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Synthesis and Reactivity of Monocyclopentadienyltantalum(V) Siloxide Complexes

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The new tantalum siloxide complex [TaCp*Me$_3$(OSiPh$_3$)] (**1**; Cp* = η^5-C$_5$Me$_5$) has been synthesized. The reaction of complex **1** with isocyanides yields the respective azatantalacyclopropanes [TaCp*(η^2-Me$_2$CNxylyl)Me(OSiPh$_3$)] (**2**; xylyl = 2,6-dimethylphenyl) and [TaCp*(η^2-Me$_2$CN*t*Bu)Me(OSiPh$_3$)] (**3**). The molecular structure of complex **2** has been established by X-ray diffraction. Complex **2** reacts with a second mol-equiv. of 2,6-xylyl isocyanide to yield [TaCp*(Nxylyl)-[N(xylyl)CMe=CMe$_2$)(OSiPh$_3$)] (**4**). The reaction of **1** with carbon monoxide gives [TaCp*(O)(OCMe=CMe$_2$)(OSiPh$_3$)] (**5**), whereas **1** reacts with B(C$_6$F$_5$)$_3$ to give the corresponding cationic compound [TaCp*Me$_2$(OSiPh$_3$)][MeB(C$_6$F$_5$)$_3$] (**6**).
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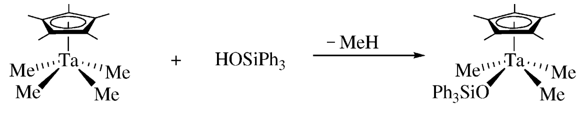
Introduction

Oxygen-donor Lewis bases such as alkoxides or aryloxides have been extensively used as versatile ligands for transition metals since the appropriate substitution patterns allow for an important modification of the steric and electronic requirements. More recently, siloxide groups have been widely used as ligands because well-defined and soluble metallasiloxanes[1,2] are analogous to the active centers in silica-grafted heterogeneous catalysts and therefore can be used to facilitate the understanding of the situation in solid materials or as precursors. These complexes are also precursors to metal oxides and silicates in sol-gel and related processes,[3] and have applications as catalysts in olefin polymerization[4] and olefin metathesis reactions,[5] amongst others. The heterogenization of well-defined homogeneous catalysts is a field of growing interest because it offers opportunities to combine the advantages of both supported and homogeneous catalysts.[6]

In spite of the growing interest in the chemistry of metal siloxide compounds only a few monocyclopentadienyltantalum complexes with siloxide ligands have been reported so far.[7] Herein we describe the synthesis of a tantalum siloxide derivative [TaCp*Me$_3$(OSiPh$_3$)] and its reactivity with unsaturated organic molecules and with B(C$_6$F$_5$)$_3$.

Results and Discussion

The tantalum derivative [TaCp*Me$_4$] reacts with 1 mol-equiv. of triphenylsilanol in toluene at room temperature to form the alkyltantalum siloxide complex **1** in a protonolysis process (Scheme 1). Complex **1** is an air-sensitive yellow solid that is soluble in the most commonly used aprotic organic solvents. It was characterized by the usual analytical and spectroscopic techniques.



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Scheme 1.

The ^{1}H NMR spectrum of **1** shows two singlets at δ = 0.66 and 0.72 ppm, which were assigned to the two methyl groups bonded to the tantalum center in the *trans* positions and to the methyl group *trans* to the siloxide moiety, respectively. The Cp* group gives rise to a singlet at δ = 1.61 ppm, whereas the aromatic protons appear as multiplets at δ = 7.15 and 7.80 ppm. The ^{13}C NMR spectrum indicates that the three phenyl groups bonded to the silicon atom are in the same chemical environment.

In order to test the reactivity of **1** we studied its behavior toward several unsaturated organic molecules. Migratory insertion of molecules such as carbon monoxide[8] or isocyanides[9] into alkyl–metal bonds, and the reactivity of the resulting acyl–metal and iminoacyl–metal functions,[10] are

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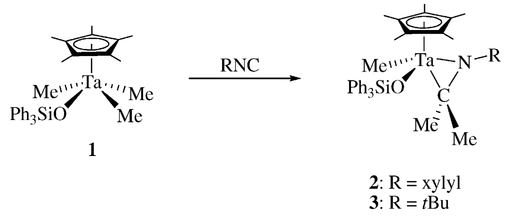
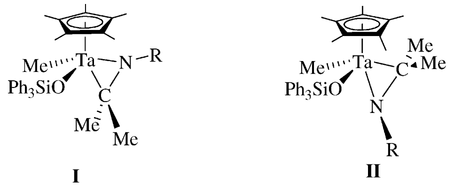
among the most important organometallic reactions, with many synthetic applications because of the C–C bond formation under mild reaction conditions. Complex **1** reacts readily with 1 equiv. of xylyl or *tert*-butyl isocyanide, at room temperature, to yield the corresponding azatantalacyclopropane complexes **2** and **3**, respectively (Scheme 2). Complex **2** was isolated as yellow crystals in 86% yield, whereas compound **3** was isolated with a yield of 74% as an orange microcrystalline compound. Both compounds were characterized by the usual analytical and spectroscopic techniques.



Scheme 2.

The spectroscopic data indicate that the structure of both derivatives is analogous. As an example, the ^{1}H NMR spectrum of **3** shows singlets at δ = 0.82, 1.28, and 1.73 ppm due to the methyl group bonded to the tantalum atom, to the *tert*-butyl moiety, and to the Cp* ligand, respectively. The inserted methyl groups give rise to two singlets at δ = 1.84 and 2.15 ppm, in agreement with their different chemical environments, whereas the aromatic proton signals appear at δ = 7.15 and 7.75 ppm. These data are in agreement with the coordination mode proposed in Scheme 2. The ^{13}C NMR spectrum shows a signal at δ = 64.5 ppm which we tentatively assign to the carbon atom of the imine ligand. This chemical shift is in agreement with that expected for an azametallacycle and is consistent with the values reported for early-d-block η^2-imine compounds.[11] These data indicate the selective adoption of either of the two geometries shown in Scheme 3.



Scheme 3.

A NOESY experiment was carried out to determine the orientation of the imine fragment. The response in the ^{1}H NOESY-1D experiment from the Cp* ligand upon irradiating the methyl groups of the xylyl or *tert*-butyl moieties indicates that orientation **I** is preferred in solution. The formation of **2** and **3** presumably takes place by a pathway involving an initial insertion of isocyanide into one Me–Ta bond to give the corresponding mono(η^2-iminoacyl) complex, followed by a second methyl migration to give an η^2-imine derivative.[12]

A single-crystal X-ray diffraction study of complex **2** was carried out in order to accurately define the bonding characteristics of the η^2-imine group. The molecular structure of complex **2** is depicted in Figure 1 and selected bond lengths and angles are listed in Table 1.

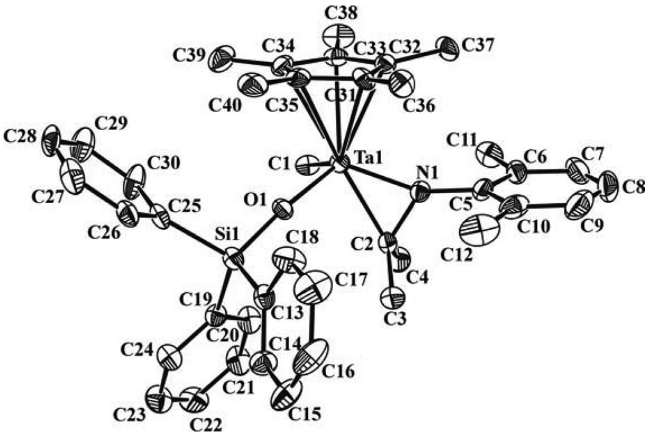


Figure 1. ORTEP diagram of [TaCp*(η^2-Me$_2$CNxylyl)Me(OSiPh$_3$)] (**2**).

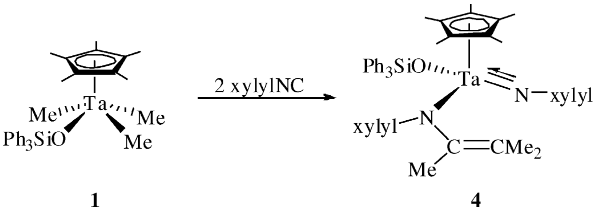
Table 1. Bond lengths [Å] and angles [°] for **2**.

Ta(1)–O(1)	1.919(5)	O(1)–Ta(1)–N(1)	117.9(3)
Ta(1)–N(1)	1.938(7)	O(1)–Ta(1)–C(1)	105.3(3)
Ta(1)–C(1)	2.171(8)	N(1)–Ta(1)–C(1)	105.5(3)
Ta(1)–C(2)	2.206(8)	O(1)–Ta(1)–C(2)	91.3(3)
Ta(1)–C(31)	2.446(7)	N(1)–Ta(1)–C(2)	40.7(3)
Ta(1)–C(32)	2.455(8)	C(1)–Ta(1)–C(2)	84.9(3)
Ta(1)–C(33)	2.485(8)	Si(1)–O(1)–Ta(1)	169.8(3)
Ta(1)–C(34)	2.540(8)	C(5)–N(1)–C(2)	124.6(7)
Ta(1)–C(35)	2.533(8)	C(5)–N(1)–Ta(1)	155.4(6)
N(1)–C(5)	1.42(1)	C(2)–N(1)–Ta(1)	79.5(5)
N(1)–C(2)	1.46(1)	N(1)–C(2)–C(4)	115.9(8)
C(2)–C(4)	1.51(1)	N(1)–C(2)–C(3)	114.0(8)
C(2)–C(3)	1.52(1)	C(4)–C(2)–C(3)	109.8(8)
		N(1)–C(2)–Ta(1)	59.8(4)
		C(4)–C(2)–Ta(1)	125.7(7)
		C(3)–C(2)–Ta(1)	121.1(7)

The molecular structure shows that complex **2** is a mononuclear compound in which the tantalum center is coordinated to the Cp* ligand, the siloxide moiety, a methyl group, and to the η^2-imine function, which is side-on bonded to the tantalum atom. It can also be seen that the CN vector of the imine group is oriented in such a way that the nitrogen atom points toward the Cp* ligand. Hence, isomer **I** (Scheme 3) is preferred in the solid state and, according to the NOESY experiments, also in solution.

The Ta(1)–C(2) bond [2.206(8) Å] is slightly longer than the Ta(1)–C(1) bond [2.171(8) Å] and is comparable to those found in [TaCp*Me$_2${η^2-Me$_2$CN(C$_6$H$_3$Me$_2$)}] [2.209(6) Å].[12] The value of the C(2)–N(1) bond length [1.463(10) Å] is within the range expected for a C–N single bond. The Ta(1)–O(1) distance [1.919(5) Å] is longer than that found in other electronically more unsaturated complexes such as [Ta{OSi(C$_6$H$_4$Me-2)$_3$}Cl$_4$·Et$_2$O] [1.812(3) Å].[13] The Si(1)–O(1)–Ta(1) angle [169.8(3)°] is somewhat smaller than that found in the above tantalum derivative [172.1(2)°], where the near linearity of the Ta–O–Si chain has been related to the presence of a significant O–Ta p_π-d_π interaction.

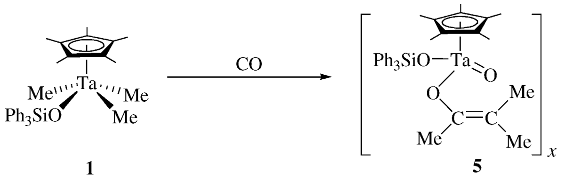
Complex **2** reacts with a second mol-equiv. of 2,6-xylyl isocyanide to give the alkenylamido complex [TaCp*(Nxylyl){N(xylyl)CMe=CMe_2}($OSiPh_3$)] (**4**), which was isolated in a 44% yield as a yellow microcrystalline solid (Scheme 4). The ^1H and ^{13}C NMR spectra of this complex indicate that seven different types of methyl groups are present in the molecule. Furthermore, the ^{13}C NMR spectrum shows signals at δ = 115.1 and 133.8 ppm due to the olefinic carbon atoms, in agreement with the formation of an alkenylamido moiety.[14]



Scheme 4.

Complex **4** can also be obtained by treatment of **1** with 2 mol-equiv. of 2,6-xylyl isocyanide (Scheme 4). In contrast to the reactivity observed for complex **2**, complex **3** does not react with an excess of *t*BuNC under the same experimental conditions.

Complex **1** also reacts readily with an excess of CO at room temperature to give the (alkenylalkoxido)(oxido) complex [TaCp*(O)(OCMe=CMe_2)($OSiPh_3$)] (**5**; Scheme 5), which was isolated in 51% yield as a yellow crystalline solid. Its ^1H NMR spectrum shows four singlets at δ = 1.52, 1.60, 1.83, and 2.03 ppm, in a 1:1:1:5 ratio, which were assigned to the three different methyl groups of the coordinated alkenylalkoxido and to the Cp* ligand. The aromatic proton signals of the siloxide group appear at δ = 7.35 and 7.65 ppm. The ^{13}C NMR spectrum of **5** shows signals at δ = 107.5 and 146.5 ppm for the olefinic carbon atoms of the OC(Me)=CMe_2 group. These spectroscopic data are in agreement with the structure proposed in Scheme 5.[15] However, the IR spectrum of compound **5** does not show strong absorptions between 1000 and 700 cm^{-1} which could be assigned to a Ta=O stretching frequency, therefore **5** is not a discrete monomer but an oligomer containing Ta–O–Ta bonds.

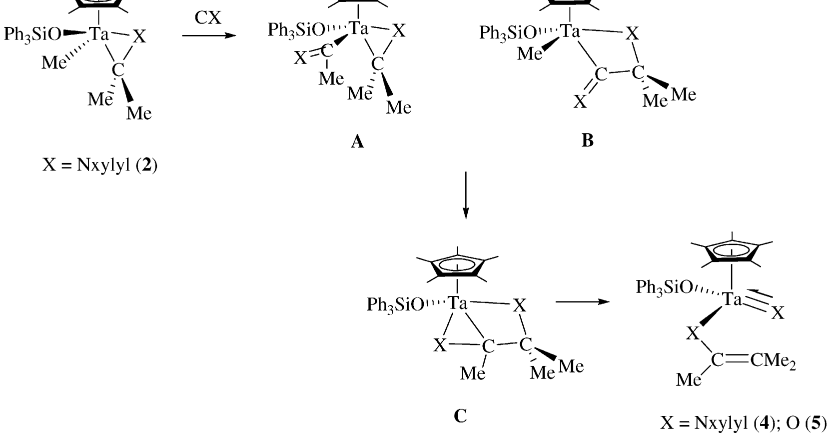


Scheme 5.

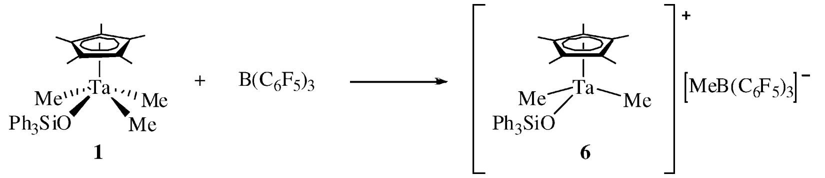
Complexes **4** and **5** are probably formed through a mechanism analogous to that proposed previously for (alkenylamido)- or (alkenylalkoxido)tantalum derivatives[14,15] (Scheme 6). Thus, insertion of a second mol-equiv. of CO or isocyanide into either the Me–Ta bond or the tantalacycle carbon bond of the (ketone)- or (imine)-tantalum complex, respectively, would yield intermediates **A** or **B**. Both intermediates would furnish intermediate **C**, which then forms derivatives **4** or **5**.

The synthesis of stable cationic alkyl complexes of the early transition metals is an objective of prime importance in organometallic chemistry as these compounds are active in many catalytic processes.[16] Thus, addition of 1 equiv. of $B(C_6F_5)_3$ to a toluene solution of compound **1** affords an insoluble brownish oil which was characterized as the ionic derivative [$TaCp^*Me_2(OSiPh_3)$][$MeB(C_6F_5)_3$] (**6**) (Scheme 7). Compound **6** is soluble in dichloromethane and $CDCl_3$ and is highly unstable in the presence of traces of water.

The ^1H and ^{13}C NMR spectra of compound **6** in $CDCl_3$ show one resonance for the two equivalent Me–Ta groups of a pseudo-tetrahedral cation. A broad signal for the methyl group of the borate anion was also observed in the ^1H NMR spectrum. The resonances in the ^{19}F NMR spectrum are in agreement with the formation of the



Scheme 6.



Scheme 7.

$[MeB(C_6F_5)_3]$ anion, the difference between the *m*- and *p*-C_6F_5 values ($\Delta\delta$ = 2.5 ppm) being consistent with the presence of separate cationic and anionic $[MeB(C_6F_5)_3]^-$ moieties.[17]

Conclusions

We have reported the synthesis of several monocyclopentadienyl complexes of tantalum containing a siloxide group as an ancillary ligand and have studied their reactivity with several unsaturated organic molecules such as isocyanides or carbon monoxide. We have also explored the synthesis of cationic alkyl derivatives.

Experimental Section

General Procedures: The preparation and handling of the described compounds was performed with rigorous exclusion of air and moisture under nitrogen using standard vacuum-line and Schlenk techniques. All solvents were dried and distilled under nitrogen. The following reagents were prepared according to literature procedures: $[TaCp^*Cl_4]$,[18] $[TaCp^*Me_4]$.[19] The commercially available compounds xylyl isocyanide and *tert*-butyl isocyanide were used as received from Aldrich. ^1H and ^{13}C NMR spectra were recorded with a 200 Mercury Varian Fourier Transform spectrometer. Trace amounts of protonated solvents were used as reference, and chemical shifts are reported in units of ppm relative to $SiMe_4$. IR spectra were recorded in the region 4000–400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer as Nujol mulls using PET cells or KBr pellets.

Synthesis of $[TaCp^*Me_3(OSiPh_3)]$ (1): Toluene (10 mL) was added to a mixture of $[TaCp^*Me_4]$ (0.753 g, 2.0 mmol) and $HOSiPh_3$ (0.553 g, 2.0 mmol) and the mixture stirred at room temperature for 3 h. The solution was then filtered and the solvent evaporated under vacuum. The residue was washed with cool pentane to afford **1** as a yellow solid (yield 1.02 g, 80%). IR (Nujol/PET): $\tilde{\nu}$ = 1589 (w), 1428 (s), 1113 (s), 1001 (m), 952 (s), 931 (s), 705 (s), 651 (w), 584 (w), 513 (m) cm^{-1}. ^1H NMR (C_6D_6, room temp.): δ = 0.66 (s, 6 H, Ta-*Me*), 0.72 (s, 3 H, Ta-*Me*), 1.61 (s, 15 H, Cp*), 7.15 (m, 9 H, Ar), 7.80 (m, 6 H, Ar) ppm. $^{13}C\{^1H\}$ NMR: δ = 11.0 (Cp*), 55.1 (Ta-*Me*), 56.5 (Ta-*Me*), 116.8 (Cp*), 128.1 (Ph), 130.1 (Ph), 135.8 (Ph), 136.2 (Ph_{ipso}) ppm. $C_{31}H_{39}OSiTa$ (636.71): calcd. C 58.48, H 6.16; found C 58.00, H 6.07.

Synthesis of $[TaCp^*(\eta^2\text{-}Me_2CNxylyl)Me(OSiPh_3)]$ (2): Toluene (15 mL) was added to a mixture of $[TaCp^*Me_3(OSiPh_3)]$ (0.290 g, 0.455 mmol) and xylylN≡C (0.059 g, 0.455 mmol) and the solution stirred at room temperature for 15 min. The solvent was then evaporated under vacuum and the residue extracted with pentane. The solution was cooled to –30 °C to yield **2** as yellow crystals (yield 0.301 g, 86%). IR (KBr): $\tilde{\nu}$ = 1589 (w), 1465 (m), 1428 (s), 1374 (w), 1115 (s), 1004 (m), 991 (m), 945 (s), 920 (s), 865 (m), 763 (m), 700 (s), 591 (w), 512 (s) cm^{-1}. ^1H NMR (C_6D_6, room temp.): δ = 0.96 (s, 3 H, Ta-*Me*), 1.49 (s, 3 H, C*Me*$_2$), 1.61 (s, 15 H, Cp*), 1.98 (s, 6 H, 2,6-*Me*$_2C_6H_3$), 2.07 (s, 3 H, C*Me*$_2$), 6.86 (m, 3 H, Ar), 7.14 (m, 9 H, Ar), 7.80 (m, 6 H, Ar) ppm. $^{13}C\{^1H\}$ NMR: δ = 10.7 (Cp*), 20.9 (2,6-*Me*$_2C_6H_3$), 27.6 (C*Me*$_2$), 29.8 (C*Me*$_2$), 39.4 (Ta-*Me*), 78.6 (*C*Me$_2$) 117.4 (Cp*), 124.0 (Ar), 127.9 (Ar), 128.6 (Ar), 129.9 (Ar), 134.3 (Ar_{ipso}), 136.0 (Ar), 137.2 (Ar_{ipso}), 151.3 (Ar_{ipso}) ppm. $C_{40}H_{48}NOSiTa$ (767.89): calcd. C 62.57, H 6.29, N 1.82; found C 62.09, H 6.49, N 1.66.

Synthesis of $[TaCp^*(\eta^2\text{-}Me_2CN\textit{t}Bu)Me(OSiPh_3)]$ (3): *t*BuN≡C (54.88 µL, 0.485 mmol) was added to a solution of $[TaCp^*Me_3(OSiPh_3)]$ (0.309 g, 0.485 mmol) in toluene (15 mL). After 15 min at room temperature, the solution became orange. The mixture was filtered and the solvent evaporated to dryness. The residue was extracted with pentane and the solution cooled to –30 °C to give **3** as an orange microcrystalline solid (yield 0.259 g, 74%). IR (KBr): $\tilde{\nu}$ = 1588 (w), 1428 (s), 1354 (m), 1249 (m), 1201 (m), 1113 (s), 1045 (w), 1030 (w), 957 (s), 940 (s), 709 (s), 535 (m), 508 (s), 411 (w) cm^{-1}. ^1H NMR (C_6D_6, room temp.): δ = 0.82 (s, 3 H, Ta-*Me*), 1.28 (s, 9 H, NC*Me*$_3$), 1.73 (s, 15 H, Cp*), 1.84 (s, 3 H, C*Me*$_2$), 2.15 (s, 3 H, C*Me*$_2$), 7.15 (m, 9 H, Ar), 7.75 (m, 6 H, Ar) ppm. $^{13}C\{^1H\}$ NMR: δ = 11.7 (Cp*), 31.7 (C*Me*$_2$), 32.3 (C*Me*$_2$), 32.7 (NC*Me*$_3$), 34.3 (Ta-*Me*), 61.9 (*C*Me$_2$), 64.5 (N*C*Me$_3$), 116.5 (Cp*), 127.8 (Ar), 129.9 (Ar), 135.9 (Ar), 136.9 (Ar_{ipso}) ppm. $C_{36}H_{48}NOSiTa$ (719.46): calcd. C 60.07, H 6.71, N 1.94; found C 59.52, H 6.70, N 2.00.

Synthesis of $[TaCp^*(Nxylyl)\{N(xylyl)CMe{=}CMe_2\}(OSiPh_3)]$ (R = 2,6-$Me_2C_6H_3$) (4): xylylN≡C (0.083 g, 0.634 mmol) was added to a toluene (15 mL) solution of $[TaCp^*Me_3(OSiPh_3)]$ (0.202 g, 0.32 mmol) and the solution stirred at room temperature for 1 h. Slow diffusion of pentane into the toluene solution yielded **4** as a yellow microcrystalline solid (yield 0.124 g, 44%). IR (KBr): $\tilde{\nu}$ = 1670 (w), 1589 (w), 1456 (m), 1427 (s), 1376 (w), 1308 (s), 1254 (w), 1188 (w), 1168 (w), 1138 (m), 1004 (s), 929 (s), 919 (s), 868 (m), 762 (m), 743 (m), 703 (s), 531 (w), 514 (s), 500 (s) cm^{-1}. ^1H NMR (C_6D_6, room temp.): δ = 1.65 [s, 3 H, C(Me)=C*Me*$_2$], 1.69 [s, 3 H, C(Me)=C*Me*$_2$], 1.81 (s, 15 H, Cp*), 1.96 [s, 3 H, C(*Me*)=CMe$_2$], 2.13 (s, 9 H, 2,6-*Me*$_2C_6H_3$), 2.36 (s, 3 H, 2,6-*Me*$_2C_6H_3$), 6.57 (m, 6 H, Ar), 7.13 (m, 9 H, Ar), 7.79 (m, 6 H, Ar) ppm. $^{13}C\{^1H\}$ NMR: δ = 12.1 (Cp*), 20.4 (2,6-*Me*$_2C_6H_3$), 21.4 (2,6-*Me*$_2C_6H_3$), 21.7 (2,6-*Me*$_2C_6H_3$), 22.2 [C(Me)=C*Me*$_2$], 22.9 [C(Me)=C*Me*$_2$], 23.8 [C(*Me*)=CMe$_2$], 115.1 [C(Me)=*C*Me$_2$], 120.1 (Cp*), 122.4 (Ar), 123.6 (Ar), 125.6 (Ar), 127.2 (Ar), 127.7 (Ar), 129.2 (Ar), 129.6 (Ar), 133.8 [*C*(Me)=CMe$_2$],134.6 (Ar_{ipso}), 135.0 (Ar_{ipso}), 136.6 (Ar), 138.2 (Ar_{ipso}), 152.7 (Ar_{ipso}), 155.6 (Ar_{ipso}) ppm. $C_{49}H_{57}N_2OSiTa$ (899.07): calcd. C 65.46, H 6.38, N 3.11; found C 65.26, H 6.34, N 3.20.

Synthesis of $[TaCp^*(O)(OCMe{=}CMe_2)(OSiPh_3)]$ (5): A toluene (15 mL) solution of $[TaCp^*Me_3(OSiPh_3)]$ (0.189 g, 0.296 mmol) was placed in a Schlenk tube under CO. The reaction mixture was left at room temperature for 24 h to yield yellow crystals of complex **5** (yield 0.140 g, 51%). IR (Nujol/PET): $\tilde{\nu}$ = 1658 (m), 1261 (m), 1200 (s), 1112 (m), 1001 (w), 937 (s), 651 (m), 584 (m), 517 (s) cm^{-1}. ^1H NMR ($CDCl_3$, room temp.): δ = 1.52 [s, 3 H, OC(Me)=C*Me*$_2$], 1.60 [s, 3 H, OC(Me)=C*Me*$_2$], 1.83 [s, 3 H, OC-(*Me*)=CMe$_2$], 2.03 (s, 15 H, Cp*), 7.35 (m, 9 H, Ar), 7.65 (m, 6 H, Ar) ppm. ^{13}C{^{1}H} NMR: δ = 10.8 (Cp*), 16.6 [OC(Me)=C*Me*$_2$], 17.3 [OC(Me)=C*Me*$_2$], 19.2 [OC(*Me*)=CMe$_2$], 107.5 [OC(Me)=*C*Me$_2$], 119.7 (Cp*), 127.9 (Ar), 129.9 (Ar), 135.4 (Ar), 136.5 (Ar$_{ipso}$), 146.5 [O*C*(Me)=CMe$_2$] ppm. $C_{33}H_{39}O_3SiTa\cdot 0.7C_7H_8$ (757.23): calcd. C 60.12, H 5.93; found C 60.24, H 5.84.

Synthesis of [TaCp*Me$_2$(OSiPh$_3$)][MeB(C$_6$F$_5$)$_3$] (6): A solution of B(C$_6$F$_5$)$_3$ (0.075g, 0.147 mmol) in toluene (10 mL) was added to a solution of [TaCp*Me$_3$(OSiPh$_3$)] (0.94g, 0.147 mmol) in toluene (15 mL) at room temperature. The oil formed after 5 min was separated from the solution and characterized as complex **6** (yield 0.112 g, 67%). ^{1}H NMR (CDCl$_3$, room temp.): δ = 0.34 (br. s, 3 H, *Me*B), 0.90 (s, 6 H, Ta-*Me*), 1.89 (s, 15 H, Cp*), 7.43 (m, 15 H, Ar) ppm. ^{13}C{^{1}H} NMR: δ = 11.7 (B-*Me*), 11.82 (Cp*), 77.7 (Ta-Me), 126.8 (Cp*), 129.6 (Ar), 131.4 (Ar), 132.8 (Ar), 135.5 (Ar$_{ipso}$) ppm. ^{19}F NMR: δ = –132.6 (m, 6 F), –164.8 (m, 3 F), –167.3 (m, 6 F) ppm.

X-ray Structure Determination for 2: Crystals of **2** were obtained from pentane. Data were collected with a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å). The crystal data, data collection, structural solution, and refinement parameters are summarized in Table 2. Data were integrated using SAINT[20] and an absorption correction was performed with the program SADABS.[21] The structure was solved by direct methods using SHELXTL,[22] and refined by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. The large residual electron density is probably due to the poor quality of the crystals. CCDC-673906 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement for **2**.

Empirical formula	$C_{40}H_{48}NOSiTa$
Formula mass	767.83
Temperature [K]	180(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	9.6650(5)
b [Å]	12.8440(7)
c [Å]	16.5020(9)
α [°]	67.348(3)
β [°]	86.194(3)
γ [°]	68.956(3)
Volume [Å^3]	1758.2(2)
Z	2
Density (calculated) [g cm^{-3}]	1.450
Absorption coefficient [mm^{-1}]	3.191
F(000)	780
Crystal size [mm]	0.14 × 0.11 × 0.09
θ range for data collection [°]	1.34–26.45
Index ranges	$-12 \le h \le 11$ $-16 \le k \le 16$ $-20 \le l \le 20$
Reflections collected	23496
Independent reflections	7212 [*R*(int) = 0.1092]
Data/restraints/parameters	7212/0/407
Goodness-of-fit on F^2	0.963
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0579$, $wR_2 = 0.1107$
Largest diff. peak/hole	2.149/–1.234

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