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Articles

Oxo and Hydroxo Tantalocene Complexes: Synthesis and Reactivity. X-ray Molecular Structures of $[(\eta^5\text{-Cp*})\text{TaCl(OH)}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)]^+\text{Cl}^-$, $(\eta^5\text{-Cp*})\text{TaCl}(=\text{O})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)$, and $[(\eta^5\text{-Cp*})\text{TaCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)]^+\text{PF}_6{}^-$

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Exposure of a THF solution of tantalocene dichloride complexes $(\eta^5\text{-Cp*})\text{TaCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)$ (**1**) and $(\eta^5\text{-Cp*})\text{TaCl}_2(\eta^5\text{-C}_5\text{H}_5)$ (**2**) to the ambient atmosphere for 12 h leads to the formation of new tantalum(V) cationic hydroxo complexes $[(\eta^5\text{-Cp*})\text{TaCl(OH)}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)]^+\text{Cl}^-$ (**3**) and $[(\eta^5\text{-Cp*})\text{TaCl(OH)}(\eta^5\text{-C}_5\text{H}_5)]^+\text{Cl}^-$ (**4**). This oxidation reaction is more rapid under oxygen atmosphere since the hydroxo complexes are obtained in better yields within only 15 min. The hydroxo complexes are easily deprotonated by base to generate oxo complexes **5** and **6**, which, in turn, react with trimethylsilyl triflate, giving the corresponding cationic silylated complexes **7** and **8**. All structures are confirmed by NMR, IR, and X-ray diffraction.

Introduction

The last two decades have witnessed major advances in catalytic oxidation, a challenging field of great importance and value since most synthetic sequences incorporate an oxidation step in one form or another. In nature, the metal-oxo group is involved in many metalloenzyme oxidations, for instance as active species such as iron complexes in cytochrome P450.[1] The mechanism occurs due to the metal center, which transfers the oxygen atom onto the organic molecule. Organometallic chemistry contributed decisively in the synthesis of metal-oxo species, which are widely used as stoichiometric and catalytic oxidants.[2] Among the numerous transition metal-oxo compounds that have been prepared, characterized, and used as catalysts, molybdenum is probably the element that has been most studied as an oxygen atom transfer agent.[3] Indeed, molybdenum complexes bearing a M=O double bond are versatile catalysts in oxidation of many substrates such as phosphines, alkanes, alkenes, and alcohols.[4] Manganese-oxo complexes have also proved to be very effective, in particular in the catalytic epoxidation of allylic alcohols whereas exclusive allylic oxidation in similar conditions occurs with chromium-oxo complexes.[5] Concerning early transition metals, many efforts have been made to synthesize and study the reactivity of such reactive oxo complexes, but almost no results have been yet published on catalytic oxidation reactions.[6] Recently, our group has described a rational synthesis of oxo niobiocene complexes of the type $\text{Cp*}_2\text{NbX}(=\text{O})$ starting from the dichloride species $\text{Cp*}_2\text{NbCl}_2$.[7] To our knowledge, examples of tantalocene complexes of the formula $\text{Cp}_2\text{TaX}(=\text{O})$ (X = one-electron ligand) are very scarce and their reactivity has not been explored.[8] As a continuation of our studies on oxo metals

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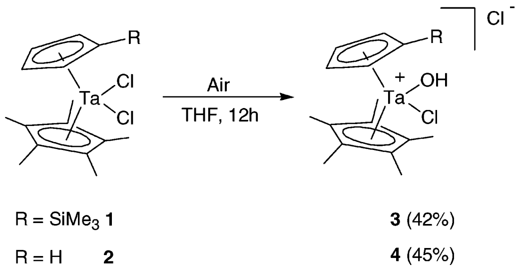
Scheme 1. Air Oxidation of the Tantalocene Dichlorides 1 and 2



of group 5, we report here our results on the formation and the reactivity of new hydroxo and oxo tantalum(V) complexes.

Results and Discussion

In a typical experiment, a THF solution of the dichloride (η^5-Cp*)$TaCl_2$(η^5-$C_5H_4SiMe_3$) (**1**) was exposed to the air for 12 h (Scheme 1). During this time, the color of the solution passed slowly from dark green to orange and a yellow precipitate was formed. Filtration of the resulting yellow suspension afforded the diamagnetic complex **3** in 42% yield. The ^{1}H NMR spectrum of **3** shows the expected singlets for the methyl groups of the permethylcyclopentadienyl ring and of the $SiMe_3$ group. The four monosubstituted cyclopentadienyl ring protons exhibit four signals strongly deshielded at δ 6.00, 6.27, 6.63, and 7.84 ppm. These NMR data are in agreement with a cationic species containing a chiral tantalum center.

Slow evaporation of the reaction mixture in THF gave crystals suitable for X-ray diffraction study. An ORTEP view of **3** is shown in Figure 1. This view shows a typical bent-metallocene structure. The Ta−O bond length of 1.869(4) Å corresponds to a single bond (a comparison of the structural data of oxo and hydroxo tantalocene complexes is given in Table 2 in the Experimental Section).[9] The tantalum atom has a pseudotetrahedral coordination if the centroids of the cyclopentadienyl rings are considered as occupying one unique coordination site.[10] The hydrogen atom is localized on the oxygen atom, and the existence of a hydrogen interaction with the chloride counterion is apparent because of the distance between them (H···Cl(2) 2.36(7) Å, O···Cl(2) 3.007(4) Å).[9] The $SiMe_3$ group lies 0.20(1) Å above the Cp plane in the bisecting plane of the Cl(1)−Ta−O angle. In 1996, on the basis of NMR data Royo et al. have depicted **3**, resulting from the air oxidation of **1** in THF, as an oxo tantalum(V) complex.[11] The hydrogen interaction observed in the solid state as mentioned above may explain the absence of a signal in the ^{1}H NMR and consequently the wrong structural proposition. Moreover, the IR spectrum of **3** is confusing since the OH band, which generally is reported at 3584−3588 cm^{-1} as a sharp and strong peak,[12] occurs as a V-shaped strong peak from 2100 to 2900 cm^{-1} presumably upon this interaction.

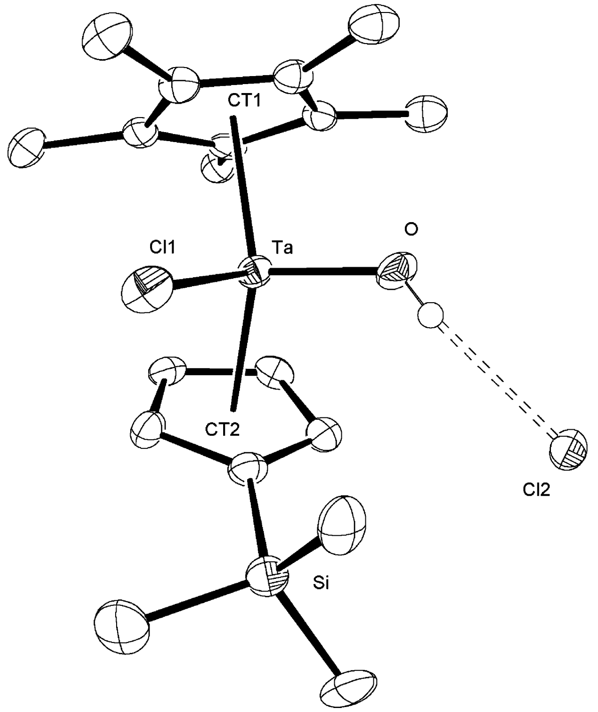


Figure 1. ORTEP view of the hydroxo complex **3**. Hydrogen atoms (except the one that is located on the oxygen atom) are omitted for clarity. Selected bond lengths [Å] and angles [deg] for compound **3**: Ta−O = 1.869(4), Ta−Cl(1) = 2.379(2), Ta−CT(1) = 2.133(5), Ta−CT(2) = 2.093(6); O−Ta−Cl(1) = 99.44(15), CT(1)-Ta−CT(2) = 131.1(2), O−Ta−CT(1) = 103.6(2), O−Ta−CT(2) = 108.3(2).

At this point, it is worth mentioning that this reactivity could be extended to other tantalocene dichlorides such as $Cp^*CpTaCl_2$ (**2**). Thus, air oxidation of compound **2** gave the expected diamagnetic hydroxo product **4** in 45% yield. Nevertheless, under the same conditions, tantalocene dichlorides (η^5-Cp)$_2TaCl_2$ and (η^5-$C_5H_4{}^tBu$)$_2$-$TaCl_2$ led only to degradation species. The permethylcyclopentadienyl ring seems to be crucial for this transformation, probably because of its electron-donating properties, which stabilizes the oxidized form.

The acidic character of the hydroxo complexes **3** and **4** has been exemplified by their reactions with bases such as NEt_3 or KOH. In these conditions, the oxo complexes **5** and **6** were obtained as white powders in good yields (Scheme 2).

The ^{1}H NMR spectra of **5** and **6** show signals for the cyclopentadienyl ring protons less deshielding than those found in the parent cationic compounds. The IR spectra of **5** and **6** exhibit new stretching bands at 807 and 819 cm^{-1} respectively, which can be assigned to the

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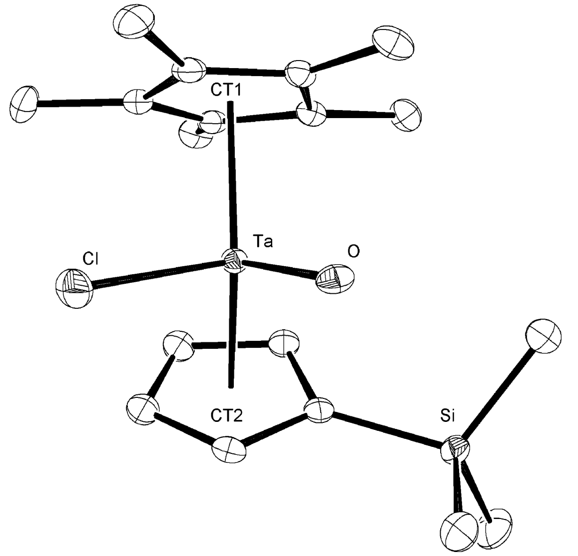
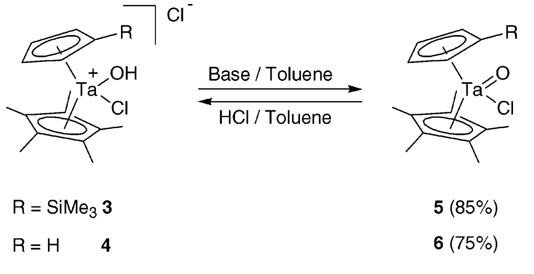


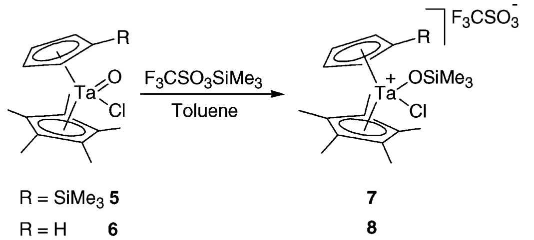
Figure 2. ORTEP view of the oxo complex **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg] for compound **5**: Ta−O = 1.759(2), Ta−Cl = 2.4198((8), Ta−CT(1) = 2.182(3), Ta−CT(2) = 2.168(3); O−Ta−Cl = 96.69(8), CT(1)-Ta−CT(2) = 128.66(11), O−Ta−CT(1) = 108.16(11), O−Ta−CT(2) = 110.05(11).

Scheme 2. Acid−Base Reactivity of the Hydroxo Complexes 3 and 4

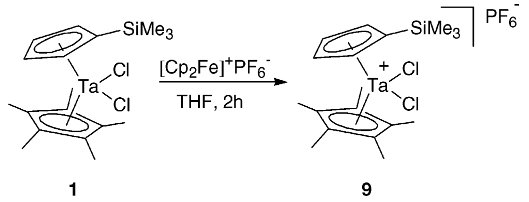


double Ta−O bond, whereas the broad one at 2100−2900 cm^{-1} has disappeared.[8c] The low frequencies of the Ta=O stretch for **5** and **6** with regard to the one observed for (Cp*)$_2$Ta(=O)Cl at 850 cm^{-1} can be explained by the lesser d-electron density on the metal determining the reduced double-bond character of the Ta−O bond. An analogous reversed substituent effect (opposite of that observed for a C=O group) has also been described in the oxo niobium series.[13] Cooling a toluene solution of the tantalum derivative **5** to −30 °C gave suitable crystals for an X-ray diffraction study (Figure 2). The Ta−O bond length of 1.759(2) Å, significantly shorter than in **3** (1.869(4) Å), corresponds to a double bond.[8b] The geometry of the complex **5** remains pseudotetrahedral, with a Ta−CpSiMe$_3$ distance slightly elongated (2.168(3) Å) compared to that in **3** (2.093(6) Å). The SiMe$_3$ group lies 0.148(5) Å above the Cp plane and is rotated nearly 90° from the bisecting plane of the Cl−Ta−O angle. It is noteworthy that the hydroxo complexes **3** and **4** can be quantitatively regenerated by bubbling HCl into a toluene solution of **5** or **6**.

Scheme 3. Reactivity of the Oxo Complexes 5 and 6



Scheme 4. Chemical Oxidation of the Tantalocene Dichloride 1



To illustrate the polarized character ($^{\delta+}$Ta−O$^{\delta-}$) of the Ta=O double bond, we reacted 1 equiv of trimethylsilyl triflate with oxo complexes **5** and **6**. The resulting cationic silylated products **7** and **8** were quantitatively isolated as yellow oils (Scheme 3).

The structures of the complexes **7** and **8** are ascertained by ^{1}H NMR analysis. In both cases, the singlet 9H at δ 0.25 ppm is assigned to the trimethyl silyl group linked to the oxygen atom. The four protons of the cyclopentadienyl ring in **7** appear as four strongly deshielded signals. These observations agree with a cationic tantalum(V) species. Other experiments with alkylated reagents or with the (isolobal H$^+$) cationic-species AuPPh$_3^+$ have been tried, but no reactivity was observed.

To determine the origin of the oxygen in the hydroxo complex **3**, we reacted the dichloride (η^5-Cp*)TaCl$_2$(η^5-C$_5$H$_4$SiMe$_3$) (**1**) with degassed water under argon. No trace of compound **3** was detected, and only degradation products were formed. Then, the cationic dichloride **9** was synthesized by ferricenium oxidation of **1** (Scheme 4), and its reactivity toward water was investigated: no formation of **3** was observed. On the contrary, it was found that when **1** reacts with dry oxygen (H$_2$O < 50 ppm), the reaction is complete within 5−10 min, as evidenced by the immediate color change to orange-yellow and the observation of a yellow precipitate. Filtration of the resulting yellow suspension afforded complex **3** in 71% yield. These experiments prove that the oxygen in the hydroxo tantalocene complexes **3** and **4** comes from O$_2$ and not from residual water.

To obtain additional insight into the oxidation mechanism, a ^{1}H NMR monitoring of the reaction of **1** with O$_2$ in CDCl$_3$ was conducted (Figure 3). The spectrum recorded a few seconds after the addition of O$_2$ shows a broad signal at δ 2.12 ppm, which can be assigned to the SiMe$_3$ group of the paramagnetic starting material **1**, and sharp signals of **3**, which already emerge from the baseline. As the reaction time increases (3 min), the signals of **3** increase and the broad signal of **1** decreases. The last spectrum recorded shows that **1** is completely consumed after only 6 min. These NMR results indicate that the initial product of oxidation of **1** is the hydroxo tantalocene **3**.

Although the oxidation mechanism remains unclear, we propose a radical pathway between O$_2$ and the d^1

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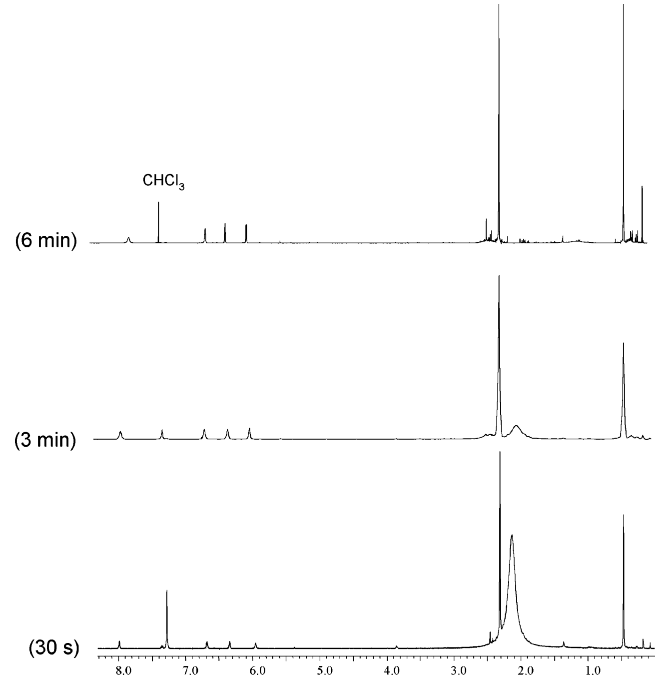

Figure 3. ^{1}H NMR spectra (298 K) recorded after different time intervals of a CDCl$_3$ solution of **1** under O$_2$ atmosphere.

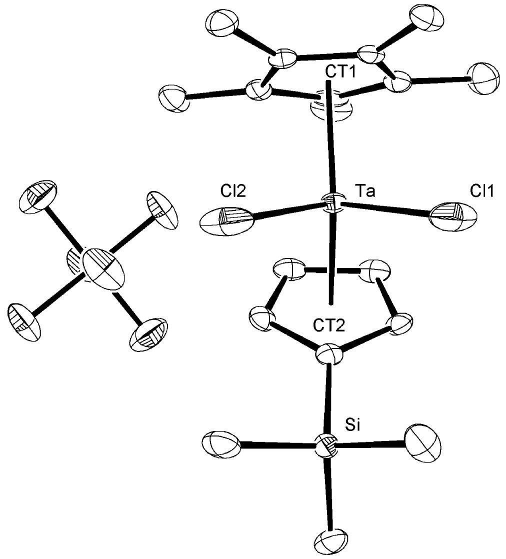

Figure 4. ORTEP view of the cationic complex **9**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg] for compound **9**: Ta−Cl(1) = 2.3242(11), Ta−Cl(2) = 2.3307(11), Ta−CT(1) = 2.123(4), Ta−CT(2) = 2.094(4); Cl(1)−Ta−Cl(2) = 97.84(6), CT(1)−Ta−CT(2) = 131.63(10), Cl(1)−Ta−CT(1) = 105.60(10), Cl(2)−Ta−CT(1) = 105.17(10), Cl(1)−Ta−CT(2) = 105.75(11), Cl(2)−Ta−CT(2) = 105.95(10).

complex (η^5-Cp*)TaCl$_2$(η^5-C$_5$H$_4$SiMe$_3$) (**1**) leading to the formation of a μ-peroxo unstable species which, after an homolytic cleavage, reacts with H$^\bullet$ to give **3**. At this stage, we can also speculate on the origin of H$^\bullet$, but we favor it being from a "sacrificed" amount of starting material rather than from residual water or from the solvent. Indeed the ^{1}H NMR analysis of the crude reaction mixture confirms that a partial degradation of **1** occurs. The O$_2$ oxidation reaction of **1**, conducted in dry conditions (i.e. flame-dried vessel, dry THF, dry O$_2$), leads to the hydroxo complex **3** in 71% yield as reported above. On the other hand, the use of wet THF (1% of water) decreases the yield by half (water has a tendency to degrade **3**). Finally this oxidation occurs whatever the solvent used (THF, CH$_2$Cl$_2$, CHCl$_3$, toluene), and if it is conducted in deuterated solvent (CDCl$_3$), no change of the OH stretching band is observed in the IR spectrum of the hydroxo tantalum complex so formed.

At this point we should mention that the one-electron-oxidized form of **1** (so-called **9**) has been fully characterized by NMR and X-ray diffraction. The ^{1}H NMR spectrum shows two 2H signals located at δ 6.53 and 6.79 ppm, which correspond to the four cylopentadienyl protons. Cooling a toluene solution of the tantalum derivative **9** to −30 °C gave suitable crystals for an X-ray diffraction study (Figure 4). The crystallographic data for **9** can be compared with those depicted for the parent neutral dichloride tantalocene (η^5-Cp*)TaCl$_2$(η^5-C$_5$H$_4$SiMe$_3$) (**1**).[11] Both molecules have the typical bent-metallocene structure with the tantalum atom lying in a pseudotetrahedral coordination if the centroids of the cyclopentadienyl rings are considered as occupying one unique coordination site.[10] The Ta−Cl distances in the cationic complex **9** (2.3307(11) and 2.3242(11) Å) are significantly shorter than in the neutral species **1** (2.447(3) and 2.418(3) Å) because of the mesomeric effect of the chloride atom due to the electronic deficiency of the metallic center. The Cl(1)−Ta−Cl(2) angle for **1** has a value of 85.3(1)° as expected for d^1 complexes, whereas the Cl(1)−Ta−Cl(2) angle is greatly more open in **9** (97.84(6)°), in agreement with values found in the literature for d^0 metallocenes.[14]

Conclusion

This study described a new route to cationic hydroxo tantalum(V) species by air oxidation of tantalocene dichloride complexes. The hydroxo complexes are easily deprotonated to generate the corresponding oxo complexes, which in turn can be either protonated back or silylated. Preliminary experiments to ascertain the mechanism for the formation of the tantalocene hydroxo compounds have shown that the oxygen of the hydroxyl group draws its origin from O$_2$ and not from water. In addition, a ^{1}H NMR study has proved that the hydroxo complex is the initial product formed when a solution of tantalocene dichloride is exposed to O$_2$ or to the ambient atmosphere. Further investigations to fully understand the mechanism of this reaction are in progress.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified argon. The solvents were dried by the appropriate procedure and distilled under argon immediately before use. Standard Schlenk techniques and conventional glass vessels were employed. Elemental analyses were carried out with a EA 1108 CHNS-O FISONS. Infrared spectra were obtained with a Bruker IFS 66v and a Perkin-Elmer 1600 FTIR instrument; abbreviations: w (weak), s (strong). Nuclear magnetic resonance spectra were recorded on Bruker 300 MHz Avance and on Bruker 300 MHz Avance

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Table 1. Crystallographic Data for Compounds 3, 5, and 9

	3	**5**	**9**
formula	$[\mathrm{C_{18}H_{29}ClOSiTa}]^+\mathrm{Cl}^-$	$\mathrm{C_{18}H_{28}ClOSiTa}$	$\mathrm{C_{18}H_{28}Cl_2SiTaPF_6}$
M	541.35	504.9	669.31
T, K	110(2)	110(2)	110(2)
cryst syst	tetragonal	monoclinic	monoclinic
space group	I_1/a	$P2_1/n$	$P2_1/c$
a, Å	20.0697(6)	9.2512(1)	8.7871(2)
b, Å		17.5808(3)	17.1558(4)
c, Å	25.8902(8)	12.0875(2)	15.6060(4)
β, deg		106.209(1)	98.767(1)
V, Å^3	10428.4(5)	1887.81(5)	2325.11(10)
Z	16	4	4
$F(000)$	4256	992	1304
D_{calc}, g/cm^3	1.379	1.776	1.912
λ, Å	0.71073	0.71073	0.71073
μ, mm^{-1}	4.468	6.027	5.128
$\sin(\theta)/\lambda$ max; Å^{-1}	0.65	0.65	0.65
index ranges h	−26; 26	−12; 10	−11; 11
k	−19; 23	−22; 22	−21; 21
l	−33; 24	−15; 15	−16; 20
RC = reflns collected	21628	15539	13881
IRC = independent RC	5949	4316	5312
	$R(\mathrm{int}) = 0.0750$	$R(\mathrm{int}) = 0.0241$	$R(\mathrm{int}) = 0.0490$
IRCGT = IRC $[I > 2\sigma(I)]$	4146	3919	4239
no. of data	5949	4316	5312
no. of restraints	0	0	0
no. of params	216	207	267
R for IRCGT	R1[a] = 0.0401 wR2[b] = 0.0874	R1[a] = 0.0251 wR2[b] = 0.0573	R1[a] = 0.0303 wR2[b] = 0.0622
R for IRC	R1[a] = 0.0756 wR2[b] = 0.0980	R1[a] = 0.0293 wR2[b] = 0.0589	R1[a] = 0.0460 wR2[b] = 0.0669
goodness-of-fit[c]	0.999	1.102	1.000
largest diff peak and hole; e Å^{-3}	1.626 and −0.934	0.739 and −1.395	0.989 and −1.777

[a] $\mathrm{R1} = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $\mathrm{wR2} = [\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0443P)^2]$ for **3**, $w = 1/[\sigma^2(F_o^2) + 3.06P + (0.0278P)^2]$ for **5**, $w = 1/[\sigma^2(F_o^2) + 0.00P + (0.0239P)^2]$ for **9** where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. [c] Goodness of fit $= [\sum w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 3, 5, [Cp*$_2$Ta(OH)Cl]$^+$OTf$^-$, and Cp*$_2$Ta(=O)H[8b,9]

	3	**5**	[Cp*$_2$Ta(OH)Cl]$^+$OTf$^-$	Cp*$_2$Ta(=O)H
Ta−O	1.869(4)	1.759(2)	1.853(8)	1.69(4)
Ta−Cl(1)	2.379(2)	2.4198(8)	2.343(4)	
Ta−H(1)				1.74
Ta−CT(1)[a]	2.133(5)	2.182(3)	2.339(11)	2.160
Ta−CT(2)[b]	2.093(6)	2.168(3)	2.346(15)	2.166
O−Ta−Cl(1)	99.44(15)	96.69(8)	96.4(3)	
O−Ta−H(1)				76.4
CT(1)−Ta−CT(2)	131.1(2)	128.66(11)	138.2(5)	139.4

[a] CT(1) is the centroid of the Cp* ring. [b] CT(2) is the centroid of the $\mathrm{C_5H_4SiMe_3}$ ring for **3** and **5**.

spectrometers at 500 MHz for ^{1}H, 202 MHz for ^{31}P, and 75 MHz for ^{13}C. The chemical shifts are reported in ppm relative to SiMe$_4$. (η^5-Cp*)TaCl$_2$(η^5-C$_5$H$_4$SiMe$_3$) (**1**)[11] and (η^5-Cp*)TaCl$_2$(η^5-C$_5$H$_5$) (**2**)[15] were prepared according to literature methods.

Synthesis of [(η^5-Cp*)TaCl(OH)(η^5-C$_5$H$_4$R)]$^+$Cl$^-$: R = SiMe$_3$ (3), R = H (4). Method a. Solutions of **1** (0.5 g, 0.95 mmol) or **2** (0.5 g, 1.10 mmol) in 30 mL of THF were stirred under air atmosphere for 12 h. The resulting yellow suspension was filtered, and the solid washed with 2 × 5 mL of THF, dried under vacuum, and identified as **3** or **4**.

Method b. Solutions of **1** (0.5 g, 0.95 mmol) or **2** (0.5 g, 1.10 mmol) in 10 mL of THF are placed in a 50 mL flask under inert atmosphere. Argon was purged and replaced by dioxygen, and the solutions were stirred for 15 min. The resulting yellow suspension was filtered, and the solid washed with 2 × 5 mL of THF, dried under vacuum, and identified as **3** or **4**.

Method c. 5 (0.5 g, 0.99 mmol) or **6** (0.5 g, 1.15 mmol) was solved in 40 mL of toluene. By bubbling HCl a yellow precipitate appeared and was filtered, and the solid washed with 2 × 5 mL of THF, dried under vacuum, and identified as **3** or **4**.

The data for **3** follow (0.21 g, 42% yield, method a; 0.36 g, 71% yield, method b; 0.32 g, 60% yield, method c). ^{1}H NMR (δ ppm, in CDCl$_3$): 0.35 (s, 9H, Si*Me*$_3$), 2.22 (s, 15H, Cp*), 6.00 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 6.27 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 6.63 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 7.84 (m, 1H, C$_5$*H*$_4$SiMe$_3$). ^{13}C{^{1}H} NMR (δ ppm, in CDCl$_3$): 0.3 (SiMe$_3$), 12.5 (C$_5$*Me*$_5$), 112.1 (Cp), 113.4 (Cp), 125.1 (Cp), 125.2 (*C*$_5$Me$_5$), 127.5 (Cp), 134.2 (Cp). IR (KBr, cm^{-1}): 3058 (s), 2957 (w), 2917 (s), 2876 (w), 2100−2900 (s), 1453 (w), 1417 (w), 1397 (w), 1249 (s), 1174 (w), 1089 (w), 1037 (w), 903 (s), 888 (w), 843 (s), 758 (w), 712 (w), 634 (w). Anal. Calcd for $\mathrm{C_{18}H_{29}Cl_2OSiTa}$: C, 39.94; H, 5.40. Found: C, 40.02; H, 5.50.

The data for **4** follow (0.22 g, 45% yield, method a; 0.33 g, 67% yield, method b; 0.29 g, 59% yield, method c). ^{1}H NMR (δ ppm, in CDCl$_3$): 2.25 (s, 15H, Cp*), 6.65 (s, 5H, Cp). ^{13}C{^{1}H} NMR (δ ppm, in CDCl$_3$): 12.5 (C$_5$*Me*$_5$), 116.1 (*C*$_5$Me$_5$), 125.5 (Cp). IR (KBr, cm^{-1}): 3081 (s), 2951 (w), 2914 (s), 2874 (w), 2100−2900 (s), 1435 (w), 1385 (w), 1026 (w), 865 (s), 717 (s), 599 (w). Anal. Calcd for $\mathrm{C_{15}H_{21}Cl_2OTa}$: C, 38.40; H, 4.51. Found: C, 38.52; H, 4.63.

Synthesis of (η^5-Cp*)TaCl(=O)(η^5-C$_5$H$_4$R): R = SiMe$_3$ (5), R = H (6). Method a. To solutions of **3** (0.5 g, 0.92 mmol) or **4** (0.5 g, 1.06 mmol) in 10 mL of toluene was added 20 mL of a 10% KOH solution. The solution was stirred for 1 h at room temperature, and then the organic phase was extracted by 3 × 20 mL of toluene. The solvent was removed under vacuum, and desired products were obtained as white powders.

Method b. To solutions of **3** (0.5 g, 0.92 mmol) or **4** (0.5 g, 1.06 mmol) in 10 mL of toluene was added an excess of triethylamine. The solution was stirred for 2 h at room temperature. Salts are filtered through a path of Celite, solvent was removed under vacuum, and desired products were obtained as white powders.

The data for **5** follow (0.31 g, 77% yield, method a; 0.39 g, 85% yield, method b). ^{1}H NMR (δ ppm, in CDCl$_3$): 0.32 (s, 9H, Si*Me*$_3$), 2.08 (s, 15H, Cp*), 5.78 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 6.10 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 6.33 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 6.51 (m, 1H, C$_5$*H*$_4$SiMe$_3$). ^{13}C{^{1}H} NMR (δ ppm, in CDCl$_3$): 0.2 (Si*Me*$_3$), 12.1 (C$_5$*Me*$_5$), 110.7 (Cp), 112.5 (Cp), 116.5 (Cp), 120.4 (*C*$_5$Me$_5$), 126.4 (Cp), 126.7 (Cp). IR (KBr, cm^{-1}): 2950 (w), 2922 (s), 2854 (w), 1453 (w), 1412 (w), 1376 (w), 1246 (s), 1177 (w), 1117 (w), 1037 (w), 908 (w), 869 (w), 842 (s), 807 (s), 763 (w), 697 (w), 630 (w). Anal. Calcd for $\mathrm{C_{18}H_{28}ClOSiTa}$: C, 42.81; H, 5.60. Found: C, 42.58; H, 5.66.

The data for **6** follow (0.32 g, 69% yield, method a; 0.34 g, 75% yield, method b). ^{1}H NMR (δ ppm, in CDCl$_3$): 2.12 (s, 15H, Cp*), 6.21 (s, 5H, Cp). ^{13}C{^{1}H} NMR (δ ppm, in CDCl$_3$): 12.0 (C$_5$*Me*$_5$), 113.1 (*C*$_5$Me$_5$), 120.7 (Cp). IR (KBr, cm^{-1}): 2950 (w), 2914 (s), 2874 (w), 1444 (w), 1374 (w), 1026 (w), 860 (s), 819 (s), 694 (s), 598 (w). Anal. Calcd for $\mathrm{C_{15}H_{20}ClOTa}$: C, 41.62; H, 4.66. Found: C, 41.50; H, 4.91.

Synthesis of [(η^5-Cp*)TaCl(OSiMe$_3$)(η^5-C$_5$H$_4$R)]$^+$F$_3$CSO$_3$$^-$: R = SiMe$_3$ (7), R = H (8). To solutions of **5** (0.5 g, 0.99 mmol) or **6** (0.5 g, 1.15 mmol) in 30 mL of toluene was added slowly 1 equiv of F$_3$CSO$_3$SiMe$_3$. The solution was stirred for 4 h at room temperature. Solvent was removed under vacuum, and desired products were obtained as a yellow oil for **7** and a green one for **8**.

The data for **7** follow (0.75 g, 97% yield). ^{1}H NMR (δ ppm, in CDCl$_3$): 0.25 (s, 9H, Si*Me*$_3$), 0.27 (s, 9H, Si*Me*$_3$), 2.33 (s, 15H, Cp*), 6.11 (m, 1H, C$_5$*H*$_4$SiMe$_3$), 6.52 (m, 1H, C$_5$*H*$_4$SiMe$_3$),

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6.83 (m, 1H, $C_5H_4SiMe_3$), 6.96 (m, 1H, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in $CDCl_3$): −0.4 (Si*Me*$_3$), 2.0 (SiMe$_3$), 12.7 (s, C_5Me_5), 115.5 (Cp), 116.9 (Cp), 121.1 (Cp), 127.6 (Cp), 128.3 (C_5Me_5), 143.9 (Cp). Anal. Calcd for $C_{22}H_{37}ClF_3O_4SSi_2Ta$: C, 36.33; H, 5.13; S, 4.41. Found: C, 36.56; H, 5.20; S, 4.26.

The data for **8** follow (0.74 g, 98% yield). ^1H NMR (δ ppm, in $CDCl_3$): 0.25 (s, 9H, Si*Me*$_3$), 2.33 (s, 15H, Cp*), 6.56 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (δ ppm, in $CDCl_3$): 1.9 (Si*Me*$_3$), 12.6 (C_5Me_5), 118.4 (C_5Me_5), 128.1 (Cp). Anal. Calcd for $C_{19}H_{29}ClF_3O_4SSiTa$: C, 45.53; H, 5.64; S, 6.39. Found: C, 45.95; H, 5.18; S, 6.76.

Synthesis of $[(\eta^5\text{-Cp*})TaCl_2(\eta^5\text{-}C_5H_4SiMe_3)]^+PF_6^-$ (9). To a solution of (η^5-Cp*)$TaCl_2$(η^5-$C_5H_4SiMe_3$) (**1**) (0.21 g, 0.40 mmol) in 10 mL of THF was added ferricenium salt $[Cp_2Fe]^+PF_6^-$ (0.13 g, 0.40 mmol), and the solution was stirred for 2 h. The resulting orange suspension was filtered, and the solid was washed with 2 × 2 mL of THF. Orange analytically pure microcrystals of **9** were obtained by recrystallization from THF (0.14 g, 52% yield). ^1H NMR (δ ppm, in $CDCl_3$): 0.40 (s, 9H, Si*Me*$_3$), 2.48 (s, 15H, Cp*), 6.53 (m, 2H, $C_5H_4SiMe_3$), 6.79 (m, 2H, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in $CDCl_3$): 0.0 (Si*Me*$_3$), 13.4 (C_5Me_5), 115.4 (Cp), 130.1 (C_5Me_5), 133.5 (Cp), 135.9 (Cp). $^{31}P\{^1H\}$ NMR (δ ppm, in $CDCl_3$): −143.3 (hept, $^1J_{F-P}$ = 712.6 Hz, PF_6^-). Anal. Calcd for $C_{18}H_{28}Cl_2F_6PSiTa$: C, 32.30; H, 4.22. Found: C, 32.63; H, 4.07.

Crystallographic Data. Single-Crystal X-ray Diffraction Study of 3, 5, and 9. Intensities were collected on an Enraf-Nonius KappaCCD diffractometer at 110 K using Mo Kα radiation. The structures were solved via a Patterson search program[16] and refined with full-matrix least-squares methods[17] based on $|F^2|$ with the aid of the WINGX program.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon atoms were included with a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). The hydrogen atom of the hydroxyl group in **3** was located in the Fourier map and freely refined with $U_{iso}(H) = 1.5U_{eq}(O)$. The essential crystallographic parameters are listed in Table 1.

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Supporting Information Available: Full details of crystallographic analyses in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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