Oxo and Hydroxo Organometallic Complexes of Tantalum: Soluble Molecular Models of Tantalum Oxide

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The tantalum complex [TaCp*Cl_2{2,6(OOC)$_2$py-κ^2O,O}] (**1**) has been synthesized by reaction of [TaCp*Cl_4], Cp* = η^5-C_5Me_5, with 2,6-pyridinedicarboxylic acid. Complex **1** reacts with AgOTf, OTf = trifluoromethylsulfate, to yield the new tantalum carboxylate derivative [TaCp*Cl(OTf){2,6(OOC)$_2$py-κ^2O,O}] (**2**) or with KOH to render the dinuclear oxo compound [TaCp*(μ-O){2,6(OOC)$_2$py-κ^2O,O}]$_2$ (**3**). The reaction of **3** with H_2O and HOTf gives the dinuclear hydroxo derivative [{TaCp*{2,6(OOC)$_2$py-κ^2O,O}}$_2$(μ-OH)$_3$](OTf) (**5**). The structures of complexes **1**, **2**, **3**, and **5** have been established by X-ray diffraction methods.

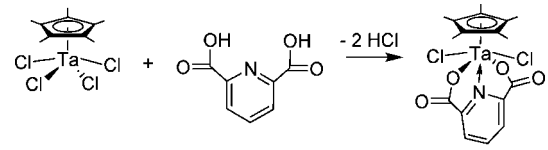
Introduction

Metal oxides are used as catalysts in a number of important industrial processes[1] and therefore, organometallic oxides are of interest because they can be considered models for studying the mechanisms and the kinetics of reactions on oxide surfaces. In recent years, the importance of oxide materials containing tantalum is increasing on account of their potential applications, for example in optical and dielectric materials based on pure Ta_2O_5,[2] ferromagnetic materials in which Ta_2O_5 additives prevent grain growth,[3] heterometallic compositions like the SrBiTaO system for capacitors in computer memory,[4] and photocatalytic materials for photoassisted water decomposition and hydrogen production.[5]

The formation of organometallic oxides can serve also as a model for the synthesis of metal oxides by condensation of hydroxo intermediate derivatives.[6] Moreover, hydroxo complexes have been postulated as key intermediates in several catalytic reactions in which water is a substrate. In this sense, the design and synthesis of water-soluble tantalum compounds is an exciting challenge for inorganic chemists and a matter of outstanding demand from materials chemistry. In this way, we report recently the successful synthesis and solid-state structural characterization of several organometallic complexes of tantalum, the first water-soluble organometallic derivatives of tantalum.[7]

Following our studies in the area, we report here the synthesis of different oxo- and hydroxo tantalum complexes stabilized by a pincer dicarboxylate group. Pincer ligands as most of multidentate ligand systems are expected to bind transition metals in a predictable manner. The steric constraints of such ligands and the nature of the donor atoms can determine to a large extent the stability and properties of the metal complexes.

Scheme 1



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Results and Discussion

The tantalum complex [TaCp*Cl_4] reacts with 2,6-(HOOC)$_2$py in CH_2Cl_2, at room temperature, to render [TaCp*Cl_2-{2,6(OOC)$_2$py-κ^2O,O} (**1**) which was isolated in good yield (73%) as a yellow solid (Scheme 1). Compound **1** is soluble in toluene, THF, or CH_2Cl_2 and less soluble in pentane or Et_2O, it is air stable in the solid state as well as in solution and it does not react with water (in 1:2 molar ratio) even in the presence of NEt_3.

Complex **1** has been characterized by the usual analytical and spectroscopic techniques. Its ^{1}H NMR spectrum exhibits a singlet at 2.55 ppm corresponding to the Cp* ligand and two multiplet signals at 8.31 and 8.38 ppm assigned to the aromatic protons of the dicarboxylate ligand. The ^{1}H and ^{13}C NMR data indicate that both carboxylate groups in the pincer ligand are in the same chemical environment, but do not allow us to

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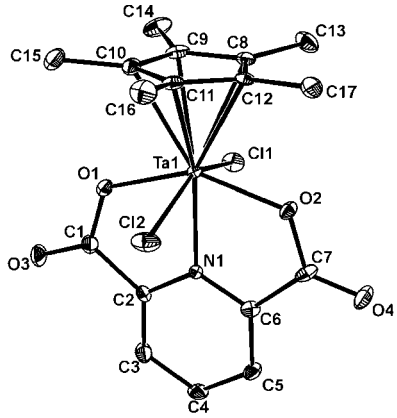


Figure 1. View of molecular diagram of **[TaCp*Cl$_2${2,6-(OOC)$_2$py-κ^2*O,O*}]** (**1**).

Table 1. Some Important Bond Distances (Å) and Angles (deg) in Complexes 1×C$_7$H$_8$ and 2×C$_7$H$_8$

1 × C$_7$H$_8$		**2 × C$_7$H$_8$**	
Bond distances			
Ta(1)−O(1)	2.043(4)	Ta(1)−O(1)	2.018(4)
Ta(1)−O(2)	2.025(4)	Ta(1)−O(3)	2.028(4)
Ta(1)−N(1)	2.159(4)	Ta(1)−N(1)	2.173(5)
Ta(1)−Cl(1)	2.421(2)	Ta(1)−O(31)	2.126(4)
Ta(1)−Cl(2)	2.414(2)	Ta(1)−Cl(1)	2.391(2)
Angles			
O(2)−Ta(1)−N(1)	73.5(2)	O(1)−Ta(1)−O(3)	146.2(2)
O(2)−Ta(1)−Cl(2)	87.5(1)	O(3)−Ta(1)−O(31)	85.5(2)
O(2)−Ta(1)−Cl(1)	86.6(1)	O(1)−Ta(1)−Cl(1)	88.07(1)
C(1)−O(1)−Ta(1)	122.5(4)	C(1)−O(1)−Ta(1)	123.6(4)
O(3)−C(1)−O(1)	124.3(5)	O(2)−C(1)−O(1)	124.2(6)

unequivocally establish the coordination mode of the dicarboxylate ligand.

The ligand coordination mode has been established by an X-ray diffraction study. An ORTEP drawing of **1 × C$_7$H$_8$** is shown in Figure 1, and some selected bond distances and angles are summarized in Table 1.

The structure consists of discrete molecules separated by van der Waals distances. The coordination around the metal is best described as a pseudo-octahedral geometry. The tantalum atom is bonded to the cyclopentadienyl ring in a η^5- mode. On the other hand, the carboxylate ligand is bonded to the metal in a tridentate fashion as a "pincer" ligand, through two oxygen atoms that are placed in the equatorial plane, and to the nitrogen of the pyridinic moiety which is in *trans*- position to the Cp* group. Besides, both chlorine atoms are in the equatorial plane, in *trans*- position to each other. The coordination environment around the tantalum center closely resembles that in [TaCp*Cl$_2${2,6-(OCH$_2$)$_2$py-κ^2*O,O*}].[7]

The Ta(1)−O(1) and Ta(1)−O(2) bond distances (2.043(4) and 2.025(4) Å, respectively) are rather short for tantalum carboxylate complexes.[8] The Ta−N bond length (2.025(4) Å) is comparable to that found in anionic nitrogen ligands.[9]

Complex **1** reacts with AgOTf in CH_2Cl_2, at room temperature, to render the triflate-containing complex [TaCp*Cl(OTf)-{2,6(OOC)$_2$py-κ^2*O,O*}] (**2**) (Scheme 2). Compound **2** has been isolated as a yellow solid that is air stable in the solid state as well as in THF or CH_2Cl_2 solution, even in the presence of an excess of water. It is soluble in CH_2Cl_2 or THF and less soluble in Et_2O or pentane and has been spectroscopically and analytically characterized. The spectroscopic data are consistent with a structure analogous to that of **1** in which one of the two chlorine atoms has been replaced by a triflate group. The ^{1}H NMR spectrum of compound **2** exhibits a singlet at 2.60 ppm corresponding to the Cp* ligand and two multiplet signals at 8.34. and 8.42 ppm assigned to the aromatic protons of the dicarboxylate ligand.

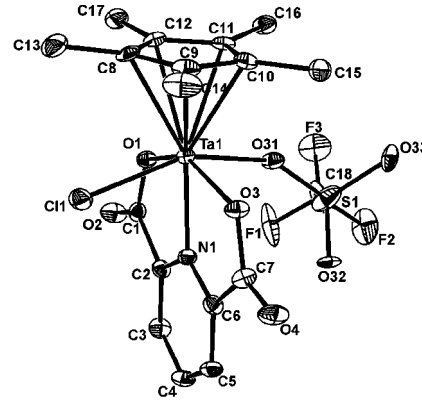
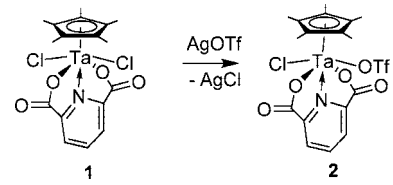


Figure 2. View of molecular diagram of **[TaCp*Cl(OTf){2,6-(OOC)$_2$py-κ^2*O,O*}]** (**2**).

Scheme 2



All attempts to obtain a cationic derivative replacing the triflate ligand in **2** by a water molecule have been, so far, unsuccessful. This behavior is different to that previously found for the bis(triflate) complex [Cp*Ta(OTf)$_2${2,6-(OCH$_2$)$_2$py-κ^2*O,O*}] where the water molecule replaces the triflate group from the coordination sphere of the tantalum center, yielding the corresponding dicationic tantalum derivative [TaCp*{2,6-(OCH$_2$)$_2$py-κ^2*O,O*}(H$_2$O)$_2$]OTf$_2$.[7]

The molecular structure of complex **2 × C$_7$H$_8$** has been confirmed by an X-ray crystallography study. An ORTEP diagram of the molecule and the atom-labeling scheme are shown in Figure 2 and Table 1 displays some selected bond distances and bond angles.

The structure is closely related to that of complex **1**. The geometry around the tantalum atom is pseudo- octahedral. Bond distances from the tantalum atom to the Cp* ligand and to the carboxylate moieties are comparable to that found in compound **1**. The Ta(1)−O(31) bond length (2.126(4) Å) is within the range expected for triflate derivatives of tantalum.[7]

Complex **1** reacts with two molar equivalents of KOH to yield the dinuclear oxo derivative [TaCp*(μ-O){2,6(OOC)$_2$py-κ^2*O,O*}]$_2$ (**3**) which is isolated as an air stable, colorless compound that is partially soluble in dichloromethane or THF and insoluble in toluene, Et_2O or pentane (Scheme 3). It has been characterized by the usual spectroscopic techniques as well as by X-ray diffraction methods.

The ^{1}H NMR spectrum of compound **3** in CD_2Cl_2 at room temperature shows a singlet signal at 1.66 ppm assigned to the Cp* ligand and two multiplet signals at 8.30 and 8.43 ppm assigned to the aromatic protons of the carboxylate ligand. The ^{13}C NMR data indicate a symmetric environment for the di-

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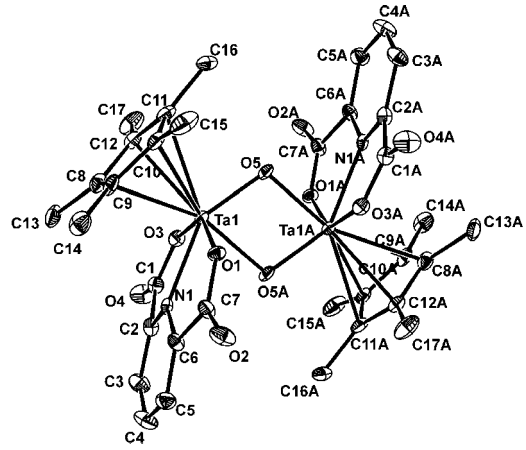


Figure 3. View of molecular diagram of **[TaCp*(μ-O){2,6-(OOC)$_2$py-κ^2*O,O*}]$_2$ (3)**.

Scheme 3

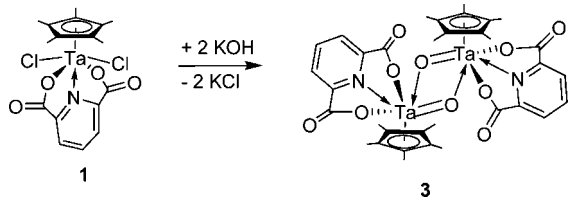


Table 2. Some Important Bond Distances (Å) and Angles (deg) in Complexes 3 × 3CH$_2$Cl$_2$ and 5 × 2 C$_4$H$_8$O

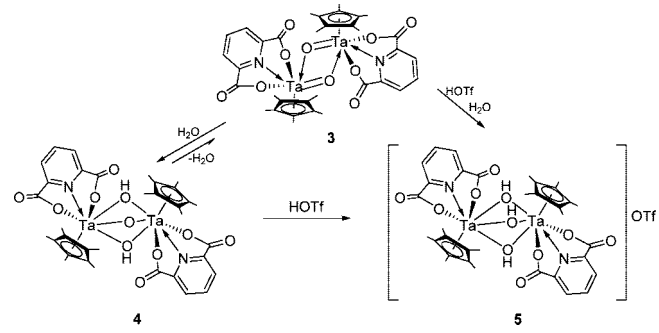
3 × 3CH$_2$Cl$_2$		5 × 2 C$_4$H$_8$O	
Bond distances			
Ta(1)−O(1)	2.066(4)	Ta(1)−O(1)	2.079(9)
Ta(1)−O(3)	2.071(5)	Ta(1)−O(3)	2.113(8)
Ta(1)−N(1)	2.226(6)	Ta(1)−N(1)	2.22(1)
Ta(1)−O(5)	1.869(5)	Ta(1)−O(10)	2.074(7)
Ta(1)−O(5)#1	2.063(4)	Ta(1)−O(9)	2.115(8)
		Ta(1)−O(11)	2.146(7)
		Ta(2)−O(9)	2.099(7)
		Ta(2)−O(10)	2.151(8)
		Ta(2)−O(11)	2.094(7)
Bond angles			
O(5)−Ta(1)−O(5)^a	75.2(2)	Ta(2)−O(9)−Ta(1)	97.5(3)
Ta(1)−O(5)−Ta(1)^a	104.8(2)	Ta(1)−O(10)−Ta(2)	97.2(3)
C(7)−O(1)−Ta(1)	124.8(5)	Ta(2)−O(11)−Ta(1)	96.7(3)
C(1)−O(3)−Ta(1)	125.4(4)	C(1)−O(3)−Ta(1)	125.7(9)
O(1)−Ta(1)−O(3)	142.21(19)	O(1)−Ta(1)−O(3)	139.3(3)
O(5)−Ta(1)−O(1)	102.8(2)		

^{a} Symmetry transformations used to generate equivalent atoms: $-x,-y+1,-z+1$.

carboxylate ligand. In order to unequivocally establish the structure of **3** we carried out an X-ray diffraction study. An ORTEP drawing is depicted in Figure 3 and some selected bond distances and bond angles are collected in Table 2.

The structure determination shows complex **3 × 3CH$_2$Cl$_2$** to be a binuclear tantalum derivative with distorted octahedral coordination geometry around each tantalum center. Two bridging oxo functions produce a flat square Ta(μ-O)$_2$Ta unit. The non linear Ta−O−Ta arrangement found in the structure of **3** is also observed in several trinuclear tantalum oxide species[10] and it is assumed to exist in the structure of the cyclopentadienyl complex [TaCp*Cl$_2$(μ-O)$_2$][11] but these non-

Scheme 4



linear bridges are generally found in complex tantalum oxo systems, simpler systems having linear Ta−O−Ta units.[12] It is to be noted that the Ta−O distances trans to the Cp* group (Ta(1)−O(5)#1, 2.063(4) Å) are much longer than those of the Ta−O bonds placed in the equatorial plane in trans position to the N atom of the pincer carboxylate ligand (Ta(1)−O(5), 1.869(5) Å). This asymmetric disposition is in agreement with the bonding mode depicted in Scheme 3. The small bite angle of the pyridinedicarboxylate ligand probably allows the oxo group to be closer to the metal center. Also, all three donor atoms in the pincer ligand are coordinated to the tantalum in equatorial position with longer bond distances than those found for the monometallic derivatives **1** and **2**. The IR spectrum of **3** shows strong bands at 749 and 714 cm^{-1} which are consistent with the proposed bonding mode.

To study the possibility of obtaining a terminal tantalum-oxo derivative,we carried out the reaction of complex **3**, at room temperature, with an excess with Py or ^{t}BuPy finding out that, under the experimental conditions, compound **3** remains unchanged.

Complex **3** can be considered as a model of tantalum oxide. In this sense, it is interesting to know how it reacts with water since hydrated tantalum oxide is highly acidic and shows interesting catalytic properties.[13] We have studied the reaction by ^{1}H NMR working at a NMR tube-scale. Complex **3** reacts with water in CDCl$_3$ to yield a mixture of **3** and a new tantalum derivative **4** for which we propose the structure depicted in Scheme 4, which fully agrees with the NMR data, the reactivity reported below, and the structural data reported for the complex [TaCp*Cl$_2$(μ-OH)]$_2$(μ-O)].[14] The ratio of complexes **3** and **4** in the mixture depends on the amount of water added. When the reaction of **3** with water is carried out in a 1:1 molar ratio,we get that the ratio of complexes **3** and **4** in the mixture is 2:5. When a large excess of water is added (1:20), the ratio becomes 2:6. However, increasing further the amount of water does not produce a higher conversion of complex **3** into **4**. All attempts to isolate **4** have been, so far, unsuccessful, resulting in all cases in the isolation of **3** as the only compound. This is, probably, due to the low solubility of compound **3** in the most commonly used organic solvents.

The ^{1}H NMR spectrum of complex **4** shows a singlet signal at 1.93 ppm corresponding to the Cp* group, and two multiplet signals at 8.29 and 8.38 ppm which can be assigned to the aromatic protons in the pincer ligand. The ^{1}H NMR spectrum

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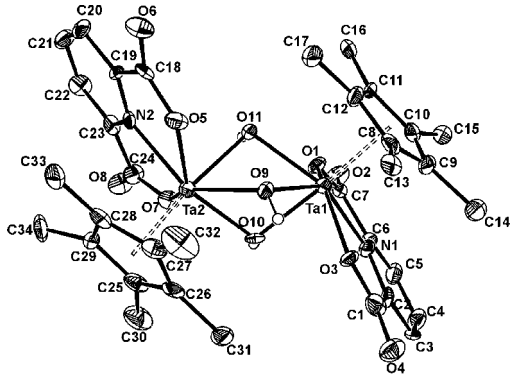

Figure 4. View of molecular diagram of **[{TaCp*{2,6-(OOC)$_2$py-κ^2*O,O*}}$_2$(μ-OH)$_3$](OTf)** (**5**).

shows also a broad signal at 2.85 ppm that can be assigned to the two hydroxilic groups. The ^{13}C NMR spectrum indicates that the two carboxylate groups in the same ligand are in different chemical environment.

Complex **3** reacts with D_2O in $CDCl_3$ to render a mixture that shows a ^{1}H NMR analogous to that reported above, but with no signal at 2.85 ppm. If we add to the mixture an equal molar amount of H_2O, we get that, after 15 min, a small signal at 2.85 ppm appears. After 1 night, this signal reaches an integral corresponding to ca. one proton.

As a possible reaction mechanism, we propose that one of the oxo ligands in **3** takes up a proton from water to form a (μ-OH) ligand and an OH^- group that is incorporated into the coordination sphere of the tantalum atoms to yield **4**. This mechanism is analogous to the one proposed for the hydroxylation of metal oxide surfaces.[15]

Complex **3** reacts with water and triflic acid in 1:1:1 molar ratio to yield the dinuclear tantalum derivative [{TaCp*{2,6-(OOC)$_2$py-κ^2*O,O*}}$_2$(μ-OH)$_3$]OTf (**5**) (Scheme 4). Complex **5** is an air stable and water soluble colorless solid. It is also soluble in dichloromethane or THF and less soluble in pentane. It has been characterized by the usual analytical and spectroscopic techniques as well as by X-ray diffraction.

Moreover, to gain insight as the reaction takes place, we have examined the reactivity of **3** toward HOTf and we have seen that it reacts with one molar equivalent of HOTf in $CDCl_3$ to render a mixture of unidentified compounds. In agreement with the above commented results and this observation, we propose that complex **3** reacts initially with water to form **4** that afterward is protonated by HOTf to render compound **5** (Scheme 4).

The ^{1}H NMR spectrum of complex **5**, in D_2O, shows a singlet signal at 1.80 ppm corresponding to the Cp* group and two multiplet signals at 8.28 and 8.55 ppm assigned to the aromatic protons of the of the carboxylate ligand. The ^{1}H NMR spectrum of **5** in $CDCl_3$ shows, besides the signals corresponding to the Cp* group and the pincer ligand, a broad peak at 5.55 ppm assigned to the hydroxylic protons. The ^{13}C NMR spectrum indicates that the two carboxylate groups in the same ligand are in different chemical environment. The IR spectrum of compound **5** shows an absorption at 3560 cm^{-1} assigned to the OH vibration. Crystals of compound **5**, suitable for an X-ray diffraction study were obtained by diffusion of pentane into a solution of **5** in THF (Figure 4). Complex **5** crystallizes with two molecules of THF. An ORTEP drawing is depicted in Figure 4 and some selected bond distances and bond angles are collected in Table 2.

The molecule is formed by two TaCp*(OOC)$_2$py units bridged by three hydroxo ligands. The Ta···Ta distance is rather short (3.168 Å) probably because of the small size of the bridging ligands. An even shorter Ta−Ta distance is found in **3** (3.1249(6) Å) as well as in other oxo and hydroxo derivatives of tantalum.[16] The Ta−OH bond distances are between 2.074(7) and 2.146(7) Å, which is the expected range for bridging hydroxo derivatives of tantalum.[16] Besides, it is interesting to notice that the Ta(2)−O(9)−Ta(1), Ta(1)−O(10)−Ta(2), and Ta(2)−O(11)−Ta(1) angles are rather small when compared to those in complex **3**. This can indicate an increased π-donation of the oxo ligand in **3** relative to that of the hydroxo group in **5**. Complex **5** is interesting because there are only a few structures reported on organometallic hydroxotantalum complexes.[6,7]

Conclusion

In conclusion, we have synthesized and characterized a series of tantalum(V) complexes with a 2,6-pyridinedicarboxylate group. It seems that the pincer coordination mode enhances the stability of the tantalum dicarboxylate bonding through the chelate effect. This remarkable stability has allowed us the synthesis of a range of organometallic oxo and hydroxo tantalum derivatives that can provided some insight into the bonding and reactivity of tantalum oxide. Moreover, it is noteworthy that the hydroxide complex [{TaCp*{2,6-(OOC)$_2$py-κ^2*O,O*}}$_2$(μ-OH)$_3$](OTf) (**5**) is stable and soluble in water.

Experimental Section

General Procedures. The preparation and handling of described compounds was performed with rigorous exclusion of air and moisture under nitrogen atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere.

The following reagent was prepared by literature procedure: [TaCp*Cl$_4$].[17] The commercially available compounds, 2,6-(HOOC)$_2$py, LiMe in diethyl ether, and HOTf were used as received from Aldrich.

^{1}H and ^{13}C NMR spectra were recorded on a Mercury Varian FT (200 MHz) spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to $SiMe_4$.

IR spectra were recorded in the region 4000−400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer.

Synthesis of [TaCp*Cl$_2${2,6-(OOC)$_2$py-κ^2*O,O*}] (1). To a mixture of [TaCp*Cl$_4$] (1.158 g, 2.52 mmol) and 2,6-(HOOC)$_2$py (0.422 g, 2.52 mmol) was added CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for 15 h. The solvent was removed under vacuum and the residue was extracted with toluene. The solvent was evaporated under vacuum and the residue was washed with pentane to yield 1.015 g (73%) of complex **1**. Cooling a saturated solution **1** to − 20 °C afforded yellow crystals suitable for X-ray diffraction. IR (KBr, $\bar{\nu}$, cm^{-1}): 1718 (vs), 1379 (w), 1300 (vs), 1130 (s), 1111 (m), 1086 (s), 915 (s), 780 (m), 759 (m), 679 (w), 594 (w), 458 (w). ^{1}H NMR ($CDCl_3$, rt, 200 MHz): δ 2.55 (s, 15 H, Cp*), 8.31 (m, 2 H, Ar), 8.38 (m, 1 H, Ar). ^{13}C{^{1}H} NMR: δ 12.9 (s, Cp*), 129.8 (s, Ar), 132.6 (s, Cp*), 144.0 (s, Ar), 146.3

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Table 3. Crystal Data and Structure Refinement for 1×C_7H_8, 2×C_7H_8, 3 × 3CH_2Cl_2, and 5 × 2 C_4H_8O

Complex	1 × C_7H_8	2 × C_7H_8	3x 3CH_2Cl_2	5 × 2 C_4H_8O
Empirical formula	$C_{24}H_{26}Cl_2NO_4Ta$	$C_{25}H_{26}ClF_3NO_7STa$	$C_{37}H_{42}Cl_6N_2O_{10}Ta_2$	C_{43} H_{55} F_3 N_2 O_{16} S Ta_2
Formula weight	644.31	757.93	1249.33	1306.85
Temperature (K)	180(2)	180(2)	180(2)	180(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	8.9484(6)	8.976(1)	11.089(1)	16.414(3)
b (Å)	10.9534(8)	14.689(2)	12.084(1)	13.115(2)
c (Å)	24.748(2)	20.673(2)	17.119(2)	22.553(4)
α (^{o})			102.968(2)	
β (^{o})	98.500(1)	91.598(2)	99.251(2)	106.737(3)
γ (^{o})			92.625(2)	
Volume (Å^3)	2399.0(3)	2724.6(6)	2198.3(4)	4649(1)
Z	4	4	2	4
Density (calculated) (g/cm^3)	1.784	1.848	1.887	1.867
Absorption coefficient (mm^{-1})	4.835	4.274	5.393	4.833
F(000)	1264	1488	1212	2576
Crystal size (mm^3)	0.33 × 0.23 × 0.23	0.33 × 0.24 × 0.11	0.25 × 0.19 × 0.07	0.30 × 0.11 × 0.04
Index ranges	$-10 \le h \le 10$	$-11 \le h \le 11$	$-13 \le h \le 13$	$-18 \le h \le 19$
	$-12 \le k \le 13$	$-18 \le k \le 18$	$-15 \le$ k ′ 15	$-14 \le k \le 15$
	$-28 \le l \le 29$	$-25 \le l \le 24$	$-21 \le l \le 17$	$-26 \le l \le 26$
Reflections collected	15365	15546	15719	19681
Independent reflections	4209 [R(int) = 0.1016]	5523 [R(int) = 0.0488]	8927 [R(int) = 0.0400]	7993 [R(int) = 0.0991]
Data/restraints/parameters	4209/0/295	5523/0/382	8927/0/524	7993/0/614
Goodness-of-fit on F^2	1.042	1.084	1.047	0.971
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0392	R1 = 0.0423	R1 = 0.0421	R1 = 0.0591
	wR2 = 0.0961	wR2 = 0.0880	wR2 = 0.0893	wR2 = 0.1107
R indices (all data)	$R1$ = 0.0432	$R1$ = 0.0648	$R1$ = 0.0641	$R1$ = 0.1177
	$wR2$ = 0.0984	$wR2$ = 0.0956	$wR2$ = 0.0982	$wR2$ = 0.1352
Largest diff. peak and hole	1.745 and −3.327	1.447 and −1.386	1.917 and −1.556	1.309 and −1.222

(s, Ar_{ipso}), 167.4 (s, OOC). Calcd for $C_{17}H_{18}O_4Cl_2NTa$: C, 36.97; H, 3.28; N, 2.67; Found: C, 36.94; H, 3.23; N, 2.70.

Synthesis of [TaCp*Cl(OTf){2,6-(OOC)$_2$py-κ^2O,O}] (2). To a solution of complex **1** (0.229 g, 0.414 mmol) in 15 mL of dichloromethane was added AgOTf (0.106 g, 0.414 mmol), and the suspension was stirred overnight, at room temperature. After that, the mixture was filtered and the solvent removed under vacuum. The residue was washed with pentane to afford a yellow solid that was characterized as **2** (0.214 g, 78%). Yellow crystals of **2** can be obtained by cooling a saturated toluene solution to −20 °C. IR (KBr, $\bar{\nu}$, cm^{-1}): 1728 (vs), 1349 (s), 1298 (vs), 1235 (s), 1210 (s), 1198 (s), 1160 (s), 1117 (m), 1080 (s), 1030 (w), 976 (s), 916 (m), 751 (m), 679 (w), 634 (s), 596 (w), 459(w). ^{1}H NMR ($CDCl_3$, rt, 200 MHz): δ 2.60 (s, 15 H, Cp*), 8.34 (m, 2 H, Ar), 8.42 (m, 1 H, Ar). ^{19}F NMR: δ −77.4. ^{13}C{^{1}H} NMR: δ 12.5 (s, Cp*), 129.6 (s, Ar), 134.1 (s, Cp*), 145.7 (s, Ar), 146.9 (s, Ar_{ipso}), 166.7 (s, OOC). Calcd for $C_{18}H_{18}O_7F_3SClNTa$: C, 32.47; H, 2.72; N, 2.10; S, 4.81. Found: C, 32.84; H, 2.95; N, 2.13; S, 4.90.

Synthesis of [TaCp*(μ-O){2,6-(OOC)$_2$py-κ^2O,O}]$_2$ (3). To a solution of complex **1** (0.375 g, 0.679 mmol) in THF (5 mL) was added a solution of KOH (0.076 g, 1.35 mmol) in water (5 mL). The mixture was stirred, at room temperature, for 24 h. After that, the mixture of solvents was evaporated to dryness and the residue extracted with CH_2Cl_2. The solvent was removed under vacuum and the residue washed with pentane to yield a white compound that was identified as **3** (0.224 g, 66%). Colorless crystals of complex **3** can be obtained from CH_2Cl_2 at − 24 °C. IR(KBr, $\bar{\nu}$, cm^{-1}): 1698 (vs), 1598 (m), 1566 (s), 1437 (s), 1397 (s), 1319 (s), 1258 (w), 1161 (m), 1073 (m), 921 (w), 846 (m), 749 (s), 714 (s), 643 (w), 593 (w). ^{1}H NMR ($CDCl_3$, rt, 200 MHz): δ 1.66 (s, 30 H, Cp*), 8.30 (m, 4 H, Ar), 8.43 (m, 2 H, Ar). ^{13}C{^{1}H} NMR: δ 10.9 (s, Cp*), 124.5 (s, Cp*), 127.45 (s, Ar), 144.3 (s, Ar), 148.9 (s, Ar_{ipso}), 166.7 (s, OOC). ^{1}H NMR (CD_2Cl_2, rt, 200 MHz): δ 1.66 (s, 30 H, Cp*), 8.30 (m, 4 H, Ar), 8.43 (m, 2 H, Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 10.8 (s, Cp*), 124.5 (s, Cp*), 127.8 (s, Ar), 144.8 (s, Ar), 148.7 (s, Ar_{ipso}), 166.8 (s, OOC). Calcd for $C_{34}H_{36}O_{10}N_2Ta_2$: C, 41.06; H, 3.65; N, 2.81. Found: C, 40.55; H, 3.54; N, 2.85.

Reaction of [TaCp*(μ-O){2,6-(OOC)$_2$py-κ^2O,O}]$_2$ with Water. To a suspension of complex **3** (0.011 g, 0.011 mmol) in $CDCl_3$ (0.8 mL) was added water (0.19 μL, 0.011 mmol) and it was stirred at room temperature until complete solution (30 min). The ^{1}H NMR was recorded indicating that the solution contains a 2:5 mixture of complex **3** and a new compound characterized as **4**: ^{1}H NMR ($CDCl_3$, rt, 400 MHz): δ 1.93 (s, 30 H, Cp*), 2.85 (br, 2 H, OH), 8.29 (m, 2 H, Ar), 8.38 (m, 4 H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.0 (s, Cp*), 125.0 (s, Cp*), 126.5 (s, Ar), 127.0 (s, Ar), 143.3 (s, Ar), 148.2 (s, Ar_{ipso}), 149.4 (s, Ar_{ipso}), 166.1 (s, OOC), 166.7 (s, OOC). To the NMR tube containing the mixture reported above was added a second molar equivalent of water (0.19 μL) and after 30 min. the ^{1}H NMR was recorded showing a ratio 2:5.6 of **3** and **4** in the mixture. After that an excess of water was added to the above NMR tube (3.42 μL) and after 30 min. the ^{1}H NMR was recorded showing that the ratio of **3** and **4** in the mixture was 2:6.

Synthesis of [{TaCp*{2,6-(OOC)$_2$py-κ^2O,O}}$_2$(μ-OH)$_3$](OTf) (5). To a solution of **3** (0.104 g, 0.209 mmol) in CH_2Cl_2 was added water (1.9 μL) and then triflic acid (9.2 μL, 0.104 mmol). After this, the solvent was evaporated to dryness and the residue washed with cool pentane to yield a white solid that was characterized as **5** (0.098 g, 81%). Colorless crystals of complex **5** were obtained by slow diffusion of pentane into a THF solution of **5**. IR(KBr, $\bar{\nu}$, cm^{-1}): 3560 (m), 1700 (vs), 1433 (w), 1345 (s), 1282 (s), 1252 (s), 1163 (s), 1077 (w), 1031 (s), 933 (w), 918 (w), 771 (w), 748 (m), 680 (w), 637 (m), 516 (w). ^{1}H NMR (D_2O, rt, 200 MHz): δ 1.66 (t, 8 H, THF), 1.80 (s, 30 H, Cp*), 3.53 (t, 8 H, THF), 8.28 (m, 4 H, Ar), 8.55 (m, 2 H, Ar).^{19}F NMR (D_2O): −79.4 (OTf). ^{13}C{^{1}H} NMR (D_2O): δ 10.3 (s, Cp*), 25.1 (s, THF), 67.9 (s, THF), 128.1 (s, Ar), 128.1 (s, Cp*), 129.0 (s, Ar), 147.0 (s, Ar), 147.3 (s, Ar_{ipso}), 149.2 (s, Ar_{ipso}), 168.4 (s, OOC), 169.1 (s, OOC). ^{1}H NMR ($CDCl_3$, rt, 200 MHz): δ 1.84 (t, 8 H, THF), 2.03 (s, 30 H, Cp*), 3.73 (t, 8 H, THF), 5.55 (br, OH, 3 H), 8.44 (m, 4 H, Ar), 8.66 (m, 2 H, Ar). ^{19}F NMR ($CDCl_3$): −78.2. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.7 (s, Cp*), 26.2 (s, THF), 68.6 (s, THF), 128.3 (s, Cp*), 128.9 (s, Ar), 130.7 (s, Ar), 147.1 (s, Ar), 148.7 (s, Ar_{ipso}), 148.2 (s, Ar_{ipso}), 166.2 (s, OOC), 168.4 (s, OOC). Anal. calcd for $C_{43}H_{55}O_{16}N_2SF_3Ta_2$: C, 39.42; H, 4.37; N, 2.24; Found: C, 39.52; H, 4.23; N, 2.14. pH (44 mg/5 mL, 20 °C) = 2.88.

X-Ray Structure Determination for 1 × C_7H_8, 2 × C_7H_8, 3 × $3CH_2Cl_2$, and 5 × 2 C_4H_8O. Data were collected on a Bruker X8 APEX II CCD-based diffractometer, equipped with a graphite monochromated Mo Kα radiation source ($\lambda = 0.71073$ Å). The crystal data, data collection, structural solution, and refinement parameters are summarized in Table 3. Data were integrated using SAINT[18] and an absorption correction was performed with the program SADABS.[19] A successful solution by direct method provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in the alternating series of least-squares cycles and difference Fourier maps.[20] All non-hydrogen atoms were refined with anisotropic displacement coefficients unless specified otherwise. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

In the case of **1** × C_7H_8 and **2** × C_7H_8, there is also a solvent molecule of toluene in the asymmetric unit. For **3** × $3CH_2Cl_2$, the asymmetric unit consists in one molecule of complex and three solvent molecules of dichloromethane. For **5** × 2 C_4H_8O, there are also two solvent molecules of THF in the asymmetric unit. In the case of **2** × C_7H_8, the triflate ligand is disordered over two positions in a 50:50 ratio and there is not possible refine all atoms anisotropically.

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Supporting Information Available: Text, tables, figures, and CIF files giving full experimental data for the crystallographic studies of compounds **1**, **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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