Insertion of CO and CNR into Tantalum−Methyl Bonds of Imido(pentamethylcyclopentadienyl)tantalum Complexes. X-ray Crystal Structures of [TaCp*(NR)Me{η^2-C(Me)=NR}] and [TaCp*Cl(O){η^2-C(Me)=NR}] (R = 2,6-$Me_2C_6H_3$)†

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[TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] reacts with 2 equiv of LiMe at −78 °C to give the imido dimethyl complex TaCp*Me_2{N(2,6-$Me_2C_6H_3$)} (**1**) in almost quantitative yield, whereas the monomethyl imido derivatives [TaCp*MeX{N(2,6-$Me_2C_6H_3$)}] (X = Cl (**2**), $OC_6H_3Me_2$ (**3**)) can be prepared by addition of HX (X = Cl, $OC_6H_3Me_2$) to toluene solutions of [TaCp*Me(NR){NR(CMe=CMe_2)}] (R = 2,6-$Me_2C_6H_3$) with elimination of the corresponding imine RN=CMeCHMe_2. Complex **1** reacts with CO to give the dinuclear ene diolate complex [TaCp*{N(2,6-$Me_2C_6H_3$)Me}]$_2${μ-η^2-OC(Me)=C(Me)O} (**5**) via intermolecular coupling between two acyl carbon atoms of the intermediate η^2-acyl complex TaCp*Me{N(2,6-$Me_2C_6H_3$)}{η^2-C(Me)=O} (**4**). However, when the same reaction was carried out with the chloro imido methyl derivative **2**, the unexpected oxo η^2-iminoacyl complex [TaCp*Cl(O){η^2-C(Me)=N-(2,6-$Me_2C_6H_3$)}] (**7**) was obtained via the barely stable intermediate η^2-acyl complex [TaCp*Cl{N(2,6-$Me_2C_6H_3$)}{η^2-C(Me)=O}] (**6**). The analogous reaction of [TaCp*Cl_2Me_2] with CO leads to the formation of the dichloro oxotantalacyclopropane complex [TaCp*Cl_2(η^2-CMe_2O)] (**8**), but the acyl intermediate species was not observed. Similarly, the azatantalacyclopropane complexes [TaCp*XMe($\eta^2$$CMe_2$-NR)] react with 1 equiv of CO to form the stable enolate derivatives [TaCp*X(NR){OC(Me)=CMe_2}] (X = Cl (**9**), Me (**10**); R = 2,6-$Me_2C_6H_3$). The stable 18-electron imido η^2-iminoacyl derivatives [TaCp*X(NR){η^2-C(Me)=NR}] (X = Me (**11**), Cl (**12**), OC(Me)=CMe_2 (**13**); R = 2,6-$Me_2C_6H_3$) are formed when the isocyanide RNC (1 equiv) is added to toluene solutions of the imido complexes **1**, **2**, and **10**, respectively. All compounds were characterized by IR and NMR (^{1}H and ^{13}C), and the molecular structures of **7** and **11** were studied by X-ray diffraction methods.

Introduction

One of the most important organometallic reactions, with many synthetic applications, is the transfer of alkyl groups from transition metals to coordinated unsaturated molecules, such as carbon monoxide[1] and isocyanides,[2] to give acyl and iminoacyl complexes whose reactivity[3] is well documented. Recently, we have reported a systematic study[4] of isocyanide insertion reactions into tantalum−methyl bonds of different halomethyl(pentamethylcyclopentadienyl)tantalum complexes TaCp*$Cl_{4-n}Me_n$, which led to the isolation of η^2-iminoacyl (n = 1), dichloro azatantalacyclopropane (n = 2), and chloro and methyl imido alkenyl amido (n = 3, 4) complexes. Further attack of the isocyanide at the terminal olefinic carbon of the alkenyl moiety of the last two complexes transforms the amido into an iminoacyl ligand containing a terminal ketimine function.

We herein report the synthesis of new imido(pentamethylcyclopentadienyl)tantalum complexes, their reactivity with CO and CNR, and the intramolecular rearrangements of the resulting complexes. The X-ray molecular structures of the complexes [TaCp*Cl(O){η^2-C(Me)=NR}] and [TaCp*(NR)Me{η^2-C(Me)=NR}] (R = 2,6-$Me_2C_6H_3$) are also described.

† Dedicated to Professor Rafael Usón on the occasion of his 70th birthday.

‡ X-ray diffraction studies.

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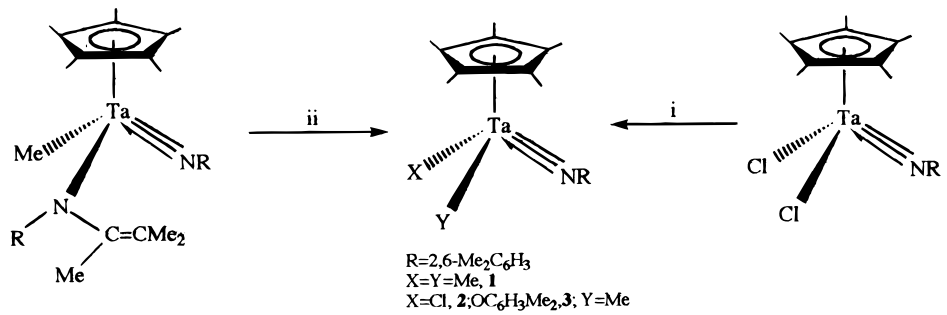
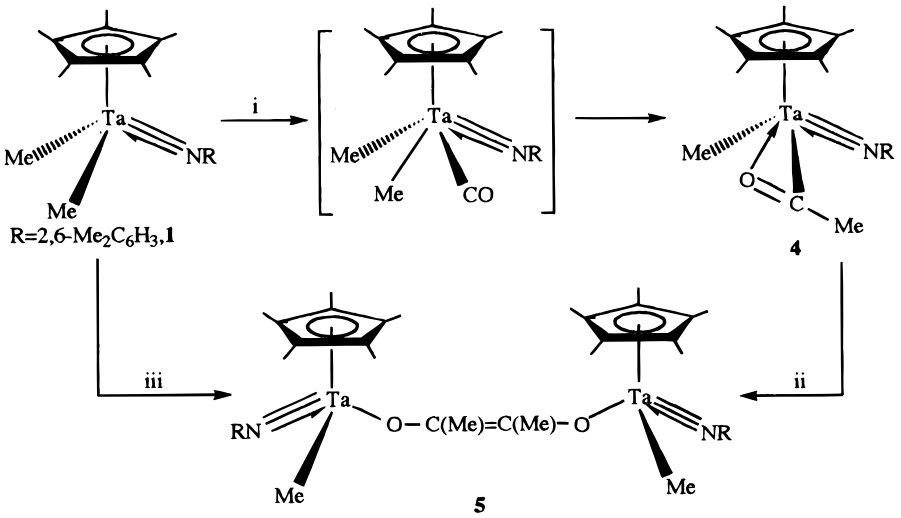
Scheme 1[a]



[a] Reagents and conditions: (i) 2 equiv LiMe (1.6 M in OEt_2), toluene, −78 °C, 30 min, room temperature, 2 h; (ii) X = Cl, 1 equiv HCl (1 M in OEt_2), toluene, −78 °C, 20 min, X = $OC_6H_3Me_2$, sealed NMR tube, 1 equiv 2,6-$Me_2C_6H_3$(OH), benzene-d_6, 60 °C, 3 days.

Scheme 2[a]



[a] Reagents and conditions: (i) sealed NMR tube, CO (1 atm), chloroform-d, N_2(l), fast; (ii) room temperature; (iii) CO (1 atm), toluene, room temperature, 16 h.

Results and Discussion

Synthesis of Imido Complexes. Reaction of [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$}] with 2 equiv of LiMe at −78 °C afforded the imido dimethyl complex [TaCp*Me_2-{N(2,6-$Me_2C_6H_3$)}] (**1**) in almost quantitative yield. When the same reaction was carried out using 1 equiv of LiMe, the same redistribution reaction observed for other halotantalum complexes[5] takes place for the expected halo methyl complex to give a 1:1 mixture of 1 and the starting product.

As shown in Scheme 1, the monomethyl imido derivatives [TaCp*MeX{N(2,6-$Me_2C_6H_3$)}] (X = Cl (**2**), OC_6H_3-Me_2 (**3**)) are easily obtained when 1 equiv of the appropriate HX reagent is added at room temperature (X = Cl) or at 60 °C (X = $OC_6H_3Me_2$) to toluene solutions of TaCp*(NR)Me[NR(CMe=CMe_2)] with elimination of the corresponding imine RN=CMeCHMe_2 (R = 2,6-$Me_2C_6H_3$).

The new imido complexes show a ν(Ta=N)[7] IR absorption at ∼1322 cm^{-1}. Their ^1H and ^{13}C NMR spectra (see Experimental Section) are consistent with the expected pseudotetrahedral structure.[8]

Reactions with CO. Complex **1** reacts with carbon monoxide (1 atm) at room temperature in toluene to give the dinuclear ene diolate complex [{TaCp*(NR)Me}$_2${μ-η^2-OC(Me)=C(Me)O}] (R = 2,6-$Me_2C_6H_3$; **5**) in good yield.

As shown in Scheme 2, this reaction takes place by intermolecular coupling between two acyl carbon atoms of the intermediate η^2-acyl complex [TaCp*Me{N(2,6-$Me_2C_6H_3$)}{η^2-C(Me)=O}] (**4**). Formation of complex **4** can be observed when the reaction is followed by NMR spectroscopy at low temperature. The NMR spectrum in $CDCl_3$ at −50 °C shows one ^1H resonance at δ 3.13 ppm and one $^{13}C\{^1H\}$ signal at δ 320 ppm, as expected for the η^2-C(Me)=O ligand.[9] Complex **4** is quantitatively transformed into the ene diolate derivative **5** on heating to room temperature, preventing its isolation as a solid.

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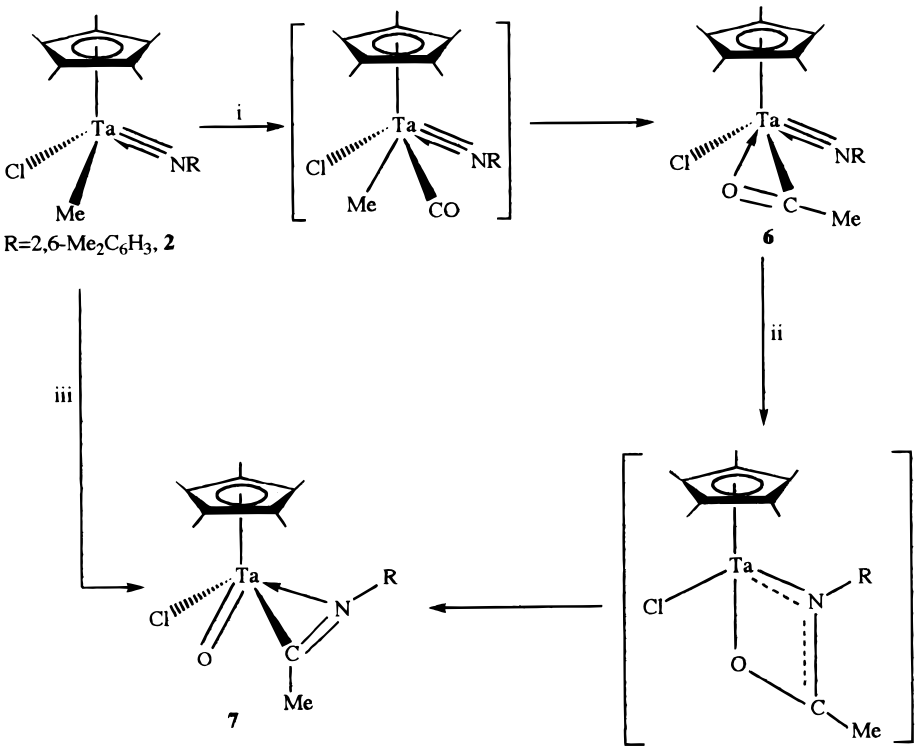
Scheme 3[a]



[a] Reagents and conditions: (i) sealed NMR tube, CO (1 atm), chloroform-*d*, −40 °C, fast; (ii) room temperature; (iii) CO (1 atm), toluene, room temperature, 12 h.

When the same reaction with CO was carried out using the chloro methyl derivative **2** as the starting compound, the expected imido acyl compound was not obtained, since it was spontaneously converted into the oxo η^2-iminoacyl complex [TaCp*Cl(O){η^2-C(Me)=N(2,6-$Me_2C_6H_3$)}] (**7**).

As shown in Scheme 3, the formation of complex **7** can be explained assuming the initial coordination of CO, followed by the migration of the methyl group bonded to the metal to the electrophilic carbonyl carbon atom to give the barely stable intermediate η^2-acyl complex [TaCp*Cl{N(2,6-$Me_2C_6H_3$)}{η^2-C(Me)=O}] (**6**). Formation of complex **6** was checked, monitoring the reaction by NMR spectroscopy. The ^{1}H NMR and ^{13}C-{^{1}H} NMR spectra of complex **6** in $CDCl_3$ at −40 °C show singlets at δ 3.12 and 316.1 ppm, respectively, as expected for the acyl ligand.[9] The nucleophilic attack of the imido nitrogen atom at the electrophilic acyl carbon atom leads to an unidentified intermediate species which spontaneously rearranges, breaking the C−O bond with simultaneous formation of M−C and the M=O double bonds to give the final η^2-iminoacyl oxo complex **7**.

The analogous reaction of TaCp*Cl_2Me_2 with CO in benzene-d_6 carried out in an NMR tube leads to the formation of the corresponding dichloro oxotantalacyclopropane complex TaCp*Cl_2(η^2-CMe_2O) (**8**), as a result of a double migration of two methyl groups, first to the electrophilic carbon atom of the coordinated CO and then to the related η^2-acyl intermediate, which could not be observed. Compound **8**, which is not further transformed, is analogous to the reported[1b,3f] tantalum acetone complex TaCp*Me_2(η^2-CMe_2O).

Similarly, the azatantalacyclopropane complexes [TaCp*XMe(η^2-CMe_2NR)] (X = Cl, Me; R = 2,6-$Me_2C_6H_3$)[4a] react with 1 equiv of CO to form the stable enolate derivatives [TaCp*X{N(2,6-$Me_2C_6H_3$)}{OC(Me)=CMe_2}] (X = Cl (**9**), Me (**10**)), which probably exhibit the same pseudotetrahedral structure known for the related isoelectronic complexes [TaCp*{N(2,6-$Me_2C_6H_3$)}{N(2,6-$Me_2C_6H_3$)CMe=CMe_2}] previously reported.[4b] We assume that the coordination of CO is followed by a double migration of one methyl group and the metallacycle alkyl group to the electrophilic carbonyl carbon atom, but when the reactions were followed by ^{1}H NMR spectroscopy, the proposed intermediate species shown in Scheme 4 could not be detected. Depending on the order of migration of both groups, either of the two different pathways lead to the same unidentified intermediate species that spontaneously rearranges, breaking the Ta−C and C−N(amido) bonds with simultaneous C=C double-bond formation, to give the resultant products **9** and **10**.

All of the complexes **4**−**10** are soluble in aromatic hydrocarbons and chlorinated solvents and only slightly soluble in saturated hydrocarbons.

The formulation of complexes **5**, **9**, and **10** as enolate derivatives is supported by the IR spectra, which show ν(C=C),[1b,3de,10] ν(C−O),[1b] and ν(Ta−O)[11] absorptions at 1587−1676, 1198−1180, and 804−816 cm^{-1}, respectively. The ^{1}H NMR spectrum of complex **5** shows one singlet at δ 2.17 ppm for the equivalent methyl substituents of the bridging enolate ligand, whereas the resonances corresponding to the nonequivalent methyl substituents of the terminal enolate ligand in complexes **9**

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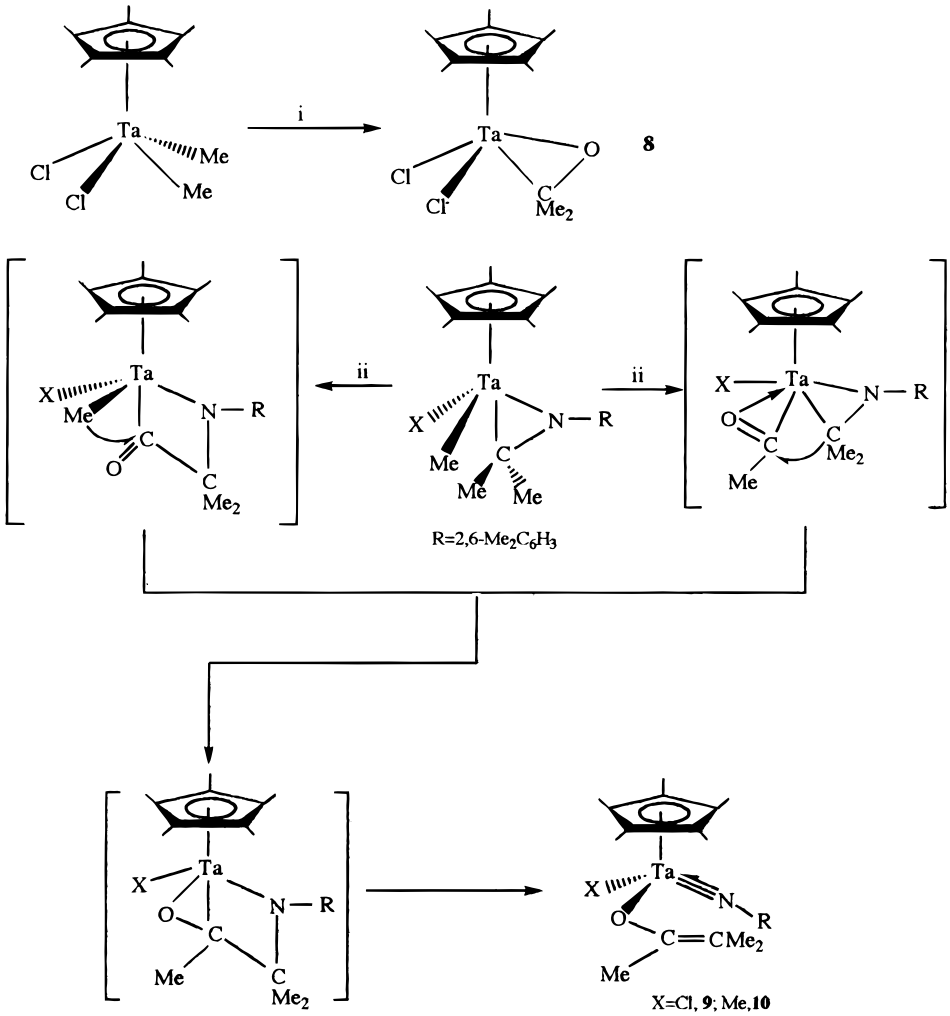
Scheme 4[a]



[a] Reagents and conditions: (i) sealed NMR tube, CO (1 atm), benzene-d_6, room temperature, fast; (ii) X = Cl, CO (1 atm), toluene, −78 °C, 2 h, X = Me, sealed NMR tube, CO (1 atm), benzene-d_6, room temperature, 2 h.

and **10** appear as three multiplets due to the existence of a rigid C=C double bond on the NMR time scale.[1b,3de,10,12]

The η^2-iminoacyl oxo complex **7** shows the ν(C=N)[9] and ν(Ta=O)[10b,13] IR absorptions at 1628 and 906 cm^{-1}, respectively. In addition, two singlets are observed in the ^{1}H and ^{13}C NMR spectra (see Experimental Section) for the *o*-methyl(phenyl) groups of the η^2-iminoacyl ligand, which are nonequivalent due to the rigid structure of **7** on the NMR time scale.

The molecular structure of **7** with the atom-numbering scheme is shown in Figure 1. Selected bond distances and angles are given in Table 1.

Complex **7** has a monomeric structure with the tantalum atom coordinated to a pentamethylcyclopentadienyl ring in an almost η^5-bonding mode (Ta−C distances ranged from 2.431(9) to 2.526(8) Å), an η^2-iminoacyl group, one chlorine atom, and one oxygen atom. When the centroid of the iminoacyl group is taken as occupying a single site, the tantalum atom can be considered to be in a three-legged piano-stool situation. The complex is chiral, and two distinct enantiomers were found in the crystals.

The η^2-iminoacyl group is coordinated in a situation similar to that found in the previously reported compound [TaCp*(NR)Me{η^2-C(CMe$_2$CMe=NR)NR}][4b] (R = 2,6-Me$_2$C$_6$H$_3$) or in compound **11** in this paper, with Ta−C(1) and Ta−N(1) distances of 2.133(9) and 2.132(7) Å, respectively, corresponding to single bonds, and a C(1)−N(1) distance of 1.276(11) Å, which implies double-bond character. The Ta−Cp*(centroid) distance is 2.156 Å, as in the compounds mentioned above.

The Ta−Cl distance is 2.409(3) Å, shorter than the distances found in [TaCp*Cl$_3$(η^2-NRCMe$_2$CNHR)],[4b] which ranged from 2.452(1) to 2.526(1) Å, but longer than those found in [TaCp*Cl$_2$(N-2,6-Me$_2$C$_6$H$_3$)],[8b] where the distances are 2.331(2) and 2.326(6) Å. The oxygen ligand is bonded to the tantalum atom with a distance of 1.731(7) Å. To the best of our knowledge only two structures with terminal Ta=O bonds have been reported: Ta(O)(NPr$^i_2$)$_2$[14] and TaCp*$_2$(O)H.[13b] In both cases a double bond was proposed with a mean distance of 1.72 Å, very similar to that found in our case. Single-bond Ta−O distances are ca. 2.18 Å, whereas mean

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Table 1. Bond Lengths (Å) and Angles (deg) for 7

Ta(1)−O(1)	1.731(7)	Ta(1)−N(1)	2.132(7)	Ta(1)−C(1)	2.133(9)
Ta(1)−Cl(1)	2.409(3)	Ta(1)−C(11)	2.431(9)	Ta(1)−C(15)	2.434(8)
Ta(1)−C(14)	2.440(9)	Ta(1)−C(13)	2.522(8)	Ta(1)−C(12)	2.526(8)
N(1)−C(1)	1.276(11)	N(1)−C(21)	1.435(11)	C(1)−C(2)	1.471(14)
C(11)−C(15)	1.402(13)	C(11)−C(12)	1.426(14)	C(11)−C(16)	1.496(14)
C(12)−C(13)	1.411(14)	C(12)−C(17)	1.499(13)	C(13)−C(14)	1.428(14)
C(13)−C(18)	1.487(14)	C(14)−C(15)	1.43(2)	C(14)−C(19)	1.496(14)
C(15)−C(20)	1.479(14)	C(21)−C(26)	1.387(14)	C(21)−C(22)	1.392(13)
C(22)−C(23)	1.39(2)	C(22)−C(27)	1.49(2)	C(23)−C(24)	1.36(2)
C(24)−C(25)	1.35(2)	C(25)−C(26)	1.39(2)	C(26)−C(28)	1.496(14)
Ta(1)−Cp*(1)[a]	2.156				
O(1)−Ta(1)−N(1)	107.2(3)	O(1)−Ta(1)−C(1)	99.5(4)	N(1)−Ta(1)−C(1)	34.8(3)
O(1)−Ta(1)−Cl(1)	101.4(3)	N(1)−Ta(1)−Cl(1)	85.5(2)	C(1)−Ta(1)−Cl(1)	120.3(3)
C(1)−N(1)−C(21)	131.4(8)	C(1)−N(1)−Ta(1)	72.6(5)	C(21)−N(1)−Ta(1)	155.4(6)
N(1)−C(1)−C(2)	127.5(9)	N(1)−C(1)−Ta(1)	72.6(5)	C(2)−C(1)−Ta(1)	159.7(8)
Cp*(1)−Ta(1)−Cl(1)	108.8	Cp*(1)−Ta(1)−N(1)	129.2	Cp*(1)−Ta(1)−O(1)	116.4
Cp*(1)−Ta(1)−C(1)	110.2				

[a] Cp* is the centroid of the η^5-C_5Me_5 ring.

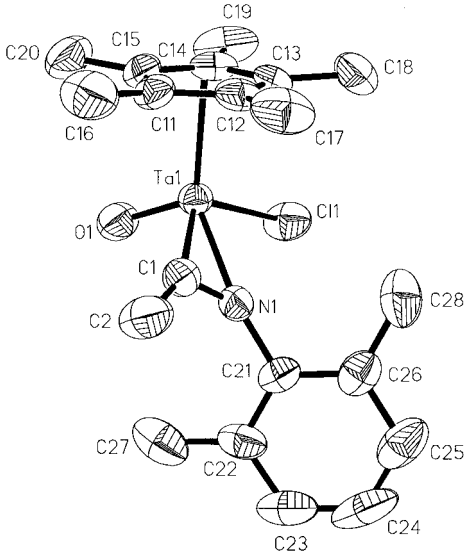
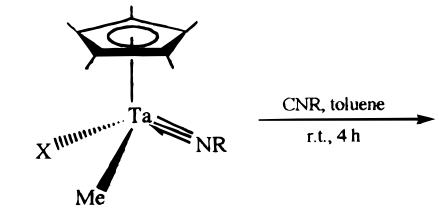
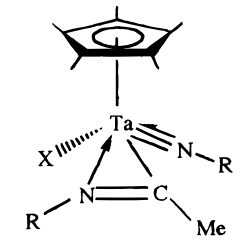


Figure 1. ORTEP view of the molecular structure of TaCp*Cl(O){η^2- C(Me)=N(2,6-$Me_2C_6H_3$)} (**7**), with the atom-numbering scheme.

Scheme 5



R=2,6-$Me_2C_6H_3$
X=Me,**1**;Cl,**2**;OC(Me)=CMe_2,**10**



X=Me, **11**; Cl, **12**; OC(Me)=CMe_2, **13**

values between 1.85[15] and 1.97 Å have been found for compounds with terminal Ta−OH bonds and for compounds with various π bond contributions, such as [TaCp*Me(CPhCPhCCH$_3$O)].[16] All these distances indicate a π donor contribution from the ligands, trying to compensate for the electron deficiency of the 16-electron metal center.

Reactions with Isocyanides. When isocyanides are added to toluene solutions of the imido complexes **1**, **2**, or **10** an instantaneous insertion reaction takes place to give the stable 18-electron imido η^2-iminoacyl derivatives [TaCp*X(NR){η^2-C(Me)=NR}] (X = Me (**11**), Cl (**12**), OC(Me)=CMe_2 (**13**); R = 2,6-$Me_2C_6H_3$) (Scheme 5).

When X = Me the migration of the second methyl group observed for TaCp*Cl_2Me_2[8b] does not take place and the presence of an excess of isocyanide does not produce a second insertion reaction in the Ta−Me or Ta−C(iminoacyl) bonds.[9,17,18] However, when X = OC(Me)=CMe_2 the methyl group bound to tantalum migrates to the electrophilic carbon atom of the isocyanide ligand, which does not attack the terminal olefinic carbon atom of the enolate ligand, in contrast with the results observed[4b] when the imido alkenylamido complexes are used.

The X-ray crystal structure of **11** with the atomic labeling scheme is shown in Figure 2. Selected bond distances and angles are given in Table 2.

The molecular structure of **11** shows the tantalum atom bonded to a Cp* ring, one methyl group, one imido group, and the η^2-coordinated iminoacyl system. The coordination around the metal atom could be considered in two ways, either with a pseudo-square-pyramidal geometry where the Cp* centroid is in the apical position, or with a tetrahedral geometry if we assume that the Cp* centroid and the center of the η^2-iminoacyl group are occupying single coordination sites. Complex **11** is chiral, and the two different enantiomers were found in the unit cell.

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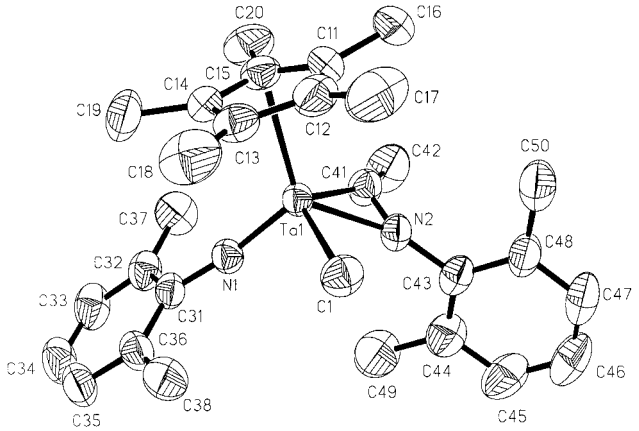

Figure 2. ORTEP view of the molecular structure of TaCp*Me(NR){η^2- C(Me)═NR} (R = 2,6-$Me_2C_6H_3$; **11**), with the atom-numbering scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 11

Ta(1)−N(1)	1.805(4)	Ta(1)−C(41)	2.153(6)
Ta(1)−N(2)	2.162(4)	Ta(1)−C(1)	2.226(5)
Ta(1)−C(15)	2.422(5)	Ta(1)−C(13)	2.430(5)
Ta(1)−C(14)	2.439(5)	Ta(1)−C(11)	2.495(6)
Ta(1)−C(12)	2.494(6)	N(1)−C(31)	1.376(6)
N(2)−C(41)	1.281(7)	N(2)−C(43)	1.428(7)
C(41)−C(42)	1.466(8)	Ta(1)−Cp1	2.148
N(1)−Ta(1)−C(41)	101.9(2)	N(1)−Ta(1)−N(2)	106.9(2)
C(41)−Ta(1)−N(2)	34.5(2)	N(1)−Ta(1)−C(1)	99.9(2)
C(41)−Ta(1)−C(1)	115.8(2)	N(2)−Ta(1)−C(1)	81.4(2)
C(31)−N(1)−Ta(1)	172.2(4)	C(41)−N(2)−C(43)	131.3(5)
C(41)−N(2)−Ta(1)	72.4(3)	C(43)−N(2)−Ta(1)	155.6(4)
N(1)−C(31)−C(36)	119.6(5)	N(1)−C(31)−C(32)	121.3(5)
N(2)−C(41)−C(42)	124.9(5)	N(2)−C(41)−Ta(1)	73.1(3)
C(42)−C(41)−Ta(1)	161.7(5)	N(1)−Ta(1)−Cp1	119.5
N(2)−Ta(1)−Cp1	129.3	C(1)−Ta(1)−Cp1	107.9

[a] Cp is the centroid of the η^5-C_5Me_5 ring.

The imido group is almost linear, the Ta−N(1)−C(31) angle being 172.2(4)°, and the Ta−N(1) (1.805(4) Å) and N(1)−C(31) (1.376(6) Å) distances are very close to those found in similar systems such as [TaCp*Cl_2(NR)] (R = 2,6-^{i}Pr$_2$C$_6$H$_3$,[7b] 2,6-$Me_2C_6H_3$[8b]) and [TaCp*Me(NR)(NRCMe═CMe_2)][4b] (R = 2,6-$Me_2C_6H_3$), corresponding to a Ta−N triple bond. The Ta−C(1) bond distance of 2.226(5) Å is the normal value for a Ta−CH_3 bond.

The situation of the η^2-iminoacyl system is parallel to that found in complex **7** with distances Ta−C(41) = 2.153(6) Å, Ta−N(2) = 2.162(5) Å, and C(41)−N(2) = 1.281(7) Å. The nitrogen atom of the iminoacyl group is located in a trans position with respect to the imido group.

The N(1), N(2), C(41), and C(1) atoms are not in a plane, but the mean plane defined by them is almost parallel to the Cp* plane, with the N(2) and the tantalum atoms above this plane at 0.25 and 0.945 Å, respectively, whereas the C(41) and C(1) atoms are below this plane by 0.357 and 0.178 Å, respectively.

The Cp* ring is bonded to tantalum in a fairly symmetric way, and the Ta−C distances ranged from 2.422(5) to 2.495(6) Å.

Conclusion

Reactions of the imido methyl tantalum(V) complexes [TaCp*MeX{N(2,6-$Me_2C_6H_3$)}] (X = Cl, Me) with CO take place through the formation of the expected acyl derivatives [TaCp*X{N(2,6-$Me_2C_6H_3$)}{η^2-C(Me)═O}] but lead to different products, depending on X. Attack of the imido nitrogen at the more electrophilic acyl carbon atom when X = Cl gives the oxo iminoacyl complex [TaCp*Cl(O){η^2-C(Me)═N(2,6-$Me_2C_6H_3$)}], whereas the higher carbenoid character of the acyl ligand when X = Me leads to the dinuclear ene diolate complex [TaCp*{N(2,6-$Me_2C_6H_3$)Me}]$_2${μ-η^2-OC(Me)═C(Me)O}. However, reactions of the related azatantalacyclopropane complexes [TaCp*XMe(η^2-CMe_2NR)] (X = Cl, Me) with CO take place with conversion into the imido enolate derivatives [TaCp*X(NR){OC(Me)═CMe_2}]. In contrast, the same imidotantalum complexes react with CN(2,6-$Me_2C_6H_3$) to give the stable 18-electron iminoacyl compounds [TaCp*X(NR){η^2-C(Me)═NR}] (X = Cl, Me) and the analogous product is also obtained when X = OC(Me)═CMe_2, without any further transformation.

Experimental Section

All operations were carried out under a dry argon atmosphere either in a Vacuum Atmosphere Dri-lab or by standard Schlenk techniques. Hydrocarbon solvents were dried and freshly distilled: *n*-hexane from sodium−potassium alloy and toluene from sodium. Reagent grade CO (SEO), LiMe (1.6 M in OEt_2, Aldrich), HCl (1 M in OEt_2, Aldrich), and 2,6-$Me_2C_6H_3$-OH (Panreac) were purchased from commercial sources and were used without further purification. Isocyanides[19] RNC (R = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$), and the starting materials TaCp*Cl_2Me_2,[20] TaCp*$Cl_{2-x}Me_x$(η^2- CMe_2-NR) (x = 0,[4a] 1,[4b] 2,[4a] R = 2,6-$Me_2C_6H_3$), TaCp*{N-(2,6-$Me_2C_6H_3$)}Cl_2,[4a] and TaCp*(NR)Me(η^1-NRCMe═CMe_2) (R = 2,6-$Me_2C_6H_3$)[4b] were prepared as described previously.

Infrared spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000−200 cm^{-1}) as Nujol mulls between CsI or polyethylene pellets. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity VXR 300 MHz and Varian Unity FT 500 MHz instruments, and chemical shifts were measured relative to residual ^{1}H and ^{13}C resonances in the deuterated solvents C_6D_6 (δ 7.15), $CDCl_3$ (δ 7.24) and C_6D_6 (δ 128), $CDCl_3$ (δ 77), respectively. Mass spectra were recorded on an HP 5988 A instrument. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer.

[TaCp*Me_2{N(2,6-$Me_2C_6H_3$)}] (1). A 1.6 M solution of LiMe in OEt_2 (6.17 mL, 9.88 mmol) was added at −78 °C to a solution of [TaCp*Cl_2{N(2,6-$Me_2C_6H_3$)}] (2.50 g, 4.94 mmol) in toluene (60 mL), and the mixture was stirred for 30 min. The color of the mixture changed quickly from red to green. It was then warmed to room temperature for 2 h, the solvent removed in vacuo, and the residue extracted into *n*-hexane (3 × 20 mL). The solution was concentrated to ca. 25 mL and cooled to −40 °C to give **1** as green crystals.

Data for **1** are as follows. Yield: 1.6 g (70%). IR (Nujol mull; ν, cm^{-1}): 1328 (vs), 1154 (m), 1094 (s), 1025 (m), 983 (m), 802 (w), 756 (s), 536 (m), 499 (s), 483 (m), 391 (w), 353 (m). ^{1}H NMR (δ, ppm; in benzene-d_6): 7.15 (d, 2H, $^2J_{H-H}$ = 7.2 Hz, **H**$_3$C$_6$Me$_2$), 6.80 (t, 1H, $^2J_{H-H}$ = 7.2 Hz, **H**$_3$C$_6$Me$_2$), 2.49 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$), 1.69 (s, 15H, C$_5$**Me**$_5$), 0.31 (s, 6H, Ta−**Me**$_2$). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-d_6): 154.02 s, 133.71 s, 126.84 s, 120.84 s (C_i, C_o, C_m, C_p, **C**$_6$H$_3$Me$_2$), 116.12 (s, **C**$_5$Me$_5$), 47.95 (s, Ta−**Me**$_2$), 18.90 (s, 2,6-**Me**$_2$C$_6$H$_3$), 10.88 (s,

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C_5**Me**$_5$). Anal. Calcd for $C_{20}H_{30}NTa$: C, 51.60; H, 6.51; N, 3.00. Found:C, 52.00; H, 6.27; N, 2.95.

[TaCp*ClMe{N(2,6-Me$_2$C$_6$H$_3$)}] (2). A 1 M solution of HCl in OEt_2 (3.92 mL, 3.91 mmol) was added at −78 °C to a solution of [TaCp*(NR)Me{η^1-NRC(Me)=CMe$_2$}] (2.50 g, 3.91 mmol) in toluene (50 mL), and the mixture was stirred for 20 min. The color of the mixture changed slowly from yellow to reddish. It was then warmed to room temperature for 2 h, the solvent removed in vacuo, and the resulting residue extracted into *n*-hexane (3 × 20 mL). The solution was filtered, concentrated to ca. 15 mL, and cooled to −40°C to give **2** as orange crystals.

Data for **2** are as follows. Yield: 1.65 g (87%). IR (Nujol mull; ν, cm^{-1}): 1325 (vs), 1262 (m), 1095 (s), 1024 (m), 800 (s), 756 (s), 484 (m), 396 (m), 350 (s). ^{1}H NMR (δ, ppm; in benzene-d_6): 7.04 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, **H**$_3$C$_6$Me$_2$), 6.93 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, **H**$_3$C$_6$Me$_2$), 2.45 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$), 1.73 (s, 15H, C$_5$**Me**$_5$), 0.84 (s, 3H, Ta−**Me**). ^{13}C NMR (δ, ppm; in benzene-d_6): 152.7 (m, C$_i$, **C**$_6$H$_3$Me$_2$), 133.8 (m, C$_o$, **C**$_6$H$_3$Me$_2$), 127.0 (dm, C$_m$, $^1J_{C-H}$ = 160.2 Hz, **C**$_6$H$_3$Me$_2$), 122.5 (d, C$_p$, $^1J_{C-H}$ = 159.7 Hz, **C**$_6$H$_3$Me$_2$), 117.7 (m, **C**$_5$Me$_5$), 42.2 (q, $^1J_{C-H}$ = 121.3 Hz, Ta−**Me**), 18.8 (qd, $^1J_{C-H}$ = 126.4 Hz, $^3J_{C-H}$ = 5.0 Hz, 2,6-**Me**$_2$C$_6$H$_3$), 10.6 (q, $^1J_{C-H}$ = 127.7 Hz, C$_5$**Me**$_5$). Anal. Calcd for $C_{19}H_{27}ClNTa$: C, 46.96; H, 5.61; N, 2.88. Found: C, 46.71; H, 5.37; N, 2.75.

[TaCp*(OC$_6$H$_3$Me$_2$)Me{N(2,6-Me$_2$C$_6$H$_3$)}] (3). In a sealed NMR tube, [TaCp*Me{N(2,6-Me$_2$C$_6$H$_3$)}{η^1-N(2,6-Me$_2$C$_6$H$_3$)C(Me)=CMe$_2$}] (0.11 g, 0.17 mmol) was treated with 2,6-Me$_2$C$_6$H$_3$OH (0.02 g, 0.17 mmol) in benzene-d_6 (0.6 mL) at 60 °C for 3 days. The reaction was monitored by ^{1}H NMR spectroscopy until quantitative conversion of the imido alkenylamido complex into **3** with simultaneous appearance of the imine RN=CMeCHMe$_2$ was observed.

Data for **3** are as follows. ^{1}H NMR (δ, ppm; in chloroform-*d*): 7.95 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, **H**$_3$C$_6$OMe$_2$), 7.00 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, **H**$_3$C$_6$Me$_2$), 6.67 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, **H**$_3$C$_6$Me$_2$), 6.54 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, **H**$_3$C$_6$OMe$_2$), 2.27 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$), 2.18 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$O), 2.02 (s, 15H, C$_5$**Me**$_5$), 0.87 (s, 3H, Ta−**Me**). ^{13}C NMR (δ, ppm; in chloroform-*d*): 159.5 (m, C$_i$, **C**$_6$H$_3$OMe$_2$), 153.6 (m, C$_i$, **C**$_6$H$_3$Me$_2$), 132.7 (m, C$_o$, **C**$_6$H$_3$Me$_2$), 128.2 (dm, C$_m$, $^1J_{C-H}$ = 156.1 Hz, **C**$_6$H$_3$OMe$_2$), 126.7 (dm, C$_m$, $^1J_{C-H}$ = 155.6 Hz, **C**$_6$H$_3$Me$_2$), 126.0 (m, C$_o$, **C**$_6$H$_3$OMe$_2$), 120.4 (d, C$_p$, $^1J_{C-H}$ = 157.5 Hz, **C**$_6$H$_3$OMe$_2$), 120.3 (d, C$_p$, $^1J_{C-H}$ = 160.7 Hz, **C**$_6$H$_3$Me$_2$), 116.8 (m, **C**$_5$Me$_5$), 32.0 (q, $^1J_{C-H}$ = 121.8 Hz, Ta−**Me**), 19.4 (qd, $^1J_{C-H}$ = 125.8 Hz, $^3J_{C-H}$ = 5.5 Hz, 2,6-**Me**$_2$C$_6$H$_3$), 17.7 (qd, $^1J_{C-H}$ = 126.3 Hz, $^3J_{C-H}$ = 5.5 Hz, 2,6-**Me**$_2$C$_6$H$_3$O), 10.9 (q, $^1J_{C-H}$ = 127.2 Hz, C$_5$**Me**$_5$).

[TaCp*X(NR){η^2-C(Me)=O}] (R = 2,6-Me$_2$C$_6$H$_3$; X = Me (4), Cl, (6)). In a typical experiment, a $CDCl_3$ solution of **1** or **2** (1.07 mmol) was placed into an NMR tube, the argon atmosphere replaced by CO, and the tube sealed. The reaction was monitored by NMR spectroscopy at −50°C until no further change was observed. Formation of the corresponding η^2-acyl complexes **4** and **6** was confirmed by their ^{1}H and ^{13}C NMR spectra.

Data for **4** are as follows. ^{1}H NMR (δ, ppm; in chloroform-*d*, −50 °C): 6.76 (m, 3H, **H**$_3$C$_6$Me$_2$), 3.13 (s, 3H, **Me**−CO), 2.24 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$), 1.95 (s, 15H, C$_5$**Me**$_5$), 0.59 (s, Ta−**Me**). ^{13}C{^{1}H} NMR (δ, ppm; in $CDCl_3$, −50 °C): 320.4 (s, O**C**−Me), 153.5 s, 131.4 s, 126.4 s, 119.8 s (C$_i$, C$_o$, C$_m$, C$_p$, **C**$_6$H$_3$Me$_2$), 113.3 (s, **C**$_5$Me$_5$), 30.5 (s, **Me**−CO), 23.3 (s, Ta−**Me**), 19.1 (s, 2,6-**Me**$_2$C$_6$H$_3$), 10.9 (s, C$_5$**Me**$_5$).

Data for **6** are as follows. ^{1}H NMR (δ, ppm; in chloroform-*d*, −40 °C): 6.75 (m, 3H, **H**$_3$C$_6$Me$_2$), 3.12 (s, 3H, **Me**−CO), 2.26 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$), 2.02 (s, 15H, C$_5$**Me**$_5$). ^{13}C{^{1}H} NMR (δ, ppm; in chloroform-*d*, −40 °C): 316.1 (s, O**C**−Me), 152.0 s, 131.1 s, 126.4, 121.5 s (C$_i$, C$_o$, C$_m$, C$_p$, **C**$_6$H$_3$Me$_2$), 116.1 (s, **C**$_5$Me$_5$), 30.4 (s, **Me**−CO), 19.1 (s, 2,6-**Me**$_2$C$_6$H$_3$), 11.1 (s, C$_5$**Me**$_5$).

[{TaCp*Me(NR)}$_2${μ-η^2-OC(Me)=C(Me)O}] (R = 2,6-Me$_2$C$_6$H$_3$ (5)). A solution of **1** (1.00 g, 2.15 mmol) in toluene (25 mL) was placed in an ampule under a CO atmosphere (1 atm) and then sealed. The reaction mixture was stirred for 16 h, and the resulting brown solution was evaporated to dryness. Recrystallization from *n*-hexane at −40 °C afforded **5** as brown crystals in 80% yield (1.70 g).

Data for **5** are as follows. IR (Nujol mull; ν, cm^{-1}): 1587 (w), 1331 (s), 1198 (m), 1026 (w), 804 (m), 495 (d), 352 (d). ^{1}H NMR (δ, ppm; in benzene-d_6): 6.93 (m, 3H, **H**$_3$C$_6$Me$_2$), 2.42 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$), 2.17 [s, 6H, OC(**Me**)=C(**Me**)O], 1.78 (s, 15H, C$_5$**Me**$_5$), 0.78 (s, 3H, Ta−**Me**). ^{13}C{^{1}H} NMR (δ, ppm; in benzene-d_6): 154.3 [s, O**C**(Me)=**C**(Me)O], 142.1 s, 132.7 s, 126.8 s, 121.1 s (C$_i$, C$_o$, C$_m$, C$_p$, **C**$_6$H$_3$Me$_2$), 116.4 (s, **C**$_5$Me$_5$), 28.8 [s, OC(**Me**)=C(**Me**)O], 19.3 (s, 2,6-**Me**$_2$C$_6$H$_3$), 17.7 (s, Ta−**Me**), 10.7 (s, C$_5$**Me**$_5$). Anal. Calcd for $C_{42}H_{60}N_2O_2Ta_2$: C, 51.11; H, 6.13; N, 2.84. Found: C, 50.80; H, 5.90; N, 2.70.

[TaCp*Cl(O){η^2-C(Me)=NC$_6$H$_3$Me$_2$}] (7). A toluene (25 mL) solution of **2** (1.00 g, 2.06 mmol) was placed into an ampule under a CO atmosphere (1 atm) and then sealed. The reaction mixture was stirred for 12 h, and the resulting orange-yellow solution was cooled to −40 °C overnight to give white crystals, which were subsequently isolated by filtration, washed with n-hexane (2 × 10 mL), and identified as **7**.

Data for **7** are as follows. Yield: 0.90 g (85%). IR (Nujol mull; ν, cm^{-1}): 1628 (s), 1023 (m), 906 (s), 352 (w), 317 (w). ^{1}H NMR (δ, ppm; in benzene-d_6): 6.85 (m, 3H, **H**$_3$C$_6$Me$_2$), 2.09 (s, 3H, **Me**C=NC$_6$H$_3$Me$_2$), 1.99 (s, 15H, C$_5$**Me**$_5$), 1.97 s, 1.61 s (6H, 2,6-**Me**$_2$C$_6$H$_3$). ^{13}C{^{1}H} NMR (δ, ppm; in chloroform-*d*): 236.8 (s, Me**C**=NC$_6$H$_3$Me$_2$), 139.6 s, 131.7 s, 128.7 s, 128.6 s, 127.8 s, 127.0 s (several phenyl carbons, **C**$_6$H$_3$Me$_2$), 117.6 (s, **C**$_5$Me$_5$), 20.8 (s, **Me**C=NC$_6$H$_3$Me$_2$), 18.2 s, 17.9 s (2,6-**Me**$_2$C$_6$H$_3$), 11.1 (s, C$_5$**Me**$_5$). MS (EI, 70 eV): *m/e* 513 ([M$^+$], 1), 498 (0.4), 367 (1.8), 363 (1.0), 351 (0.6), 146 (100). Anal. Calcd for $C_{20}H_{27}NOClTa$: C, 46.75; H, 5.30; N, 2.73. Found: C, 46.52; H, 5.25; N, 2.63.

[TaCp*Cl$_2$(η^2-CMe$_2$O)] (8). A C_6D_6 (0.6 mL) solution of TaCp*Cl$_2$Me$_2$ (0.08 g, 0.19 mmol) was placed in a NMR tube under a CO atmosphere (1 atm), and then the tube was sealed. The color of the mixture changed quickly from green to orange, and the reaction was monitored by ^{1}H NMR spectroscopy until TaCp*Cl$_2$Me$_2$ was totally transformed into the η^2-acetone complex **8**.

Data for **8** are as follows. ^{1}H NMR (δ ppm, in benzene-d_6): 1.95 (s, 6H, C**Me**$_2$O), 1.68 (s, 15H, C$_5$**Me**$_5$).

[TaCp*Cl{N(2,6-Me$_2$C$_6$H$_3$)}{OC(Me)=CMe$_2$}], 9. [TaCp*ClMe{η^2-CMe$_2$N(2,6-Me$_2$C$_6$H$_3$)}] (0.08 g, 0.15 mmol) and C_6D_6 (0.6 mL) were placed in a NMR tube under a CO atmosphere (1 atm), and then the tube was sealed. The reaction was instantaneous, and the formation of **9** in quantitative yield was confirmed by NMR.

Data for **9** are as follows: IR (Nujol mull; ν, cm^{-1}): 1673 (m), 1337 (vs), 1250 (m), 1180 (vs), 1095 (m), 1025 (m), 980 (w), 951 (m), 817 (s), 760 (s), 342 (s). ^{1}H NMR (δ, ppm; in chloroform-*d*): 6.90 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, **H**$_3$C$_6$Me$_2$), 6.60 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, **H**$_3$C$_6$Me$_2$), 2.26 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$), 2.13 (s, 15H, C$_5$**Me**$_5$), 1.91 [m, 3H, O(**Me**)C=CMe$_2$], 1.7 m, 1.5 m [6H, **Me**$_2$C=C(Me)O]. ^{13}C NMR (δ, ppm; in chloroform-*d*): 151.8 (m, C$_i$, **C**$_6$H$_3$Me$_2$), 149.5 [m, O**C**(Me)=CMe$_2$], 133.3 (m, C$_o$, **C**$_6$H$_3$Me$_2$), 126.4 (dm, C$_m$, $^1J_{C-H}$ = 155.7 Hz, **C**$_6$H$_3$Me$_2$), 121.4 (d, C$_p$, $^1J_{C-H}$ = 156.8 Hz, **C**$_6$H$_3$Me$_2$), 119.3 (m, **C**$_5$Me$_5$), 107.2 [m, Me$_2$**C**=C(Me)], 18.8 [m, **Me**$_2$C=C(Me)O], 18.9 [m, **Me**$_2$C=C(Me)O], 18.2 (qd, $^1J_{C-H}$ = 126.3 Hz, $^3J_{C-H}$ = 5.3 Hz, 2,6-**Me**$_2$C$_6$H$_3$), 17.4 [m, O(**Me**)C=CMe$_2$], 10.8 (q, $^1J_{C-H}$ = 127.9 Hz, C$_5$**Me**$_5$).

[TaCp*Me{N(2,6-Me$_2$C$_6$H$_3$)}{OC(Me)=CMe$_2$}], 10. A toluene (40 mL) solution of [TaCp*Me$_2$(η^2-CMe$_2$N(2,6-Me$_2$C$_6$H$_3$)}] (1.50 g, 2.96 mmol) was placed in a Schlenk tube under a CO atmosphere (1 atm), and the mixture then was stirred at room temperature for 2 h. The resulting green solution was evaporated to dryness and the residue recrystallized from cold *n*-hexane (20 mL) to give **10** as a green microcrystalline solid.

Data for **10** are as follows. Yield: 1.44 g (91%). IR (Nujol mull; ν, cm^{-1}): 1676 (m), 1335 (vs), 1258 (w), 1179 (vs), 1096 (m), 1026 (m), 985 (w), 947 (m), 816 (s), 758 (s), 494 (m), 353

Table 3. Crystal and Experimental Data and Structure Refinement Procedures for Compounds 7 and 11

	7	11
formula	$C_{20}H_{27}ClNOTa$	$C_{29}H_{39}N_2Ta$
cryst habit	prismatic	prismatic
color	white	yellow
temp, K	293(2)	293(2)
cryst size, mm	0.35 × 0.32 × 0.28	0.37 × 0.32 × 0.25
symmetry	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
unit cell determn	least-squares fit from 25 rflns	
unit cell dimens		
a, b, c, Å	8.913(2), 15.550(3), 14.430(3)	17.476(3), 8.662(2), 18.568(9)
β, deg	96.74(3)	105.51(2)
V, Å^3	1986.1(7)	2708.4
Z	4	4
D_{calcd}, g cm^{-3}	1.718	1.463
mw	513.83	596.57
$F(000)$	1008	1200
μ, cm^{-1}	56.75	40.76
scan mode	ω scans; $\theta_{max} = 37°$	ω scans; $\theta_{max} = 27°$
no. of rflns		
measd	3659	6121
indep	3260 ($R_{int} = 0.1456$)	5824 ($R_{int} = 0.0580$)
no. of data/restraints/params	3247/0/217	5810/0/300
range of hkl	$0 < h < 10, -18 < k < 0, -16 < l < 16$	$-22 < h < 0, 0 < k < 11, -23 < l < 23$
std rflns	2 rflns every 120 min, no variation	
R indices ($I > 2\sigma(I)$)	R1 = 0.0369, wR2 = 0.0831	R1 = 0.0344, wR2 = 0.0804
R indices (all data)	R1 = 0.0785, wR2 = 0.1325	R1 = 0.0653, wR2 = 0.1460
max peak in final diff map, e/Å^3	0.725	1.671
min peak in final diff map, e/Å^3	−0.683	−1.776
goodness of fit on F^2	1.297	1.204
weighting scheme[a]	$w = 1/[\sigma^2(F_o^2) + (0.010P)^2 + 12.188P]$	$w = 1/[\sigma^2(F_o)^2 + (0.040P)^2 + 3.663P]$

[a] $P = (F_o^2 + 2F_c^2)/3$.

(m). ^{1}H NMR (δ, ppm; in benzene-d_6): 7.09 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, **H**$_3$C$_6$Me$_2$), 6.75 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, **H**$_3$C$_6$Me$_2$), 2.42 (s, 6H, 2,6-**Me**$_2$C$_6$H$_3$), 1.90 [m, 3H, O(**Me**)C=CMe$_2$], 1.81 (s, 15H, C$_5$**Me**$_5$), 1.74 [m, 3H, **Me**$_2$C=C(Me)O], 1.57 [m, 3H, **Me**$_2$C=C(Me)O], 0.84 (s, 3H, Ta−**Me**). ^{13}C NMR (δ, ppm; in benzene-d_6): 153.9 (m, C$_i$, **C**$_6$H$_3$Me$_2$), 149.0 [m, O**C**(Me)=CMe$_2$], 132.5 (m, C$_o$, **C**$_6$H$_3$Me$_2$), 126.6 (dm, C$_m$, $^1J_{C-H}$ = 152.5 Hz, **C**$_6$H$_3$Me$_2$), 120.1 (d, C$_p$, $^1J_{C-H}$ = 157.5 Hz, **C**$_6$H$_3$Me$_2$), 116.4 (m, **C**$_5$Me$_5$), 105.9 [m, Me$_2$**C**=C(Me)O], 28.8 (q, $^1J_{C-H}$ = 120.8 Hz, Ta−Me), 19.05 [m, **Me**$_2$C=C(Me)O], 18.99 [m, **Me**$_2$C=C(Me)O], 18.90 (qd, $^1J_{C-H}$ = 126.6 Hz, $^3J_{C-H}$ = 5.5 Hz, 2,6-**Me**$_2$C$_6$H$_3$),-17.4 [m, O(**Me**)C=CMe$_2$], 10.8 (q, $^1J_{C-H}$ = 127.3 Hz, C$_5$**Me**$_5$). Anal. Calcd for $C_{24}H_{36}NOTa$: C, 53.82; H, 6.79; N, 2.61. Found: C, 53.31; H, 2.55; N, 6.67.

[TaCp*X{N(2,6-Me$_2$C$_6$H$_3$)}{η^2-C(Me)=N(2,6-Me$_2$C$_6$H$_3$)}] (X = Me (11), Cl (12), OC(Me)=CMe$_2$ (13)). A sample of **1**, **2**, or **10** (1.07 mmol) was dissolved in 25 mL of toluene in a Schlenk tube. After the addition of a toluene (10 mL) solution of CN-2,6-Me$_2$C$_6$H$_3$ (0.14 g, 0.07 mmol), the color of the mixture changed quickly from brown-green to orange. The reaction mixture was stirred for 4 h at room temperature and evaporated to dryness. The oily residue was extracted into n-hexane (2 × 10 mL) and cooled to −40 °C to give **11**−**13** as yellow crystals.

Data for **11** are as follows. Yield 0.54 g (85%). IR (Nujol mull; ν, cm^{-1}): 1620 (s), 1333 (s), 980 (w), 480 (w), 354 (w). ^{1}H NMR (δ, ppm; in benzene-d_6): 6.85 (m, 6H, 2 **H**$_3$C$_6$Me$_2$), 2.40 [sbr, 6H, 2,6-**Me**$_2$H$_3$C$_6$N=C(Me)], 2.11 (s, 3H, **Me**C=NC$_6$H$_3$-Me$_2$), 1.89 (s, 15H, C$_5$**Me**$_5$), 1.79 s, 1.64 s (6H, 2,6- **Me**$_2$H$_3$-C$_6$N=Ta), 0.61 (s, 3H, Ta−**Me**). ^{13}C{^{1}H} NMR (δ, ppm; in chloroform-d): 241.6 [s, **C**(Me)=NC$_6$H$_3$Me$_2$], 154.7 s, 141.3 s, 130.6 s, 128.4 s, 126.4 s, 125.7 s, 119.2 s (several phenyl carbons, **C**$_6$H$_3$Me$_2$), 112.7 (s, **C**$_5$Me$_5$), 20.3 (s, **Me**C=NC$_6$H$_3$Me$_2$), 19.1 [s, 2,6-**Me**$_2$H$_3$C$_6$N=C(Me)], 18.3 s, 18.0 s (2,6-**Me**$_2$H$_3$C$_6$N=Ta), 17.7 (s, Ta−**Me**), 10.9 (s, C$_5$**Me**$_5$). MS (EI, 70 eV): m/e 596 ([M$^+$], 12.30), 581 (12.9), 435 (14.2), 146 (77.8), 105 (100). Anal. Calcd for $C_{29}H_{39}N_2Ta$: C, 58.38; H, 6.59; N, 4.70. Found: C, 57.80; H, 6.50; N, 4.60.

Data for **12** are as follows. Yield: 0.83 g (86%). IR (Nujol mull; ν, cm^{-1}): 1626 (s), 1328 (s), 976 (w), 485 (w), 358 (w), 306 (m). ^{1}H NMR (δ, ppm; in benzene-d_6): 6.80 (m, 6H, 2 **H**$_3$C$_6$Me$_2$), 2.67 sbr, 2.25 sbr [6H, 2,6-**Me**$_2$H$_3$C$_6$N=C(Me)], 1.81 s, 1.79 s (6H, 2,6-**Me**$_2$H$_3$C$_6$N=Ta), 2.06 [s, 3H, **Me**C=NC$_6$H$_3$-Me$_2$], 1.90 (s, 15H, C$_5$**Me**$_5$). ^{13}C{^{1}H} NMR (δ, ppm; in chloroform-d): 240.4 [s, **C**(Me)=NC$_6$H$_3$Me$_2$], 153.0 s, 140.3 s, 129.7 s, 128.5 s, 127.7 s, 126.2 s, 120.3 s (several phenyl carbons, **C**$_6$H$_3$Me$_2$), 115.0 (s, **C**$_5$Me$_5$), 20.7 (s, **Me**C=NC$_6$H$_3$Me$_2$), 19.1 s, 18.8 s [2,6-**Me**$_2$H$_3$C$_6$N=C(Me)], 18.4 s, 18.1 s (2,6-**Me**$_2$H$_3$-C$_6$N=Ta), 20.7 (s, **Me**C=NC$_6$H$_3$Me$_2$), 11.1 (s, C$_5$**Me**$_5$). MS (EI, 70 eV): m/e 619 ([M$^+$], 0.3), 582 (0.3), 472 (0.6), 435 (0.6), 146 (100), 105 (48.6). Anal. Calcd for $C_{28}H_{36}N_2ClTa$: C, 54.51; H, 5.88; N, 4.54. Found: C, 54.70; H, 6.10; N, 4.45.

Data for **13** are as follows. Yield: 0.60 g (84%). IR (Nujol mull; ν, cm^{-1}): 1678 (m), 1630 (s), 1332 (s), 1250 (m), 1180 (m), 1026 (m), 982 (w), 817 (s), 760 (s), 480 (w), 340 (s). ^{1}H NMR (δ, ppm; in benzene-d_6): 7.08−6.69 (m, 6H, 2 **H**$_3$C$_6$Me$_2$), 2.40 [sbr, 6H, 2,6-**Me**$_2$C$_6$H$_3$N=C(Me)], 2.09 (s, 3H, **Me**C=NC$_6$H$_3$-Me$_2$), 1.96 (s, 15H, C$_5$**Me**$_5$), 1.90 [m, 3H, OC(**Me**)=CMe$_2$], 1.84 [m, 3H, **Me**$_2$C=C(Me)O], 1.82 (s, 6H, 2,6-**Me**$_2$H$_3$C$_6$N=Ta), 1.49 [m, 3H, **Me**$_2$C=C(Me)O]. ^{13}C NMR (δ, ppm; in benzene-d_6): 247.1 [q, $^2J_{C-H}$ = 6.1 Hz, **C**(Me)=NC$_6$H$_3$Me$_2$], 151.0 [m, O**C**(Me)=CMe$_2$], 154.2 m, 142.5 m (C$_i$, **C**$_6$H$_3$Me$_2$), 130.5 m, 129.6 m (C$_o$, **C**$_6$H$_3$Me$_2$), 128.5 dm, 127.9 dm (C$_m$, $^1J_{C-H}$ = 158 Hz, **C**$_6$H$_3$Me$_2$), 126.0 d, 120.4 d (C$_p$, $^1J_{C-H}$ = 158.5 Hz, **C**$_6$H$_3$-Me$_2$), 115.2 (m, C$_5$**Me**$_5$), 100.4 [m, Me$_2$**C**=C(Me)O], 21.13 (q, $^1J_{C-H}$ = 127.9 Hz, **Me**C=NC$_6$H$_3$Me$_2$), 19.86 [m, **Me**$_2$C=C-(Me)O], 19.84 [m, OC(**Me**)=CMe$_2$], 19.42 [br, 2,6-**Me**$_2$C$_6$H$_3$N=C-(Me)], 18.98 [m, **Me**$_2$C=C(Me)O], 18.7 (qd,$^1J_{C-H}$ = 126.6 Hz, $^3J_{C-H}$ = 4.6 Hz, 2,6-**Me**$_2$H$_3$C$_6$N=Ta), 18.09 (qd, $^1J_{C-H}$ = 127.1 Hz, $^3J_{C-H}$ = 4.9 Hz, 2,6-**Me**$_2$H$_3$C$_6$N=Ta), 11.1 (q, $^1J_{C-H}$ = 126.8 Hz, C$_5$**Me**$_5$). Anal. Calcd for $C_{33}H_{45}N_2OTa$: C, 59.45; H, 6.80; N, 4.20. Found: C, 59.54; H, 6.85; N, 4.12.

Crystal Structure Determination of Compounds 7 and 11. Crystallographic and experimental details of the crystal structure determinations are given in Table 3. Suitable crystals of complexes **7** and **11** were mounted on an Enraf-Nonius CAD 4 automatic four-circle diffractometer with bisecting geometry, equipped with a graphite-oriented monochromator and Mo Kα radiation (λ = 0.710 73 Å). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made.

The structures were solved by direct methods (SHELXS 90)[21] and refined by full-matrix least-squares against F^2 (SHELXL 93).[22] All non-hydrogen atoms were refined anisotropically. In the last cycle of refinement the hydrogen atoms were positioned geometrically and refined using a riding model with fixed thermal parameters ($U = 0.08$ Å^2).

Calculations were carried on an ALPHA AXP (Digital) workstation.

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(22) Sheldrick, G. M. SHELXL 93; University of Göttingen, Göttingen, Germany, 1993.

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Supporting Information Available: Hydrogen atom coordinates (Tables S1-7 and S1-11), anisotropic displacement parameters (Tables S2-7 and S2-11), complete bond distances and angles (Tables S3-7 and S3-11), and final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms (Tables S5-7 and S5-11) for complexes **7** and **11** (9 pages). Ordering information is given on any current masthead page.

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