast to the above case, the NMR spectra of bis-triflate complexes **7** and **8** are simpler due to the equivalence of the aromatic rings. In fact only three signals appear in the ^{1}H NMR spectrum of **8**, one singlet for the Cp* protons at 2.32 ppm and two doublets ($^4J_{H-H} = 2.41$ Hz) at 6.75 ppm and 6.77 ppm corresponding to the aromatic ring protons.

Additionally, in the ^{19}F NMR spectra of all the triflate derivatives it is worth noting the presence of only one signal corresponding to the fluorine atoms of the triflate ligands at −77.7 ppm for the mono-triflates (**5**, **6**) and at −76.7 ppm for the bis-triflates (**7**, **8**).

Finally, the molecular structure of **6** (see Figure 3) was effectively established by X-ray crystallography studies, which revealed the covalent nature of the TfO−Ta bond, as the Ta−O(3) distance 2.097(4) Å is comparable with those published for analogous covalent triflate-tantalum complexes.[15,9] The tantalum atom is bonded to the cyclopentadienyl ring in a η^5-mode. The tbcp ligand is bonded to the metal center in a *fac* κ^3-fashion. The oxygen atoms are located in the equatorial plane and are *cis* to one another. The central sulfur atom occupies the position *trans* to the Cp* group. The coordination around the metal is best described as a pseudo-octahedral geometry, with the tantalum atom 0.494(2) Å out of the plane defined by the atoms C(13), O(1), O(2), and O(3). The Ta(1)−O(1) and Ta(1)−O(2) bond distances [1.952(4) and 2.021(4) Å, respectively] are within the normal range for tantalum alkoxide complexes,[9,12] and the slight difference between these values can be justified by the steric requirements of the triflate ligand. The Ta(1)−S(1) bond length [2.693(1) Å] is comparable to that found in complexes **2**, **3**, and others previously described by our group for similar ligands [2.641(7) Å].[13]

Finally, the reactivity of methyl-containing complexes **3** and **4** toward unsaturated compounds such as isocyanides was considered. Surprisingly, while the most soluble complex **3** did not react with these reagents under different experimental conditions, compound **4** reacted readily in toluene at 100 °C with 2,6-dimethylphenyl isocyanide (xylylNC) in a 1:1 molar ratio to give the azatantalacyclopropane complex [TaCp*(κ^2-$Me_2CNxylyl$)(κ^3-tbcp)] (**9**), which was isolated as an air- and moisture-sensitive white solid in almost quantitative yield (Scheme 5).

The ^{1}H and ^{13}C NMR spectroscopic data for compound **9** point to a κ^2-coordination for the generated azatantalacyclopropane moiety. The ^{1}H NMR spectrum shows a singlet signal at 1.76 ppm, which is assigned to the Cp* protons, and two singlet signals corresponding to the methyl groups present in the molecule, one at 1.07 ppm for the methyl groups bonded to the quaternary carbon atom of the azatantalacyclopropane moiety and the other at 2.28 ppm for the methyl groups of the xylyl moiety. The ^{13}C NMR spectrum shows, as its outstanding feature, a signal at 86.04 ppm corresponding to the quaternary carbon atom of the azatantalacyclopropane moiety. The high-field shift of this resonance points to a κ^2-C,N-coordination of the group.[16] This structural disposition was confirmed by X-ray diffraction. An ORTEP view of the molecule is depicted in Figure 4, and some selected bond distances are listed in Table 4.

The molecular structure of **9** is best described as pseudo-octahedral, with the Cp* ligand and the carbon atom of the azatantalacyclopropane moiety C(1) placed in the apical positions. The most remarkable feature of this molecule is the coordination mode of the tbcp ligand, which is *mer* κ^3-fashion with the oxygen and sulfur atoms located in the equatorial plane. The oxygen atoms are located *trans* to each other, while the sulfur atom is in a *trans* disposition with respect to the nitrogen atom. The Ta−O distances [Ta−O(1) 2.00(1) Å, Ta−O(2) 2.05(1) Å] are in the expected range, while the Ta−S(1) distance [2.725 (4) Å] is somewhat longer than those found in complexes **2**, **3**, and **6**, possibly due to the different disposition of the tbcp ligand. The Ta−N(1) [1.89(1) Å], Ta(1)−C(1) [2.19(1) Å], and C(1)−N(1) [1.46(2) Å] bond distances are comparable to those found in other nitrogen ligand tantalum complexes.[17] Finally, the tantalum atom is practically in the equatorial plane, i.e., 0.30(1) Å out of the plane defined by the S(1), O(1), and O(2) atoms, but the N(1) atom is −0.82(2) Å out of this plane.

A plausible mechanism for the formation of **9** would initially involve complex **4** reacting with 1 molar equiv of 2,6-dimethylphenyl isocyanide by insertion into one Ta−Me bond to form an intermediate κ^2-C,N-iminoacyl-containing complex (see Scheme 5). However, all attempts to isolate this proposed intermediate were unsuccessful. A second methyl migration would then occur, forming the isolated κ^2-C,N-azatantalacyclopropane species **9** (Scheme 5). Nevertheless, when the reaction of **4** with *tert*-butyl isocyanide was carried out in THF

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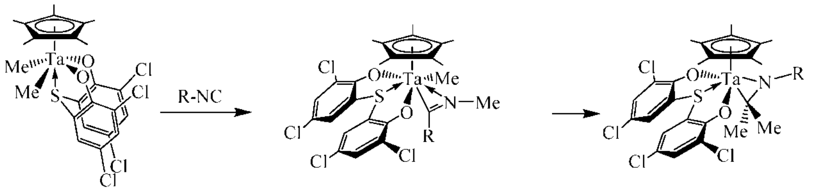
Scheme 5



4

R = xylyl (not detected)
R = ^{t}Bu (**10**)

R = xylyl (**9**)
R = ^{t}Bu (**11**)

at 65 °C during 96 h, both the κ^2-iminoacyl [TaCp*Me(κ^2-MeCN^{t}Bu)(κ^3-tbcp)] (**10**) and κ^2-azatantalacyclopropane [TaCp*(κ^2-Me$_2$CN^{t}Bu)(κ^3-tbcp)] (**11**) species were detected in the reaction mixture (Scheme 5). Complex **10** could be isolated as a pure solid after the appropriate workup, while characterization of **11** in solution by NMR was also possible (see Experimental Section) and the ^{1}H NMR data support the presence in its structure of a κ^2-C,N-azatantalacyclopropane fragment as a result of a double-insertion process. The spectroscopic data for **10** point to a κ^2-C,N-coordination of the iminoacyl group, which is consistent with the literature precedents in which early transition metal iminoacyl complexes are described to be normally stabilized by coordination of the nitrogen atom to the metal center in a κ^2-coordination mode.[18] The IR spectrum of **10** shows an absorption in the region near 1500 cm^{-1}, which can be assigned to ν(C=N), and the resonance of the iminoacyl carbon appears at 236.59 ppm in the ^{13}C NMR spectrum.[8]

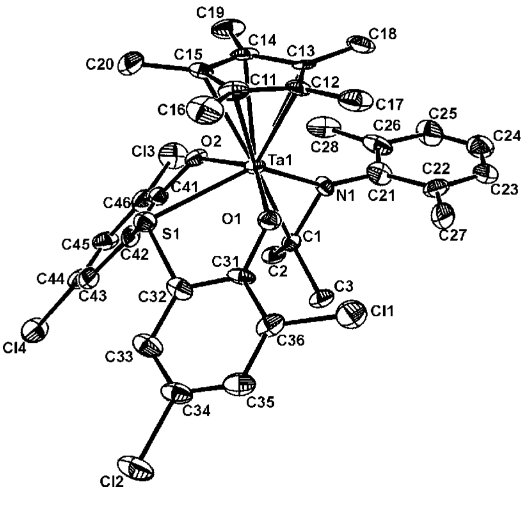


Figure 4. ORTEP drawing of complex **9** with the atomic labeling scheme. Hydrogen atoms are omitted for clarity; thermal ellipsoids are at the 30% level of probability.

Table 2. Bond Lengths and Angles for 3

bond distances [Å]		bond angles [deg]	
Ta(1)−O(2)	2.003(4)	O(2)−Ta(1)−O(1)	91.7(2)
Ta(1)−O(1)	2.025(4)	O(2)−Ta(1)−C(2)	84.8(2)
Ta(1)−C(2)	2.242(7)	O(1)−Ta(1)−C(2)	149.01(2)
Ta(1)−C(1)	2.249(6)	O(2)−Ta(1)−C(1)	149.8(2)
Ta(1)−S(1)	2.677(1)	O(1)−Ta(1)−C(1)	85.3(2)
S(1)−C(17)	1.777(6)	C(2)−Ta(1)−C(1)	82.6(2)
S(1)−C(8)	1.779(6)	C(17)−S(1)−C(8)	102.8(3)
O(1)−C(3)	1.348(6)	C(17)−S(1)−Ta(1)	97.7(2)
O(2)−C(22)	1.334(6)	C(8)−S(1)−Ta(1)	97.63(17)
		C(3)−O(1)−Ta(1)	130.4(4)
		C(22)−O(2)−Ta(1)	131.8(4)

Table 3. Bond Lengths and Angles for 6

bond distances [Å]		bond angles [deg]	
Ta(1)−O(1)	1.952(4)	O(1)−Ta(1)−O(2)	91.0(2)
Ta(1)−O(2)	2.021(4)	O(1)−Ta(1)−O(3)	155.0(1)
Ta(1)−O(3)	2.097(4)	O(2)−Ta(1)−O(3)	81.4(12)
Ta(1)−S(1)	2.693(1)	O(1)−Ta(1)−C(13)	90.4(2)
S(1)−C(7)	1.765(7)	O(2)−Ta(1)−C(13)	148.3(2)
S(1)−C(6)	1.790(6)	O(3)−Ta(1)−C(13)	84.0(2)
		C(7)−S(1)−C(6)	99.6(3)
		C(7)−S(1)−Ta(1)	97.1 (2)
		C(1)−O(1)−Ta(1)	131.0(3)
		C(12)−O(2)−Ta(1)	131.2(4)
		S(2)−O(3)−Ta(1)	154.5(3)

Table 4. Bond Lengths and Angles for 9

bond distances [Å]		bond angles [deg]	
Ta(1)−N(1)	1.89(1)	N(1)−Ta(1)−C(1)	41.2(5)
Ta(1)−C(1)	2.19(1)	O(1)−Ta(1)−O(2)	139.7(4)
Ta(1)−O(1)	2.00(1)	O(1)−Ta(1)−N(1)	99.6(5)
Ta(1)−O(2)	2.05(1)	O(2)−Ta(1)−N(1)	99.2(5)
Ta(1)−S(1)	2.725(4)	S(1)−Ta(1)−N(1)	137.3(4)
C(1)−N(1)	1.46(2)	S(1)−Ta(1)−C(1)	96.2(4)

Conclusion

New monocyclopentadienyltantalum complexes containing tridentate bis(phenolato) ligands, namely, tbcp (=2,2′-thiobis(4,6-dichloro-phenolato) and tbop (=2,2′-thiobis(6-*tert*-octylphenolato), with choro, methyl, and triflate as co-ligands have been isolated and characterized. In all of these complexes the tridentate ligand adopts a *facial* κ^3-coordination mode.

Furthermore, a significant difference in reactivity between the two types of methyl-containing derivatives toward unsaturated molecules has been observed. In fact, the less soluble complex (the tbcp-containing derivative **4**) reacted with isocyanides to give azatantalacyclopropane-containing tantalum complexes, while the more soluble complex (the tbop-containing derivative **3**) did not react. This observation could indicate a possible influence of the ring substituents on the electronic density on the tantalum center, and we are currently working on several reactivity studies with other kinds of unsaturated molecules.

Experimental Section

General Remarks. All compounds were prepared and handled with rigorous exclusion of air and moisture under a nitrogen atmosphere by using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under nitrogen.

The following reagents were prepared by literature procedures: [TaCp*Cl$_4$][19] and [TaCp*Me$_4$].[20] The commercially available compounds 2,6-dimethylphenyl isocyanide (xylyl-NC), *tert*-butyl isocyanide, triflic acid, 2,2′-thiobis(4,6-dichlorophenol), and 2,2′-thiobis(6-*tert*-octylphenol) were used as received from Aldrich.

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

(19) Burt, R. J.; Chatt, J.; Leigh, G. J.; Teuben, J. H.; Westerhof, A. *J. Organomet. Chem.* **1977**, *129*, C33.

(20) Sanner, R. D.; Carter, S. T.; Burton, W. J. *J. Organomet. Chem.* **1982**, *240*, 157.

Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded in the region 4000−400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer as Nujol mulls using PET cells. ^{1}H, ^{19}F, and ^{13}C NMR spectra were obtained on a 200 MHz Mercury Varian Fourier transform spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to SiMe$_4$.

[TaCp*Cl$_2$(κ^3-tbop)] (1). To a solution of [TaCp*Cl$_4$] (0.359 g, 0.78 mmol) and tbopH$_2$ (0.347 g, 0.78 mmol) in toluene (10 mL) was added 2 equiv of Et$_3$N (218 μL, 1.56 mmol). The mixture was stirred at 100 °C for 12 h and allowed to cool to room temperature. The suspension was filtered and the residue extracted with toluene (2 × 10 mL). The resulting toluene solution was evaporated, and the yellow oil was washed with cold pentane to afford a yellow solid (0.513 g, 79%), which was characterized as **1**. Crystals of complex **1** that were suitable for X-ray diffraction were obtained by crystallization from pentane.

^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.66 (s, 18H, 6CH$_3$ *t*-octyl), 1.16 (s, 6H, 2CH$_3$ *t*-octyl), 1.19 (s, 6H, 2CH$_3$ *t*-octyl), 1.53 (s, 4H, 2CH$_2$ *t*-octyl), 2.23 (s, 15H, Cp*), 6.58 (d, $^3J_{\mathrm{H-H}}$ = 8.60 Hz, 2H, ar), 7.04 (dd, $^3J_{\mathrm{H-H}}$ = 8.60 Hz, $^4J_{\mathrm{H-H}}$ = 2.31 Hz, 2H, ar), 7.51 (d, $^4J_{\mathrm{H-H}}$ = 2.31 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 11.86 (Cp*), 31.51 (*C*Me$_3$ *t*-octyl), 31.91 (C*Me$_3$* *t*-octyl), 32.06 (C*Me$_2$* *t*-octyl), 32.27 (C*Me$_2$* *t*-octyl), 38.18 (*C*Me$_2$ *t*-octyl), 56.94 (*C*H$_2$ *t*-octyl), 118.65 (Cp*), 123.80 (C$_{\mathrm{ipso}}$ S), 126.17 (ar), 129.26 (ar), 129.50 (ar), 144.52 (C$_{\mathrm{ipso}}$ *t*-octyl), 165.70 (C$_{\mathrm{ipso}}$O). Anal. Calcd for C$_{38}$H$_{55}$Cl$_2$O$_2$STa (827.77): C, 55.14; H, 6.70; S, 3,87. Found: C, 55.25; H, 6.65; S, 3.88.

[TaCp*Cl$_2$(κ^3-tbcp)] (2). To a solution of [TaCp*Cl$_4$] (0.427 g, 0.93 mmol) and tbcpH$_2$ (0.332 g, 0.93 mmol) in toluene (10 mL) was added 2 equiv of Et$_3$N (259 μL, 1.8 mmol). The mixture was stirred at 100 °C for 12 h and allowed to cool to room temperature. The suspension was filtered and the residue extracted twice with toluene (2 × 10 mL). The resulting toluene solution was evaporated to afford a yellow solid (0.569 g, 82%), which was characterized as **2**. Crystals of complex **2** that were suitable for X-ray diffraction were obtained by crystallization from toluene.

^{1}H NMR (C$_6$D$_6$, 293 K): δ 2.31 (s, 15H, Cp*), 6.78 (d, $^4J_{\mathrm{H-H}}$ = 2.44 Hz, 2H, ar), 6.80 (d, $^4J_{\mathrm{H-H}}$ = 2.44 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 12.29 (Cp*), 124.15 (Cp*), 124.32 (C$_{\mathrm{ipso}}$S), 126.09 (C$_{\mathrm{ipso}}$ Cl^6), 129.67 (C$_{\mathrm{ipso}}$Cl^4), 130.15 (ar), 132.49 (ar), 165.79 C$_{\mathrm{ipso}}$(O). Anal. Calcd for C$_{22}$H$_{19}$Cl$_6$O$_2$STa (741.08): C, 35.65; H, 2.58; S, 4.33. Found: C, 35.18; H, 2.84; S, 4,53.

[TaCp*Me$_2$(κ^3-tbop)] (3). A mixture of [TaCp*Me$_4$] (0.314 g, 0.83 mmol) and tbopH$_2$ (0.369 g, 0.83 mmol) in toluene (10 mL) was stirred at 100 °C for 8 h. The toluene was evaporated to afford a yellow solid (0.585 g, 89%), which was characterized as **3**. Crystals of complex **3** that were suitable for X-ray diffraction were obtained by crystallization from toluene/pentane.

^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.07 (s, 6H, Ta-*Me*), 0.71 (s, 18H, 6CH$_3$ *t*-octyl), 1.25 (s, 6H, 2CH$_3$ *t*-octyl), 1.28 (s, 6H, 2CH$_3$ *t*-octyl), 1.61 (s, 4H, 2CH$_2$ *t*-octyl), 1.99 (s, 15H, Cp*), 6.63 (d, $^3J_{\mathrm{H-H}}$ = 8.56 Hz, 2H, ar), 7.05 (dd, $^3J_{\mathrm{H-H}}$ = 8.56 Hz, $^4J_{\mathrm{H-H}}$ = 2.37 Hz, 2H, ar), 7.73 (d, $^4J_{\mathrm{H-H}}$ = 2.37 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 11.22 (Cp*), 31.79 (C*Me$_2$* *t*-octyl), 31.90 (C*Me$_2$* *t*-octyl), 32.09 (C*Me$_3$* *t*-octyl), 32.49 (*C*Me$_3$ *t*-octyl), 35.51 (Ta-*Me$_2$* *t*-octyl), 38.24 (*C*Me$_2$ *t*-octyl), 57.20 (*C*H$_2$ *t*-octyl), 119.27 (Cp*), 120.68 (C$_{\mathrm{ipso}}$S), 121.88 (ar), 128.30 (ar), 129.57 (ar), 142.94 (C$_{\mathrm{ipso}}$ *t*-octyl), 167.08 (C$_{\mathrm{ipso}}$O). Anal. Calcd for C$_{40}$H$_{61}$O$_2$STa (786.92): C, 61.05; H, 7.81; S, 4.07. Found: C, 60.62; H, 7.73; S, 3.97.

[TaCp*Me$_2$(κ^3-tbcp)] (4). A mixture of [TaCp*Me$_4$] (0.454 g, 1.20 mmol) and tbcpH$_2$ (0.429 g, 1.20 mmol) in toluene (10 mL) was stirred at 100 °C for 8 h. The toluene was evaporated to afford a yellow solid (0.813 g, 96%), which was characterized as **4**.

^{1}H NMR (C$_6$D$_6$, 293 K): δ −0.11 (s, 6H, Ta-*Me*), 1.97 (s, 15H, Cp*), 6.89 (d, $^4J_{\mathrm{H-H}}$ = 2.46 Hz, 2H, ar), 7.06 (d, $^4J_{\mathrm{H-H}}$ = 2.46 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 11.33 (Cp*), 37.83 (Me-Ta), 122.38 (C$_{\mathrm{ipso}}$S), 122.88 (Cp*), 124.69 (C$_{\mathrm{ipso}}$Cl^6), 124.87 (C$_{\mathrm{ipso}}$ Cl^4), 129.79 (ar), 132.28 (ar), 156.12 (C$_{\mathrm{ipso}}$O). Anal. Calcd for C$_{24}$H$_{25}$Cl$_4$O$_2$STa (700.28): C, 41.16; H, 3.60; S, 4.58. Found: C, 41.14; H, 3.49; S, 4.52.

[TaCp*Me(κ^3-tbop)(TfO)] (5). To a solution of [TaCp*Me$_2$(κ^3-tbop)] (**3**) (0.150 g, 0.19 mmol) in toluene (10 mL) at −78 °C was added 1 equiv of triflic acid (16.8 μL, 0.19 mmol), and the mixture was stirred for 15 min at this temperature. After warming slowly to room temperature the toluene was evaporated and the residue was washed with pentane (8 mL) to give a yellow solid (0.121 g, 69%), which was characterized as **5**.

^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.61 (s, 9H, 3CH$_3$ *t*-octyl), 0.72 (s, 9H, 3CH$_3$ *t*-octyl), 0.74 (s, 3H, Ta-*Me*), 1.13 (s, 3H, CH$_3$ *t*-octyl), 1.16 (s, 6H, 2CH$_3$ *t*-octyl), 1.22 (s, 3H, CH$_3$ *t*-octyl), 1.51 (s, 2H, CH$_2$ *t*-octyl), 1.58 (s, 2H, CH$_2$ *t*-octyl), 1.99 (s, 15H, Cp*), 6.36 (d, $^3J_{\mathrm{H-H}}$ = 8.58 Hz, 1H, ar), 6.59 (d, $^3J_{\mathrm{H-H}}$ = 8.59 Hz, 1H, ar), 6.96 (dd, $^3J_{\mathrm{H-H}}$ = 8.58 Hz, $^4J_{\mathrm{H-H}}$ = 2.43 Hz, 1H, ar), 7.06 (dd, $^3J_{\mathrm{H-H}}$ = 8.59 Hz, $^4J_{\mathrm{H-H}}$ = 2.33 Hz, 1H, ar), 7.50 (d, $^4J_{\mathrm{H-H}}$ = 2.43 Hz, 1H, ar), 7.55 (d, $^4J_{\mathrm{H-H}}$ = 2.33 Hz, 1H, ar). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 10.98 (Cp*), 31.39 (C*Me$_3$* *t*-octyl), 31.50 (C*Me$_3$* *t*-octyl), 31.76 (C*Me$_2$* *t*-octyl), 31.85 (C*Me$_2$* *t*-octyl), 31.92 (*C*Me$_3$ *t*-octyl), 32.13 (*C*Me$_3$ *t*-octyl), 32.26 (C*Me$_2$* *t*-octyl), 32.27 (C*Me$_2$* *t*-octyl), 38.15 (*C*Me$_2$ *t*-octyl), 38.20 (*C*Me$_2$ *t*-octyl), 38.39 (*Me*-Ta), 56.87 (CH$_2$ *t*-octyl), 118.33 (C$_{\mathrm{ipso}}$S), 118.92 (C$_{\mathrm{ipso}}$S), 125.08 (Cp*), 125.22 (ar), 128.80 (ar), 129.65 (ar), 129.88 (ar), 130.42 (ar), 144.36 (C$_{\mathrm{ipso}}$*t*-octyl), 145.29 (C$_{\mathrm{ipso}}$*t*-octyl), 161.07 (C$_{\mathrm{ipso}}$O), 163.08 (C$_{\mathrm{ipso}}$O). ^{19}F NMR (C$_6$D$_6$, 293 K): δ −77.7. Anal. Calcd for C$_{40}$H$_{58}$F$_3$O$_5$S$_2$Ta (920.96): C, 52.17; H, 6.35; S, 6.96. Found: C, 51.50; H, 6.19; S, 6.69.

[TaCp*Me(κ^3-tbcp)(TfO)] (6). To a solution of [TaCp*Me$_2$(κ^3-tbcp)] (**4**) (0.185 g, 0.26 mmol) in toluene (10 mL) at −78 °C was added 1 equiv of triflic acid (23.3 μL, 0.26 mmol), and the mixture was stirred for 15 min at this temperature. After warming slowly to room temperature the toluene was evaporated and the residue washed with pentane (8 mL) to give a yellow solid (0.209 g, 92%), which was characterized as **6**. Crystals of complex **6** that were suitable for X-ray diffraction were obtained by crystallization from toluene.

^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.62 (s, 3H, Ta-*Me*), 2.08 (s, 15H, Cp*), 6.73 (d, $^4J_{\mathrm{H-H}}$ = 2.45 Hz, 2H, ar), 6.80 (d, $^4J_{H-H}$ = 2.45 Hz, 2H, ar) 6.89 (d, $^4J_{\mathrm{H-H}}$ = 2.39 Hz, 2H, ar), 6.99 (d, $^4J_{\mathrm{H-H}}$ = 2.39 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 11.46 (Cp*), 40.74 (Me-Ta), 122.81 (C$_{\mathrm{ipso}}$S), 123.69 (C$_{\mathrm{ipso}}$S), 124.62 (C$_{\mathrm{ipso}}$Cl^6), 124.81 (C$_{\mathrm{ipso}}$Cl^6), 125.50 (Cp*), 126.31 (C$_{\mathrm{ipso}}$Cl^4), 127.07 (C$_{\mathrm{ipso}}$Cl^4), 129.12 (ar), 130.70 (ar), 132.72 (ar), 132.84 (ar), 160.26 C$_{\mathrm{ipso}}$(O). ^{19}F NMR (C$_6$D$_6$, 293 K) δ −77.7. Anal. Calcd for C$_{24}$H$_{22}$Cl$_4$F$_3$O$_5$S$_2$Ta·C$_7$H$_8$ (926.44): C, 40.19; H, 3.26; S, 6.92 Found: C, 40.46; H, 2.99; S, 7.06.

[TaCp*(κ^3-tbop)(TfO)$_2$] (7). To a solution of [TaCp*Me$_2$(κ^3-tbop)] (**3**) (0.156 g, 0.19 mmol) in toluene (10 mL) was added 2 equiv of triflic acid (35 μL, 0.39 mmol), and the mixture was stirred for 12 h at room temperature. The toluene was removed under vacuum to give a yellow solid (0.099 g, 47%), which was identified as **7**.

^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.66 (s, 18H, 6CH$_3$ *t*-octyl), 1.09 (s, 6H, 2CH$_3$ *t*-octyl), 1.14 (s, 6H, 2CH$_3$ *t*-octyl), 1.52 (s, 4H, 2CH$_2$ *t*-octyl), 2.18 (s, 15H, Cp*), 6.44 (d, $^3J_{\mathrm{H-H}}$ = 8.60 Hz, 2H, ar), 7.02 (dd, $^3J_{H-H}$ = 8.60 Hz, $^4J_{\mathrm{H-H}}$ = 2.25 Hz, 2H, ar), 7.32 (d, $^4J_{\mathrm{H-H}}$ = 2.25 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 11.02 (Cp*), 31.17 (*C*Me$_3$ *t*-octyl), 31.86 (C*Me$_3$* *t*-octyl), 32.23 (br, C*Me$_2$* *t*-octyl), 38.33 (*C*Me$_2$ *t*-octyl), 56.88 (*C*H$_2$ *t*-octyl), 118.30 (Cp*), 125.41 (C$_{\mathrm{ipso}}$ S), 129.64 (ar), 129.88 (ar), 130.15(ar), 146.80 (C$_{\mathrm{ipso}}$ *t*-octyl), 163.04 (C$_{\mathrm{ipso}}$O). ^{19}F NMR (C$_6$D$_6$, 293 K) δ −76.7. Anal. Calcd for C$_{40}$H$_{55}$F$_6$O$_8$S$_3$Ta (1054.99): C, 45.54; H, 5.25; S, 9.12. Found: C, 45.58; H, 5.25; S, 9.25.

[TaCp*(κ^3-tbcp)(TfO)$_2$] (8). To a solution of [TaCp*Me$_2$(κ^3-tbcp)] (**4**) (0.167 g, 0.23 mmol) in toluene (10 mL) was added 2

Table 5. Crystal Data and Structure Refinement for 2, 3, 6, and 9

	2	3	6	9
molecular formula	$C_{22}H_{19}Cl_6O_2STa$	$C_{40}H_{58}O_2STa\cdot 0.5C_7H_8$	$C_{24}H_{22}Cl_4F_3O_5S_2Ta\cdot C_7H_8$	$C_{33}H_{34}Cl_4N_2Ta\cdot C_5H_{12}$
fw	741.08	829.01	926.44	903.57
temperature (K)	298(2)	180(2)	180(2)	180(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	11.657(1)	11.4237(9)	10.8183(6)	20.039(7)
b (Å)	10.922(1)	10.6823(8)	17.3283(9)	8.668(3)
c (Å)	19.804(3)	34.124(3)	36.413(2)	21.588(7)
β (deg)	97.305(2)	95.166(1)	92.806(1)	94.896(5)
volume (Å^3)	2500.9(6)	4147.3(6)	6817.9(6)	3736(2)
Z, density (calcd) (g/cm^3)	4, 1.968	4, 1.316	8, 1.805	4, 1.606
absorp coeff (mm^{-1})	5.139	2.732	3.716	3.318
F(000)	1432	1690	3648	1816
cryst size (mm^3)	0.37 × 0.26 × 0.06	0.32 × 0.30 × 0.25	0.34 × 0.23 × 0.14	0.97 × 0.25 × 0.10
index ranges	$-15 \le h \le 15$	$-14 \le h \le 14$	$-13 \le h \le 13$	$-21 \le h \le 20$
	$-14 \le k \le 12$	$-13 \le k \le 9$	$-17 \le k \le 21$	$-9 \le k \le 9$
	$-26 \le l \le 26$	$-42 \le l \le 42$	$-45 \le l \le 45$	$-23 \le l \le 23$
no. of reflns collected	15 016	29 147	46 550	18 630
no. of indep reflns	5912 [R(int) = 0.0477]	8463 [R(int) = 0.0717]	13 905 [R(int) = 0.0747]	4924 [R(int) = 0.0755]
no. of data/restraints/params	5912/0/294	8463/256/470	13 905/0/843	4924/0/435
goodness-of-fit on F^2	1.004	1.026	1.018	1.131
final R indices [$I > 2\sigma(I)$]	R1 = 0.0421	R1 = 0.0462	R1 = 0.0440	R1 = 0.0692
	wR2 = 0.0841	wR2 = 0.1060	wR2 = 0.0810	wR2 = 0.1744
largest diff peak and hole (e Å^{-3})	1.331, −1.477	0.416, −0.758	1.737, −0.931	3.279, −1.363

equiv of triflic acid (42.1 μL, 0.47 mmol), and the mixture was stirred for 12 h at room temperature. The toluene was removed under vacuum to give a yellow solid (0.197 g, 85%), which was identified as **8**.

^{1}H NMR (C_6D_6, 293 K): δ 2.32 (s, 15H, Cp*), 6.75 (d, $^4J_{H-H}$ = 2.41 Hz, 2H, ar), 6.77 (d, $^4J_{H-H}$ = 2.41 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ 11.69 (Cp*), 116.58 (Cp*), 122.91 (C_{ipso}S), 123.67 ($C_{ipso}Cl^6$), 125.94 ($C_{ipso}Cl^4$), 129.80 (ar), 133.10 (ar), 160.31 C_{ipso}(O). ^{19}F NMR (C_6D_6, 293 K): δ −76.7. Anal. Calcd for $C_{24}H_{19}Cl_4F_6O_8S_3Ta\cdot 3/4C_7H_8$ (1037.455): C, 33.35; H, 2.39; S, 9.13. Found: C, 33.04; H, 2.66; S, 9.25.

[TaCp*(κ^2-Me$_2$CNxylyl)(κ^3-tbcp)] (9). To a solution of [TaCp*Me$_2$(κ^3-tbcp)] (**4**) (0.315 g, 0.44 mmol) in toluene (10 mL) was added 1 equiv of xylyl-N≡C (0.059 g, 0.44 mmol). The mixture was stirred at 100 °C for 24 h, and the toluene was removed to give a white solid (0.347 g, 99%), which was characterized as **9**. Crystals of complex **9** that were suitable for X-ray diffraction were obtained by crystallization from toluene.

IR (PET-Nujol, ν, cm^{-1}): 1263 (m), 1118 (w), 1072 (m), 885 (m), 762 (m). ^{1}H NMR (C_6D_6, 293 K): δ 1.07 (s, 6H, *Me*C), 1.76 (s, 15H, Cp*), 2.28 (s, 6H, Me$_{xylyl}$), 6.94 (m, 3H, ar$_{xylyl}$), 7.03 (d, $^4J_{H-H}$ = 2.43 Hz, 2H, ar), 7.12 (d, $^4J_{H-H}$ = 2.43 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ 9.96 (Cp*), 20.59 (*Me*$_{xylyl}$), 25.59 (*Me*$_2$CN), 86.04 (*C*N), 118.72 (Cp*), 119.46 (C_{ipso}S), 122.87 (ar), 124.54 ($C_{ipso}Cl^6$), 126.13 (ar), 128.47 ($C_{ipso}Cl^4$), 128.75 (C_{ipso}N), 131.43 (ar), 135.76 (ar), 147.95 (C_{ipso}Me), 161.78 (C_{ipso}O). Anal. Calcd for $C_{33}H_{34}Cl_4NO_2STa$ (831.45): C, 47.67; H, 4.12; N, 1.68; S, 3.86. Found: C, 47.01; H, 4.07; N, 1.70; S, 3.94.

[TaCp*Me(κ^2-MeCN^{t}Bu)(κ^3-tbcp)] (10). To a solution of [TaCp*Me$_2$(κ^3-tbcp)] (**4**) (0.322 g, 0.46 mmol) in THF (10 mL) was added 1 equiv of ^{t}BuN≡C (52 μL, 0.46 mmol). The mixture was stirred at 65 °C for 96 h, and the THF was removed. The residue was washed with Et$_2$O (20 mL) to give a white solid (0.040 g, 11%), which was characterized as **10**.

IR (PET-Nujol, ν, cm^{-1}): 1572 (m), 1316 (m), 1261 (m), 1115 (w), 1072 (w) 753 (s). ^{1}H NMR (C_6D_6, 293 K): δ −0.02 (s, 3H, Ta-*Me*), 0.78 (s, 9H, ^{t}Bu), 1.88 (s, 15H, Cp*), 2.09 (s, 3H, MeCN), 6.80 (d, $^4J_{H-H}$ = 2.53 Hz, 2H, ar), 6.98 (d, $^4J_{H-H}$ = 2.53 Hz, 2H, ar). ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ 11.37 (Cp*), 17.93 (*Me*-Ta), 27.80 (*Me*CN), 29.07 (*Me*$_3$C), 61.18 (Me$_3$*C*), 116.95 (Cp*), 118.86 (C_{ipso}S), 119.35 (C_{ipso}S), 123.88 ($C_{ipso}Cl^6$), 125.28 ($C_{ipso}Cl^{6'}$), 125.86 ($C_{ipso}Cl^4$), 126.06 ($C_{ipso}Cl^4$), 129.19 (ar), 129.74 (ar), 131.42 (ar), 131.63 (ar), 164.53 (C_{ipso}O), 166.79 (C_{ipso}O), 236.59 (*C*N). Anal. Calcd for $C_{29}H_{34}Cl_4NO_2STa$ (783.41): C, 44.46; H, 4.37; N, 1.79; S, 4.09. Found: C, 43.84; H, 4.29; 1.83; S, 4.02.

Spectroscopic Characterization of [TaCp*(κ^2- Me$_2$CN^{t}Bu)(κ^3-tbcp)] (11). This complex was detected by NMR in the Et$_2$O fraction when complex **10** was purified.

^{1}H NMR (C_6D_6, 293 K): δ 0.68 (s, 9H, ^{t}Bu), 2.01 (s, 15H, Cp*), 2.63 (s, 6H, MeCN), 6.71 (m, 2H, ar), 7.02 (m, 2H, ar).

Crystal Structure Determination. A summary of crystal data collection and refinement parameters for all compounds is given in Table 5. Single crystals for **2**, **3**, **6**, and **9** were obtained by crystallization from saturated solutions in toluene. The single crystals were mounted on a glass fiber and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Data were integrated using SAINT,[21] and an absorption correction was performed with the program SADABS.[22] The software package SHELXTL version 6.10[23] was used for space group determination, structure solution, and refinement by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters except for compound **3**, which showed a high level of disorder in the orientation of the *tert*-octyl chains and the toluene solvent, and it was not possible to refine all non-hydrogen atoms with anisotropic thermal parameters.

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(21) *SAINT+* v7.12a, Area-Detector Integration Program; Bruker-Nonius AXS: Madison, WI, 2004.

(22) Sheldrick, G. M. *SADABS* version 2004/1, A Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, 2004.

(23) *SHELXTL-NT* version 6.12, Structure Determination Package; Bruker-Nonius AXS: Madison, WI, 2001.