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η^2-Iminoacyl and η^2-Acyl Monocyclopentadienyl Tantalum Complexes Bearing Oxo and Oxo-Borane Ligands

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Dedicated to J. Antonio Abad, an excellent scientist and friend

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Alkyl-chloro ligand exchange by the reaction of [TaCp'R_2{O·B(C_6F_5)$_3$}] (R = CH_2Ph, Me) with Ph_3CCl gave the monoalkyl compounds [TaCp'RCl{O·B(C_6F_5)$_3$}] (R = CH_2Ph, Me). Insertion of CNAr (Ar = 2,6-$Me_2C_6H_3$) and CO into a Ta–C bond of the mono- and dialkyl complexes gave the iminoacyl compounds [TaCp'X{η^2-C(R)=NAr}{O·B(C_6F_5)$_3$}] (X = R = CH_2Ph, Me; X = Cl, R = CH_2Ph) and the acyl compounds [TaCp'X{η^2-C(R)=O}{O·B(C_6F_5)$_3$}] (X = R = CH_2Ph, Me; X = Cl, R = CH_2Ph), respectively. The related chloro compound [TaCp'Cl{η^2-C(Me)=NAr}{O·B(C_6F_5)$_3$}] was isolated from the reaction of the oxo derivative [TaCp'Cl{η^2-C(Me)=NAr}(O)] with the Lewis acid B(C_6F_5)$_3$. Addition of CNAr or pyridine to [TaCp'(CH_2Ph){η^2-C(CH_2Ph)=NAr}{O·B(C_6F_5)$_3$}] afforded the borane-free complex [TaCp'(CH_2Ph){η^2-C(CH_2Ph)=NAr}(O)] and the acid-base adduct L·B(C_6F_5)$_3$ (L = py, CNAr). The molecular structures of [TaCp'Cl{η^2-C(Me)=NAr}{O·B(C_6F_5)$_3$}] and [TaCp'(CH_2Ph){η^2-C(CH_2Ph)=O}{O·B(C_6F_5)$_3$}] were obtained from X-ray diffraction studies.

Introduction

The formation of C–C bonds through insertion of isocyanides (CNR) and carbon monoxide (CO) into M–C bonds is well-documented, and this reaction initially affords iminoacyl and acyl complexes, respectively.[1] For a given metal atom, the stability and further evolution of these compounds are determined by the nature of the ancillary ligands. Many reaction pathways may follow to give a broad variety of products:[1] (a) migratory insertion of a second alkyl or aryl group to give η^2-imine or η^2-ketene complexes;[2–5] (b) intra- or intermolecular coupling of iminoacyl or acyl units affording diaza- or dioxobutene complexes;[6,7] (c) transfer of the NR or O moieties to the metal centre;[8–11] (d) insertion of a second CNR[12–16] or CO[17] molecule into the new M–C bond formed after the first insertion process and (e) hydrogen migration.[18,19]

We reported the results of our studies on the insertion reactions of CNR into the Ta–C(methyl) bond of monocyclopentadienyl complexes of the type [TaCp*Cl_xMe_{4-x}][8–10] for which processes (a) and (c) were observed. Similar reactions with imido compounds of the type [TaCp*MeX(N*t*Bu)] (X = Cl, Me, OR, NH*t*Bu) gave the imine-η^2-iminoacyl derivatives [TaCp*(N*t*Bu)X{η^2-C[C(Me)=NR]=NR}].[20] With regard to the CO insertion reactions, double migration of the alkyl group [process (a)] was observed for [TaCp*Cl_2Me_2],[10] whereas the coupling of the acyl groups [process (b)] occurred for [TaCp*Me_2(NR)] (R = 2,6-$Me_2C_6H_3$) to give the dinuclear compound [TaCp*(NR)Me]$_2${μ-η^2-OC(Me)=C(Me)O},[10] and ligand exchange [process (c)] for complexes [TaCp*ClMe(NR)] (R = 2,6-$Me_2C_6H_3$,[10] *t*Bu)[11] led to the oxo compounds [TaCp*Cl(O){η^2-C(Me)=NR}]. Furthermore, the η^2-(methyl)acyl complexes remained elusive and were only detected as intermediates by NMR spectroscopy, whereas the related η^2-iminoacyl complexes are stable.

It was observed that for monocyclopentadienyl imido tantalum derivatives addition of a second CNR molecule into the iminoacyl compounds [TaCp*(NR)X{η^2-C(Me)=NR}] (R = 2,6-$Me_2C_6H_3$, *t*Bu; X = Cl, Me) resulted in differing behaviours depending on the R group of the imido ligand. No reaction was found for R = 2,6-$Me_2C_6H_3$,[10] whereas a second insertion occurred for R = *t*Bu.[20] Conversely, the imido complexes [TaCp*MeX(NR)] (R = 2,6-$Me_2C_6H_3$, *t*Bu; X = Cl, Me) reacted with CO to give the dinuclear compound [TaCp*(NR)Me]$_2${μ-η^2-OC(Me)=C(Me)O} for X = Me[10] and one of the few mononuclear derivatives [TaCp*Cl(O){η^2-C(Me)=NR}] containing a terminal tantalum-oxo double bond for X = Cl.[10,11]

The versatility and potential applications of all these results determined by the R and X substituents of the imido

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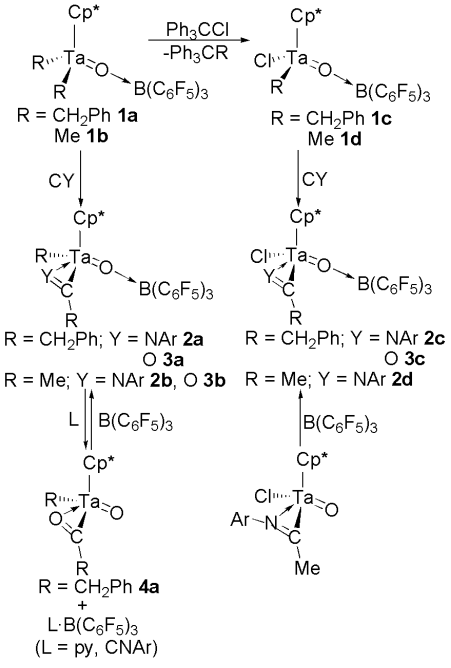
complexes [TaCp*MeX(NR)] led us to extend our studies to similar insertion reactions of CNR and CO into the Ta–alkyl bonds of the related oxo-borane compounds [TaCp*X_2{O·B(C_6F_5)$_3$}] that have recently been isolated.[21]

Results and Discussion

The monoalkyl oxo-borane compounds [TaCp*RCl{O·B(C_6F_5)$_3$}] (R = CH_2Ph **1c**, Me **1d**) were synthesised by an alkyl-chloro metathesis reaction of [TaCp*R_2{O·B(C_6F_5)$_3$}] (R = CH_2Ph **1a**, Me **1b**) with one equiv. of Ph_3CCl as chlorinating agent (Scheme 1). The reaction for **1c** proceeded smoothly at room temperature to give a pale yellow solid in good yield, whereas complex **1d** could not be isolated in the solid state. The formation of **1d** was demonstrated on a small scale by ^{1}H NMR spectroscopy with a C_6D_6 solution of **1b** that was treated with Ph_3CCl and heated to 40 °C. All attempts made to obtain the monomethyl complex through alkylation of [TaCp*Cl_2{O·B(C_6F_5)$_3$}] and redistribution reactions between [TaCp*Cl_2{O·B(C_6F_5)$_3$}] and [TaCp*Me_2{O·B(C_6F_5)$_3$}] failed. The ^{11}B and ^{19}F NMR spectra of complexes **1c** and **1d** are consistent with the presence of a tetracoordinate boron atom,[21–31] and the ^{1}H NMR spectra with the monosubstitution of only one of the alkyl ligands.



Scheme 1.

The alkyl complexes [TaCp*R_2{O·B(C_6F_5)$_3$}] (R = CH_2Ph **1a**, Me **1b**) and [TaCp*(CH_2Ph)Cl{O·B(C_6F_5)$_3$}] (**1c**) immediately reacted at room temperature with one equiv. of the isocyanide CNAr (Ar = 2,6-$Me_2C_6H_3$) to give the corresponding η^2-iminoacyl compounds [TaCp*X{η^2-C(R)=NAr}{O·B(C_6F_5)$_3$}] (X = R = CH_2Ph **2a**, Me **2b**; X = Cl, R = CH_2Ph **2c**) in high yields by insertion of the isocyanide ligand into a Ta–C bond (Scheme 1). These pale yellow complexes are air and thermally stable in solution. The ^{13}C NMR resonance at ca. δ = 240 ppm is the most apparent spectroscopic feature and confirms the presence of the η^2-iminoacyl ligand in complexes **2**.

We previously reported[10] on the isolation of the related oxo complex [TaCp*Cl{η^2-C(Me)=NAr}(O)] from the reaction of the monomethyl compound [TaCp*ClMe(NAr)] with CO through a process that involved insertion of CO into the Ta–Me bond and further rearrangement of the η^2-acyl intermediate with intramolecular oxo-imido exchange. Since the starting oxo-borane chloro-methyl complex could not be isolated, thus preventing access to the oxo-borane compound [TaCp*Cl{η^2-C(Me)=NAr}{O·B(C_6F_5)$_3$}] (**2d**) by insertion of CNAr into the Ta–C bond of the corresponding alkyl-chloro compound, we tried to obtain this compound by an alternative route. With this aim, we investigated the reaction of the oxo iminoacyl compound [TaCp*Cl{η^2-C(Me)=NAr}(O)] with B(C_6F_5)$_3$, which afforded **2d** in high yield. The formation of **2d** was confirmed by ^{13}C and ^{19}F NMR spectroscopy. The ^{13}C NMR spectrum shows the resonance corresponding to the C_{sp^2} atom of the η^2-iminoacyl ligand (δ = 240.1 ppm) to be slightly low-field shifted with respect to that of the starting compound [TaCp*Cl{η^2-C(Me)=NAr}(O)] (δ = 236.8 ppm). An analogous behaviour was observed in the ^{1}H NMR spectrum for the methyl-iminoacyl group, which was shifted from δ = 2.65 ppm in [TaCp*Cl{η^2-C(Me)=NAr}(O)] to δ = 2.94 ppm in **2d**.

The molecular structure of compound [TaCp*Cl{η^2-C(Me)=NAr}{O·B(C_6F_5)$_3$}] (Ar = 2,6-$Me_2C_6H_3$) (**2d**) was obtained by X-ray diffraction studies. Figure 1 depicts an ORTEP drawing of **2d** with selected bond lengths and angles. Compound **2d** exhibits the typical geometry known for group 5 half-sandwich iminoacyl compounds with a tetrahedral coordination environment around the tantalum atom. Considering the centroid of the Cp* ring and the midpoint of the C(10)–N bond as coordination sites, the other two positions are occupied by the chloro and oxo ligands. The N atom of the η^2-iminoacyl group is located in a *trans* position with respect to the oxo ligand, as in analogous half-sandwich imido complexes and in [TaCp*Cl{η^2-C(Me)=NAr}(O)]. Furthermore, the oxygen atom is attached to the boron atom of the B(C_6F_5)$_3$ group.

All the values of the bond lengths and angles of compound **2d** are very close to the corresponding bond lengths and angles found for the parent compound [TaCp*Cl{η^2-C(Me)=NAr}(O)][10] except for the Ta–O bond, which is longer in [TaCp*Cl{η^2-C(Me)=NAr}(O)] [1.731(7) Å] than in **2d** [1.809(5) Å] as a consequence of the coordination of the oxygen atom to the B(C_6F_5)$_3$ ligand.[21,23–28,30,31] The linear Ta–O–B angle [174.4(6)°] and the B–O bond length [1.52(1) Å] are typical of oxo-borane compounds.[21–31] The Ta–O bond in **2d** is longer than that in the oxo-borane compound [TaCp*Cl_2{O·B(C_6F_5)$_3$}][21] [1.784(2) Å]. This bond length is similar to the lower end of the range of Ta–O bond lengths for compounds with Ta–O–Ta bridges (1.82–2.10 Å)[32–35] and with terminal Ta–OH bonds (1.85–1.97 Å).[36–38] However, the single bond Ta–O distances are ca. 2.18 Å,

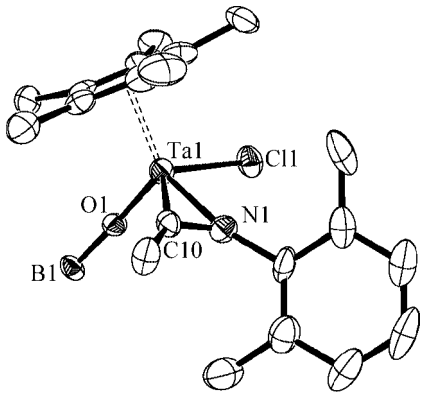


Figure 1. ORTEP diagram of the X-ray structure of compound **2d**. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms and C_6F_5 groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ta–O 1.809(5), Ta–N 2.127(7), Ta–C(10) 2.120(9), Ta–Cl 2.392(2), B–O 1.525(11), N–C(10) 1.26(1), N–Ta–C(10) 34.5(3), C(10)–N–Ta 72.4(5), N–C(10)–Ta 73.1(5), B–O–Ta 174.4(6).

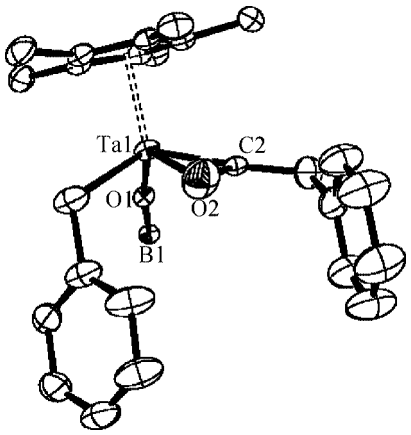


Figure 2. ORTEP diagram of the X-ray structure of compound **3a**. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms and C_6F_5 groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ta–O(1) 1.816(2), Ta–O(2) 2.110(3), Ta–C(1) 2.229(4), Ta–C(2) 2.011(3), B–O(1) 1.512(4), O(2)–C(2) 1.209(4), O(2)–Ta–C(2) 34.02(12), C(2)–O(2)–Ta 68.5(2), O(2)–C(2)–Ta 77.5(2), B–O(1)–Ta 173.02(19).

and thus a bond order of two should be considered for the Ta–O bond in **2d**.

The reaction of the dialkyl [TaCp*R_2{O·B(C_6F_5)$_3$}] (R = CH_2Ph **1a**, Me **1b**) and the monobenzyl [TaCp*(CH_2Ph)Cl{O·B(C_6F_5)$_3$}] (**1c**) complexes with CO in toluene gave the η²-acyl compounds [TaCp*X{η²-C(R)=O}{O·B(C_6F_5)$_3$}] (X = R = CH_2Ph **3a**, Me **3b**; X = Cl, R = CH_2Ph **3c**) after ca. 24 h at room temperature in moderate yields (Scheme 1). These pale yellow compounds were air and thermally stable below 120 °C for several hours. The ^{13}C NMR spectra showed a resonance at ca. δ = 305 ppm corresponding to the C_{sp^2} atom of the η²-acyl fragment. The slowness of the insertion reactions of CO is in contrast with the rapid transformations observed for complexes **1** with isocyanide and the behaviour observed[10,11] for the reactions of the imido compounds [TaCp*MeX(NR)] (R = 2,6-$Me_2C_6H_3$, *t*Bu; X = Cl, Me) with CO. This difference may be attributed to the lower oxophilicity of the tantalum atom in compounds **1** that is caused by the presence of the oxo ligand.

The X-ray structure of compound **3a** is shown in Figure 2. The environment around the Ta atom is analogous to that described for compound **2d** (see above) with the oxygen atom of the acyl group located *trans* to the oxo-borane ligand, as expected. The Ta–O(1) bond length of 1.816(2) Å is similar to that observed for compound **2d**, and the O(1)–B bond length [1.512(4) Å] and Ta–O(1)–B angle [173.0(2)°] have values that are normally seen for these types of compounds.[21–31]

The whole set of angles and bond lengths of the [Ta-(η²-acyl)] group is in line with compounds of this type[1] and is similar to those found in the other two tantalum-acyl complexes for which X-ray structures are known, [TaCp*Me{η²-C(CH_2CMe_2Ph)=O}{N(2,6-$Me_2C_6H_3$)}][39] and [TaCp*Cl_3{η²-C(CH_2CMe_3)=O}].[40] However, in the particular case of the isostructural imido derivative [TaCp*Me{η²-C(CH_2CMe_2Ph)=O}{N(2,6-$Me_2C_6H_3$)}], the Ta–O bond [2.21(1) Å] is slightly longer than the corresponding bond in compound **3a** [2.110(3) Å], because of the different *trans* effect and higher donor capacity of the imido ligand.

The insertion of a second CNAr or CO molecule into these new acyl and iminoacyl oxo-borane complexes was not observed, in contrast with the behaviour observed for the analogous *tert*-butyl imido complexes.[20] Rather, all complexes **2**–**3** released the acid-base adduct L·B(C_6F_5)$_3$ (L = py, CNAr) in the presence of donor ligands such as isocyanide or pyridine.[41] Only in the case of compound **2a** were we able to isolate the borane-free 18-electron compound [TaCp*(CH_2Ph){η²-C(CH_2Ph)=NAr}(O)] (**4a**), with a terminal oxo-tantalum bond. The remaining oxo-borane complexes decomposed under similar conditions. The ^{13}C NMR spectrum of the new oxo iminoacyl compound **4a** showed the η²-iminoacyl C_{sp^2} resonance at δ = 240.3 ppm. A comparison of this ^{13}C resonance and that assigned to the CH_2–iminoacyl group in the ^{1}H NMR spectrum with the corresponding resonances in the parent compound **2a**, showed a behaviour that is opposite to that observed for **2d** and [TaCp*Cl{η²-C(Me)=NAr}(O)].

Conclusions

The dialkyl oxo-borane compounds [TaCp*R_2{O·B(C_6F_5)$_3$}] can be transformed into the monoalkyl derivatives [TaCp*RX{O·B(C_6F_5)$_3$}] by alkyl-chloro exchange with Ph_3CCl. All of these complexes reacted with one molecule of isocyanide or carbon monoxide to give the η²-iminoacyl or η²-acyl compounds, respectively. No further insertion processes have been observed. This behaviour is analogous to that observed for the imido compounds [TaCp*MeX(NR)] (R = 2,6-$Me_2C_6H_3$; X = Cl, Me), although in the oxo-borane compounds the insertion of CO gave stable η²-acyl derivatives because of the presence of a Ta–O multiple bond, which prevents further rearrangement.

Experimental Section

All manipulations were carried out under argon, and solvents were distilled from appropriate drying agents. NMR spectra were recorded at 300.13 (^{1}H NMR), 188.31 (^{19}F NMR), 75.47 (^{13}C NMR) and 128.38 Hz (^{11}B NMR) at room temperature with a Varian Unity 300 (^{1}H, ^{13}C, ^{19}F) or Bruker Advance 400 (^{11}B NMR) instrument. Chemical shifts (δ, $CDCl_3$) are given in ppm, relative to internal TMS (^{1}H and ^{13}C NMR), and external $CFCl_3$ (^{19}F NMR) and $BF_3{\cdot}OEt_2$ (^{11}B NMR). Elemental analyses were performed with a Perkin–Elmer 240C instrument. Compounds [TaCp*Me$_4$],[42] [TaCp*(CH$_2$Ph)$_2${O·B(C$_6$F$_5$)$_3$}],[21] [TaCp*Me$_2${O·B(C$_6$F$_5$)$_3$}],[21] [TaCp*Cl{η^2-C(Me)=NAr}(O)][10] and B(C$_6$F$_5$)$_3$[43] were prepared by literature methods, and H$_2$O·B(C$_6$F$_5$)$_3$[44] was prepared from H$_2$O and B(C$_6$F$_5$)$_3$ in toluene at room temperature and used in situ without further purification.

[TaCp*Cl(CH$_2$Ph){O·B(C$_6$F$_5$)$_3$}] (1c): A suspension of Ph_3CCl (0.14 g, 0.50 mmol) and [TaCp*(CH$_2$Ph)$_2${O·B(C$_6$F$_5$)$_3$}] (**1a**) (0.50 g, 0.49 mmol) in toluene (5 mL) was stirred overnight at room temperature, with a colour change from yellow to brown. Later, all volatile components were removed under vacuum until the volume was ca. 1 mL, leaving a dark oil that was washed with hexane (2 × 10 mL) to yield **1c** as a brownish solid (0.36 g, 76%). $C_{35}H_{22}BClF_{15}OTa$ (970.75): calcd. C 43.31, H 2.28; found C 42.99, H 2.25. ^{1}H NMR: δ = 2.14 (s, 15 H, C$_5$*Me*$_5$), 2.52 (d, $^2J_{H,H}$ = 14.0 Hz, 1 H, C*H*$_2$Ph), 2.80 (d, $^2J_{H,H}$ = 14.0 Hz, 1 H, C*H*$_2$Ph), 6.74 (m, 2 H, C$_6$*H*$_5$), 7.02 (m, 3 H, C$_6$*H*$_5$) ppm. ^{11}B NMR: δ = 0.10 [O·B(C$_6$F$_5$)$_3$] ppm; ^{13}C NMR{^{1}H}: δ = 11.5 (C$_5$*Me*$_5$), 82.3 (*C*H$_2$Ph), 125.7 (*C*$_5$Me$_5$), 127.1 (*C*$_6$H$_5$), 128.2 (*C*$_6$H$_5$),128.3 (*C*$_6$H$_5$), 131.4 (*C*$_6$H$_5$), 135.0 (*C*$_6$F$_5$), 138.3 (*C*$_6$F$_5$), 145.9 (*C*$_6$F$_5$), 149.1 (*C*$_6$F$_5$) ppm; ^{19}F NMR: δ = –132.9 (*o*-C$_6$F$_5$), –157.7 (*p*-C$_6$F$_5$), –163.3 (*m*-C$_6$F$_5$) ppm.

[TaCp*ClMe{O·B(C$_6$F$_5$)$_3$}] (1d): A solution of Ph_3CCl (0.080 g, 0.028 mmol) and [TaCp*Me$_2${O·B(C$_6$F$_5$)$_3$}] (**1d**) (0.025 g, 0.028 mmol) in C_6D_6 was heated at 45 °C for 18 h. Total transformation of **1b** to **1d** was then observed. ^{1}H NMR (C_6D_6): δ = 1.26 (s, 3 H, Ta–*Me*), 2.13 (s, 15 H, C$_5$*Me*$_5$) ppm. ^{11}B NMR (C_6D_6): δ = 0.05 [O·B(C$_6$F$_5$)$_3$] ppm. ^{19}F NMR (C_6D_6): δ = –133.0 (*o*-C$_6$F$_5$), –157.2 (*p*-C$_6$F$_5$), –163.3 (*m*-C$_6$F$_5$) ppm.

[TaCp*(CH$_2$Ph){η^2-C(CH$_2$Ph)=NAr}{O·B(C$_6$F$_5$)$_3$}] (Ar = 2,6-Me$_2$C$_6$H$_3$) (2a): A solution of [TaCp*(CH$_2$Ph)$_2${O·B(C$_6$F$_5$)$_3$}] (**1a**) (0.50 g, 0.49 mmol) in toluene (5 mL) was treated with CNAr (0.065 g, 0.50 mmol), and the mixture was stirred for 1 h at room temperature. All volatile components were removed under vacuum, and the remaining solid was washed with hexane (2 × 10 mL) to give **2a** as a white solid (0.49 g, 87%). $C_{51}H_{38}BF_{15}NOTa$ (1157.59): calcd. C 52.91, H 3.31, N 1.21; found C 52.67, H 3.21, N 1.09. ^{1}H NMR: δ = 1.34 (s, 3 H, *Me*$_2$C$_6$H$_3$), 1.41 (s, 3 H, *Me*$_2$C$_6$H$_3$), 1.93 (s, 15 H, C$_5$*Me*$_5$), 2.78 (d, $^2J_{H,H}$ = 12.5 Hz, 1 H, Ta–C*H*$_2$Ph), 2.93 (d, $^2J_{H,H}$ = 12.5 Hz, 1 H, Ta–C*H*$_2$Ph), 4.46 (d, $^2J_{H,H}$ = 17.4 Hz, 1 H, C–C*H*$_2$Ph), 4.56 (d, $^2J_{H,H}$ = 17.4 Hz, 1 H, C–C*H*$_2$Ph), 6.47–7.03 (m, 13 H, C$_6$*H*$_3$ and C$_6$*H*$_5$) ppm. ^{13}C NMR{^{1}H}: δ = 11.1 (C$_5$*Me*$_5$), 17.6 (*Me*$_2$C$_6$H$_3$), 18.8 (*Me*$_2$C$_6$H$_3$), 42.2 (C–*C*H$_2$Ph), 54.8 (Ta–*C*H$_2$Ph), 120.1 (*C*$_5$Me$_5$), 123.5–149.2 (*C*$_6$H$_5$, Me$_2$*C*$_6$H$_3$ and *C*$_6$F$_5$), 237.7 (Ta–*C*=N) ppm. ^{19}F NMR: δ = –130.7 (*o*-C$_6$F$_5$), –158.3 (*p*-C$_6$F$_5$), –163.8 (*m*-C$_6$F$_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1601 (C=N) cm^{-1}.

[TaCp*Me{η^2-C(Me)=NAr}{O·B(C$_6$F$_5$)$_3$}] (Ar = 2,6-Me$_2$C$_6$H$_3$) (2b): The procedure used for **2a**, but starting from [TaCp*Me$_2${O·B(C$_6$F$_5$)$_3$}] (**1b**) (0.50 g, 0.57 mmol) and CNAr (0.079 g, 0.060 mmol), gave **2b** (0.52 g, 91%). $C_{39}H_{30}BF_{15}NOTa$ (1005.41): calcd. C 46.59, H 3.09, N 1.39; found C 46.40, H 3.00, N 1.28. ^{1}H NMR: δ = 0.79 (s, 3 H, Ta–*Me*), 1.48 (s, 3 H, *Me*$_2$C$_6$H$_3$), 1.69 (s, 3 H, *Me*$_2$C$_6$H$_3$), 1.95 (s, 15 H, C$_5$*Me*$_5$), 2.72 (s, 3 H, C–*Me*), 7.06 (m, 2 H, Me$_2$C$_6$*H*$_3$), 7.13 (m, 1 H, Me$_2$C$_6$*H*$_3$) ppm. ^{13}C NMR{^{1}H}: δ = 11.0 (C$_5$*Me*$_5$), 17.2 (*Me*$_2$C$_6$H$_3$), 18.6 (*Me*$_2$C$_6$H$_3$), 20.0 (Ta–*Me*), 31.6 (C–*Me*), 118.7 (*C*$_5$Me$_5$), 127.6–148.8 (Me$_2$*C*$_6$H$_3$ and *C*$_6$F$_5$), 238.3 (Ta–*C*=N) ppm. ^{19}F NMR: δ = –131.7 (*o*-C$_6$F$_5$), –158.4 (*p*-C$_6$F$_5$), –163.8 (*m*-C$_6$F$_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1629 (C=N) cm^{-1}.

[TaCp*Cl{η^2-C(CH$_2$Ph)=NAr}{O·B(C$_6$F$_5$)$_3$}] (Ar = 2,6-Me$_2$C$_6$H$_3$) (2c): The procedure used for **2a**, but starting from [TaCp*Cl(CH$_2$Ph){O·B(C$_6$F$_5$)$_3$}] (**1c**) (0.50 g, 0.52 mmol) and CNAr (0.072 g, 0.55 mmol), gave **2c** (0.51 g, 89%). $C_{44}H_{31}BClF_{15}NOTa$ (1101.91): calcd. C 47.96, H 2.84, N 1.27; found 47.00, H 2.75, N 1.24. ^{1}H NMR: δ = 1.55 (s, 3 H, *Me*$_2$C$_6$H$_3$), 1.64 (s, 3 H, *Me*$_2$C$_6$H$_3$), 2.09 (s, 15 H, C$_5$*Me*$_5$), 4.59 (d, $^2J_{H,H}$ = 18.5 Hz, 1 H, C–C*H*$_2$Ph), 4.72 (d, $^2J_{H,H}$ = 18.5 Hz, 1 H, C–C*H*$_2$Ph), 6.76–7.06 (m, 8 H, C$_6$*H*$_3$ and C$_6$*H*$_5$) ppm. ^{13}C NMR{^{1}H}: δ = 11.4 (C$_5$*Me*$_5$), 17.8 (*Me*$_2$C$_6$H$_3$), 21.4 (*Me*$_2$C$_6$H$_3$), 43.3 (C–*C*H$_2$Ph), 123.2 (*C*$_5$Me$_5$), 125.3–149.2 (*C*$_6$H$_5$, Me$_2$*C*$_6$H$_3$ and *C*$_6$F$_5$), 236.7 (Ta–*C*=N) ppm. ^{19}F NMR: δ = –130.6 (*o*-C$_6$F$_5$), –157.9 (*p*-C$_6$F$_5$), –163.4 (*m*-C$_6$F$_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1644 (C=N) cm^{-1}.

[TaCp*Cl{η^2-C(Me)=NAr}{O·B(C$_6$F$_5$)$_3$}] (Ar = 2,6-Me$_2$C$_6$H$_3$) (2d): A solution of [TaCp*Cl{η^2-C(Me)=NAr}(O)] (0.25 g, 0.49 mmol) and B(C$_6$F$_5$)$_3$ (0.28 g, 0.51 mmol) in toluene (5 mL) was stirred at room temperature for 1 h. Later, the solution was filtered, layered with hexane (5 mL) and cooled to –10 °C, obtaining **2d** as yellow crystals (0.40 g, 74%). $C_{38}H_{27}BClF_{15}NOTa{\cdot}(C_7H_8)_2$ (1210.09): calcd. C 51.61, H 3.58, N 1.16; found C 51.01, H 3.22, N 1.19. ^{1}H NMR: δ = 1.62 (s, 3 H, *Me*$_2$C$_6$H$_3$), 1.91 (s, 3 H, *Me*$_2$C$_6$H$_3$), 2.18 (s, 15 H, C$_5$*Me*$_5$), 2.94 (s, 3 H, C–*Me*), 7.13 (m, 2 H, Me$_2$C$_6$*H*$_3$), 7.20 (m, 1 H, Me$_2$C$_6$*H*$_3$) ppm. ^{13}C NMR{^{1}H}: δ = 11.5 (C$_5$*Me*$_5$), 17.6 (*Me*$_2$C$_6$H$_3$), 19.2 (C–*Me*), 21.1 (*Me*$_2$C$_6$H$_3$), 113.3 (*C*$_5$Me$_5$), 128.7–149.4 (Me$_2$*C*$_6$H$_3$ and *C*$_6$F$_5$), 240.1 (Ta–*C*=N) ppm. ^{19}F NMR: δ = –131.5 (*o*-C$_6$F$_5$), –158.4 (*p*-C$_6$F$_5$), –164.0 (*m*-C$_6$F$_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1638 (C=N) cm^{-1}.

[TaCp*(CH$_2$Ph){η^2-C(CH$_2$Ph)=O}{O·B(C$_6$F$_5$)$_3$}] (3a): A flask containing a solution of [TaCp*(CH$_2$Ph)$_2${O·B(C$_6$F$_5$)$_3$}] (**1a**) (0.50 g, 0.49 mmol) in toluene (10 mL) was charged with CO, and the mixture was stirred for 24 h at room temperature. The solution was then filtered, all volatile components were removed under vacuum to leave ca. 4 mL of solution and the solution was layered with hexane (4 mL) and cooled to –10 °C to give **3a** as yellow crystals (0.39 g, 70%). $C_{43}H_{29}BF_{15}O_2Ta{\cdot}C_7H_8$ (1146.56): calcd. C 52.38, H 3.25; found C 52.43, H 3.17. ^{1}H NMR: δ = 1.88 (s, 15 H, C$_5$*Me*$_5$), 2.54 (d, $^2J_{H,H}$ = 12.1 Hz, 1 H, Ta–C*H*$_2$Ph), 2.70 (d, $^2J_{H,H}$ = 12.1 Hz, 1 H, Ta–C*H*$_2$Ph), 4.59 (d, $^2J_{H,H}$ = 19.4 Hz, 1 H, C–C*H*$_2$Ph), 4.88 (d, $^2J_{H,H}$ = 19.4 Hz, 1 H, C–C*H*$_2$Ph), 6.70–6.90 (m, 6 H, C$_6$*H*$_5$), 7.20–7.45 (m, 4 H, C$_6$*H*$_5$) ppm. ^{13}C NMR{^{1}H}: δ = 10.8 (C$_5$*Me*$_5$), 49.2 (C–*C*H$_2$Ph), 60.0 (Ta–*C*H$_2$Ph), 120.0 (*C*$_5$Me$_5$), 123.5–148.9 (*C*$_6$H$_5$ and *C*$_6$F$_5$), 306.9 (Ta–*C*=O) ppm. ^{19}F NMR: δ = –133.0 (*o*-C$_6$F$_5$), –157.7 (*p*-C$_6$F$_5$), –163.4 (*m*-C$_6$F$_5$) ppm. IR (KBr): $\tilde{\nu}$ = 1643 (C=O) cm^{-1}.

[TaCp*Me{η^2-C(Me)=O}{O·B(C$_6$F$_5$)$_3$}] (3b): The procedure used for **3a**, but starting from [TaCp*Me$_2${O·B(C$_6$F$_5$)$_3$}] (**1b**) (0.50 g, 0.57 mmol) and CO, gave **3b** as a white solid (0.41 g, 80%). $C_{31}H_{21}BF_{15}O_2Ta$ (902.23): calcd. C 41.27, H 2.35; found C 40.87, H 2.30. ^{1}H NMR: δ = 0.81 (s, 3 H, Ta–*Me*), 1.90 (s, 15 H, C$_5$*Me*$_5$), 3.23 (s, 3 H, C–*Me*) ppm. ^{13}C NMR{^{1}H}: δ = 10.6 (C$_5$*Me*$_5$), 28.7 (Ta–*Me*), 37.6 (C–*Me*), 119.4 (*C*$_5$Me$_5$), 134.3–149.8 (*C*$_6$F$_5$), 313.8 (Ta–*C*=O) ppm. ^{19}F NMR: δ = –133.2 (*o*-C$_6$F$_5$), –157.7 (*p*-C$_6$F$_5$), –163.4 (*m*-C$_6$F$_5$). IR (KBr): $\tilde{\nu}$ = 1644 (C=O) cm^{-1}.

[TaCp*Cl{η²-C(CH₂Ph)=O}{O·B(C₆F₅)₃}] (3c): The procedure used for **3a**, but starting from [TaCp*Cl(CH₂Ph){O·B(C₆F₅)₃}] (**1c**) (0.50 g, 0.52 mmol) and CO, gave **3c** as a yellowish solid (0.40 g, 78%). $C_{36}H_{22}BClF_{15}O_2Ta$ (998.76): calcd. C 43.29, H 2.22; found C 43.17, H 2.24. ^{1}H NMR: δ = 2.05 (s, 15 H, C_5Me_5), 4.41 (d, $^2J_{H,H}$ = 19.0 Hz, 1 H, C–CH_2Ph), 4.91 (d, $^2J_{H,H}$ = 19.0 Hz, 1 H, C–CH_2Ph), 7.05–7.40 (m, 5 H, C_6H_5) ppm. ^{13}C NMR{^{1}H}: δ = 10.5 (C_5Me_5), 49.2 (C–CH$_2$Ph), 123.7 (C_5Me$_5$), 127.8–130.0 (C_6H$_5$), 135.8, 138.3, 139.2, 141.7, 146.8 and 150.1 (C_6F_5), 310.5 (Ta–C=O) ppm. ^{19}F NMR: δ = –132.5 (o-C_6F_5), –156.9 (p-C_6F_5), –162.9 (m-C_6F_5) ppm. IR (KBr): $\tilde{\nu}$ = 1658 (C=O) cm^{-1}.

[TaCp*(CH₂Ph){η²-C(CH₂Ph)=NAr}(O)] (Ar = 2,6- Me₂C₆H₃) (4a): A solution of [TaCp*(CH$_2$Ph){η^2-C(CH$_2$Ph)=NAr}-{O·B(C$_6$F$_5$)$_3$}] (**2a**) (0.25 g, 0.22 mmol) in toluene (5 mL) was treated with pyridine (0.026 g, 0.33 mmol), and the mixture was stirred for 2 h at room temperature. All volatile components were removed under vacuum until ca. 1 mL remained, and hexane (10 mL) was added to precipitate a white solid that was washed with a hexane/toluene mixture (2 × 10 mL, 9:1) to give **4a** (0.10 g, 72%). $C_{33}H_{38}NOTa$ (645.62): calcd. C 61.39, H 5.93, N 2.17; found C 61.00, H 5.83, N 2.21. ^{1}H NMR: δ = 1.25 (s, 3 H, $Me_2C_6H_3$), 1.72 (d, $^2J_{H,H}$ = 11.9 Hz, 1 H, Ta–CH_2Ph), 1.80 (s, 3 H, $Me_2C_6H_3$), 1.99 (s, 15 H, C_5Me_5), 2.77 (d, $^2J_{H,H}$ = 11.9 Hz, 1 H, Ta–CH_2Ph), 3.75 (d, $^2J_{H,H}$ = 17.6 Hz, 1 H, C–CH_2Ph), 4.25 (d, $^2J_{H,H}$ = 17.6 Hz, 1 H, C–CH_2Ph), 6.50–7.26 (m, 13 H, C_6H_3 and C_6H_5) ppm. ^{13}C NMR{^{1}H}: δ = 10.9 (C_5Me_5), 17.2 ($Me_2C_6H_3$), 18.4 ($Me_2C_6H_3$), 39.3 (C–CH$_2$Ph), 48.8 (Ta–CH$_2$Ph), 121.1 (C_5Me$_5$), 126.1–149.8 (C_6H$_5$ and Me$_2C_6$H$_3$), 240.3 (Ta–C=N) ppm. IR (KBr): $\tilde{\nu}$ = 1631 (C=N) cm^{-1}.

Crystal Structure Determination for 2d and 3a: Selected crystals were covered with perfluoropolyether oil and mounted on a Nonius KAPPA-CCD single crystal diffractometer. The crystal structure was solved by direct methods and refined using full-matrix least-squares on F^2 (SHELXL-97). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. Two molecules of toluene crystallised with every molecule of **2d**; both solvent molecules were found in the difference Fourier map but one of them was very disordered and it was not possible to get a chemically sensible model for it, so the Squeeze procedure[45] was used to remove its contribution to the structural factors. In **3a** some restraints on the solvent molecule were applied. Crystal data for both compounds are given in Table 1. CCDC-272817 (for **2d**) and CCDC-272818 (for **3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for compounds **2d** and **3a**.

Compound	**2d**	**3a**
Empirical formula	$C_{52}H_{43}BClF_{15}NOTa$	$C_{50}H_{37}BF_{15}O_2Ta$
Formula mass	1210.08	1146.56
λ [Å]	0.71069	0.71069
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
T [K]	200(2)	150(2)
a [Å]	9.565(1)	12.739(2)
b [Å]	13.7547(3)	13.171(2)
c [Å]	19.545(3)	15.104(2)
α [°]	77.483(7)	88.20(1)
β [°]	79.50(1)	82.58(2)
γ [°]	71.389(4)	63.20(1)
V [Å^3]	2361.1(5)	2242.1(6)
Z	2	2
Calcd. density [mg m^{-3}]	1.572	1.698
Absorption coefficient [mm^{-1}]	2.478	2.555
θ range [°]	3.52–27.50	3.61–27.50
Reflections collected/unique reflections	13375/8067	19150/10201
R(int.)	0.0863	0.0228
Data/restraints/parameters	8067/3/586	10201/239/622
GOF	1.101	1.042
Final R indices	R_1 = 0.0575	R_1 = 0.0292
[$I > 2\sigma(I)$]	wR_2 = 0.1211	wR_2 = 0.0678
Largest diff. peak/hole [e Å^{-3}]	1.596/–1.899	1.303/–1.364

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