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# Synthesis and Reactivity of Monocyclopentadienyl Tantalum Complexes with Pincer Dialkoxide Ligands

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The new tantalum dialkoxide complexes $Cp^*TaCl_2(OCH_2)_2py$ (**1**), *trans*-$Cp^*TaMe_2(OCH_2)_2py$ (**2**), and *cis*-$Cp^*TaMe_2(OCH_2)_2py$ (**3**) ($Cp^* = \eta^5\text{-}C_5Me_5$; $(OCH_2)_2py$ = 2,6-pyridinedimethoxide) have been synthesized. The molecular structures of complexes **1** and **2** have been studied by X-ray diffraction methods. The reaction of complex **3** with carbon monoxide renders $Cp^*Ta(\eta^2\text{-}Me_2CO)(OCH_2)_2py$ (**4**), while with isocyanides yields the respective azatantalacyclopropanes $Cp^*Ta(\eta^2\text{-}Me_2CNxylyl)(OCH_2)_2py$ (**6**) (xylyl = 2,6-dimethylphenyl) and $Cp^*Ta(\eta^2\text{-}Me_2CN^tBu)(OCH_2)_2py$ (**7**). The molecular structure of complex **4** has been established by X-ray diffraction. The coordinated ketone in **4** can be reduced to 2-propanol in the presence of water. On the other hand, compound **3** reacts with triflic acid (HOTf) to render the corresponding cationic derivative $[Cp^*TaMe(OCH_2)_2py]OTf$ (**8**).

## Introduction

The modulation of the electronic and steric properties of the metal center through modification of the ancillary ligands is one of the main issues in organometallic chemistry. In this search of new ligands to tune the reactivity of the metal center, alkoxide and aryloxide groups are among the most widely used in organometallic and coordination chemistry.[1] Alkoxides and aryloxides are extremely versatile ligands for transition metals since adequate substitution patterns allow for an important modification of the steric and electronic requirements.[2] Accordingly, they have been utilized extensively in the synthesis of group 4[3] and group 5[4] metal complexes. More recently, chelating ligands are the focus of much attention as ancillary ligand frameworks for group 4 and 5 metal centers.[5] In particular, tantalum complexes are known to mediate a number of interesting catalytic transformations including olefin polymerization,[6] metathesis of imines and olefins,[7] or arene hydrogenation,[8] among others. Despite these facts, a somewhat limited range of ancillary ligands have been employed in order to modulate the reactivity of the tantalum center.

In the last years we have developed studies based on the synthesis of several families of cyclopentadienyl-containing early transition metal complexes with different classes of assisted ligands, namely, pyrimidinethiolate[9] or pyridyl-alkoxide.[10] Now we are interested

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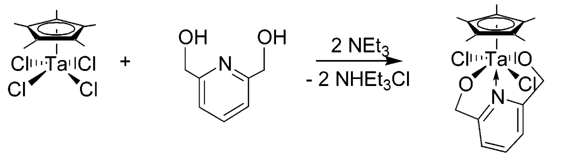
**Scheme 1**



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in the study of the reactivity of monocyclopentadienyltantalum derivatives toward dialkoxide ligands, and herein we report the synthesis and characterization of some assisted dialkoxide monocyclopentadienyltantalum complexes as well as some interesting insertion reactions along with the formation of a cationic complex.

## Results and Discussion

The tantalum complex Cp*TaCl$_4$ reacts with 2,6-bis(hydroxymethyl)pyridine, in the presence of 2 equiv of NEt$_3$, to yield complex **1**, which was isolated in good yield (77%) as a white solid (Scheme 1).

Complex **1** has been characterized by the usual analytical and spectroscopic techniques. Its $^1$H NMR spectrum exhibits resonances at 2.31 (s), 5.77 (s), 6.03 (m), and 6.63 (m) ppm attributable to the pentamethylcyclopentadienyl ligand, the methylene groups, and the aromatic protons of the dialkoxide ligand, respectively. The ratio of the integrals is consistent with the proposed stoichiometry. The multiplicity and number of the methylene proton signals point to a trans disposition of the chloride ligands and to the coordination of the dialkoxide ligand through both oxygen atoms and the pyridinic nitrogen atom in trans position to the cyclopentadienyl ligand (see Scheme 1) in a pseudo-octahedral environment for the tantalum center. In this way, the dialkoxide ligand shows a tridentate mer-coordination, and it is bonded to the metal center in a "pincer" fashion. The $^{13}$C NMR spectrum is also in agreement with the proposed disposition.

The "pincer" ligands constitute an emergent class of potentially terdentate ligands that have been explored mainly with late transition metals.[11] Surprisingly, given the ubiquity of the alkoxide ligands in early transition metal chemistry, only a few dialkoxides with this geometry have been reported.[12]

The proposed coordination mode has been confirmed by an X-ray diffraction study. An ORTEP drawing of **1** is shown in Figure 1, and 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 pseudo-octahedral geometry. The tantalum atom is bonded to the cyclopentadienyl ring in an $\eta^5$-mode. On the other hand, the alkoxide ligand is bonded to the metal in a tridentate fashion as a "pincer" ligand, through both oxygen atoms that are placed in the equatorial plane and the nitrogen of the pyridinic moiety, which is in trans position to the Cp* group. In addition, both chlorine atoms are in the equatorial plane, in trans position to each other. The Ta(1)−O(1) and Ta(1)−O(2) bond distances (1.952(3) and 1.936(3) Å, respectively) are within the normal range for tantalum alkoxide complexes.[13] The Ta−N bond length (2.173(4) Å) is rather short and comparable to that found in anionic nitrogen ligands.[14]

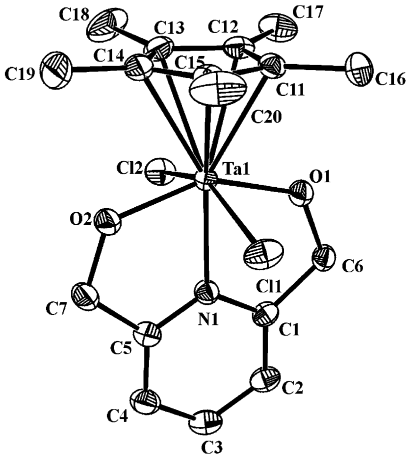
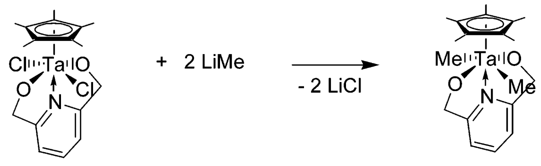


**Figure 1.** Perspective ORTEP drawing of the molecular structure of complex **1**.

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

| | |
|---|---|
| Ta(1)−C(12) | 2.446(4) |
| Ta(1)−Cl(1) | 2.463(1) |
| Ta(1)−C(13) | 2.481(5) |
| Ta(1)−O(2) | 1.936(3) |
| Ta(1)−O(1) | 1.952(3) |
| Ta(1)−N(1) | 2.173(4) |
| Ta(1)−C(11) | 2.448(4) |
| Ta(1)−C(15) | 2.485(5) |
| Ta(1)−Cl(2) | 2.498(1) |
| Ta(1)−C(14) | 2.503(5) |
| O(1)−C(6) | 1.400(5) |
| O(2)−C(7) | 1.402(6) |
| O(2)−Ta(1)−O(1) | 148.0(1) |
| O(2)−Ta(1)−N(1) | 73.8(1) |
| O(1)−Ta(1)−N(1) | 74.2(1) |
| C(6)−O(1)−Ta(1) | 124.8(3) |
| C(7)−O(2)−Ta(1) | 125.2(3) |

**Scheme 2**



1 2

Reaction of complex **1** with 2 equiv of LiMe yields the corresponding alkyl-alkoxide derivative **2** (see Scheme 2). Complex **2** was isolated as an air-sensitive white solid, very soluble in toluene or THF and less soluble in pentane.

The $^1$H NMR spectrum of compound **2** shows singlet signals at −0.13, 2.06, and 5.43 ppm attributable to the methyl groups bonded to the tantalum atom, the pen-

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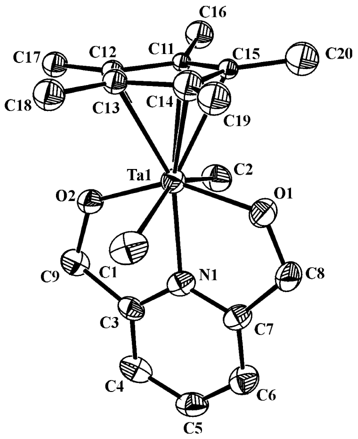


**Figure 2.** Perspective ORTEP drawing of the molecular structure of complex **2**.

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

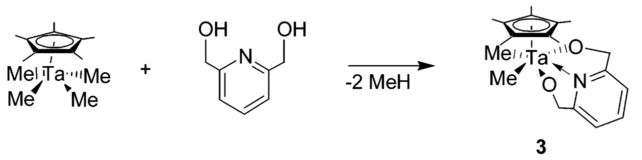
| | |
|---|---|
| Ta(1)−O(1) | 1.953(5) |
| Ta(1)−O(2) | 1.970(5) |
| Ta(1)−N(1) | 2.168(6) |
| Ta(1)−C(2) | 2.269(8) |
| Ta(1)−C(1) | 2.270(8) |
| Ta(1)−C(14) | 2.41(2) |
| Ta(1)−C(15) | 2.47(1) |
| Ta(1)−C(13) | 2.48(2) |
| Ta(1)−C(11) | 2.48(1) |
| O(1)−Ta(1)−O(2) | 148.2(2) |
| O(1)−Ta(1)−N(1) | 73.8(2) |
| O(2)−Ta(1)−N(1) | 74.4(2) |
| O(1)−Ta(1)−C(2) | 86.5(3) |
| O(2)−Ta(1)−C(2) | 86.0(3) |
| C(8)−O(1)−Ta(1) | 124.2(4) |
| C(9)−O(2)−Ta(1) | 124.2(5) |

tamethylcyclopentadienyl ligand, and the methylene groups of the dialkoxide ligand, respectively. On the other hand, the resonances corresponding to the aromatic protons are located at 6.06 and 6.67 ppm as multiplet signals. The fact that the methylene protons give rise to a singlet signal suggests a trans disposition of the methyl groups and to the coordination of the dialkoxide ligand through both oxygen atoms and the pyridinic nitrogen atom in trans position to the cyclopentadienyl ligand (see Scheme 1), in an analogous way to that found for complex **1**.

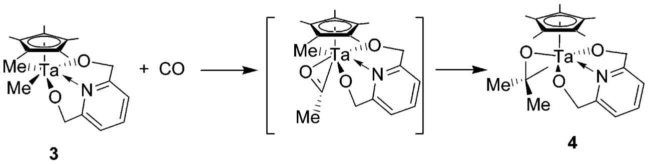
A single-crystal X-ray analysis of compound **2** confirmed the proposed structure. The geometry around the tantalum atom is analogous to that described for complex **1**. An ORTEP diagram of the structure of complex **2** is shown in Figure 2. Selected bond distances and angles are summarized in Table 2. The Ta(1)−O(1) and Ta(1)−O(2) bond distances (1.953(5) and 1.970(5) Å, respectively) are slightly longer than that found in complex **1** but are also within the expected range for tantalum alkoxide complexes.[13] On the other hand, the Ta(1)−C(1) and Ta(1)−C(2) bond lengths are comparable to that found in other tantalum-alkyl complexes.[15]

To study the reactivity of the Ta−C bonds in complex **2** with unsaturated organic molecules, we carried out some NMR scale experiments. Surprisingly, complex **2** does not react with xylylisocyanide or carbon monoxide, at room temperature in C$_6$D$_6$, over a period of 48 h.

**Scheme 3**



**Scheme 4**



Another general way of to achieve the synthesis of alkoxide derivatives of early transition metals is the reaction of metal alkyl complexes with alcohols to yield the corresponding alkane and the alkoxide complex. The proposed mechanism for the protonolysis of carbon−metal bonds requires initial donation of an oxygen lone pair to the metal center.[16] This methodology has been proven useful in the synthesis of alkyl alkoxide tantalum complexes. Thus, the tantalum complex Cp*TaMe$_4$ reacts with 2,6-bis(hydroxymethyl)pyridine in 1:1 ratio according to Scheme 3 to render complex **3**, which is isolated in 72% yield. Previously, we have described an analogous reaction using the titanium complex Cp*TiMe$_3$ as starting material.[17]

Complex **3** is an air sensitive, white solid, rather soluble in THF or toluene and less soluble in pentane or Et$_2$O. The $^1$H NMR spectrum shows singlet signals at 0.00 and 2.00 ppm, which are assigned to the methyl groups bonded to the tantalum center and to the pentamethylcyclopentadienyl ligand, respectively, while the methylene protons give rise to two doublet signals centered at 5.44 and 5.60 ppm (this is in contrast to the singlet observed in complexes **1** and **2**). On the other hand, aromatic protons are located at 6.13 and 6.58 ppm as multiplet signals.

According to the spectroscopic data, we propose complex **3** to be a monomer in which two oxygen atoms of the dialkoxide ligand and the pyridine nitrogen atom are bonded to the tantalum center in the equatorial plane of a symmetrical pseudo-pentagonal pyramid environment. As in complexes **1** and **2**, the tripodal alkoxide ligand behaves as a “pincer” ligand. An alternative pseudo-octahedral environment with the methyl ligands located in both equatorial and axial coordination sites in a dynamic exchange cannot be definitively excluded, although no change of the $^1$H NMR spectra took place upon lowering the temperature from room temperature to −80 °C.

In contrast to the behavior of **2**, complex **3** reacts readily with an excess of CO at room temperature to give a $\eta^2$-acetone complex, Cp*Ta($\eta^2$-Me$_2$CO)(OCH$_2$)$_2$py (**4**). This complex was isolated in good yield (74%) as an orange crystalline solid. Its $^1$H NMR spectrum shows singlet signals at 1.91 and 2.03 ppm in a 2:5 ratio assigned to the methyl groups of the coordinated ketone

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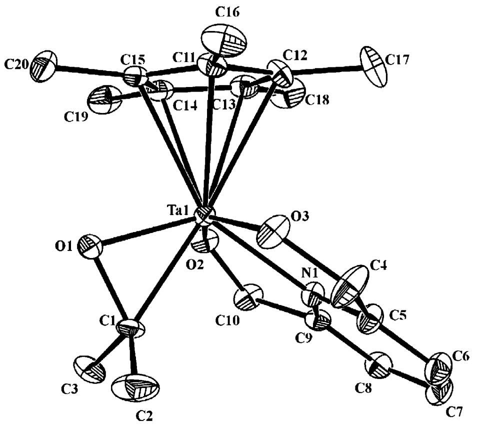


**Figure 3.** Perspective ORTEP drawing of the molecular structure of complex **4**.

and to the Cp* ligand. On the other hand, methylene groups give rise to two doublet signals at 5.20 and 5.37 ppm, while the aromatic protons appear at 6.10 and 6.73 ppm; these data are in agreement with the coordination mode proposed in Scheme 4. On the other hand, the $^{13}$C NMR spectrum of **4** shows a signal for the carbonyl carbon atom at 118.3 ppm. This high-field CO resonance falls into the range expected for oxymetallacyclopropane complexes (80−120 ppm).[18] Probably, complex **4** is formed through the initial insertion of the carbonyl ligand into the tantalum methyl bond to yield the corresponding acyl derivative. A second methyl migration would render the ketone complex[18b] (see Scheme 4). All attempts to isolate the proposed acyl intermediate have been unsuccessful.

A single-crystal X-ray analysis of compound **4** confirmed the proposed structure. It is, as far as we know, the first tantalum $\eta^2$-acetone complex that has been characterized by an X-ray diffraction analysis. An ORTEP diagram of the molecule is shown in Figure 3, and selected bond distances and angles are summarized in Table 3.

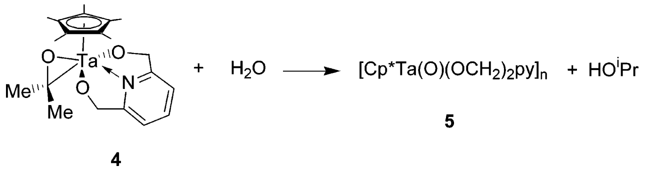
The molecular structure shows it to be a mononuclear compound in which the tantalum center is coordinated by the Cp* ligand, the dialkoxide moiety, and the $\eta^2$-ketone function. In the first place, it is worth noticing that the relative arrangement of the Cp* ligand and the dialkoxide moiety around the metal center is different from that of complexes **1** and **2**. Another interesting feature of the structure is the presence of an acetone group with the keto function side-on bonded to the tantalum atom.

The C(1)−O(1) bond distance (1.441(5) Å) is rather long, and it falls into the range expected for C−O single bonds.[19] On the other hand, the large deviation from planarity of the acetone ligand together with the $^{13}$C chemical shift of the carbonyl carbon (118.3 ppm) suggest a metallaoxirane bonding mode. In addition, the Ta(1)−O(1), Ta(1)−O(2), and Ta(1)−O(3) bond distances (1.936(3), 1.990(3), and 1.986(3) Å, respectively) are within the range expected for tantalum(V) alkoxide complexes. The Ta(1)−N(1) bond length is somewhat longer than that found in complexes **1** and **2**, but it falls into the range expected for tantalum(V) pyridyl complexes.[20]

**Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4**

| | |
|---|---|
| Ta(1)−O(1) | 1.936(3) |
| Ta(1)−O(2) | 1.990(3) |
| Ta(1)−O(3) | 1.986(3) |
| Ta(1)−C(1) | 2.155(4) |
| Ta(1)−N(1) | 2.218(3) |
| Ta(1)−C(11) | 2.534(4) |
| Ta(1)−C(12) | 2.564(4) |
| Ta(1)−C(13) | 2.542(4) |
| Ta(1)−C(14) | 2.455(4) |
| Ta(1)−C(15) | 2.476(3) |
| O(1)−C(1) | 1.441(5) |
| O(2)−C(10) | 1.398(5) |
| O(3)−C(4) | 1.390(5) |
| N(1)−C(5) | 1.326(5) |
| N(1)−C(9) | 1.344(5) |
| C(1)−C(2) | 1.501(7) |
| C(1)−C(3) | 1.518(7) |
| C(4)−C(5) | 1.506(6) |
| C(9)−C(10) | 1.501(6) |
| O(1)−Ta(1)−O(2) | 104.4(1) |
| O(1)−Ta(1)−O(3) | 99.8(1) |
| O(2)−Ta(1)−O(3) | 143.5(1) |
| O(1)−Ta(1)−N(1) | 129.6(1) |
| O(2)−Ta(1)−N(1) | 71.9(1) |
| O(3)−Ta(1)−N(1) | 71.6(1) |
| C(1)−Ta(1)−N(1) | 89.0(1) |

### Scheme 5



Compound **4** does not react with an excess of CO, at room temperature and atmospheric pressure, over a period of 48 h. However, complex **4** reacts with water to yield the oxo derivative [Cp*Ta(O)(OCH$_2$)$_2$py]$_n$ (**5**), while the coordinated ketone in **4** is reduced to 2-propanol (Scheme 5). $^1$H and $^{13}$C NMR spectra of **5** are in agreement with a coordination of the dialkoxide moiety, analogous to that proposed for complexes **3** and **4** (see Experimental Section), while the elemental analysis is that expected for the proposed stoichiometry. According to the IR spectrum, **5** is not a discrete monomer. This is consistent with the fact that no strong absorption is found between 900 and 700 cm$^{-1}$, as it should be expected for the Ta═O stretching frequency. An oligomeric structure based on bridges Ta−O−Ta may be proposed.

Complex **3** reacts also with 1 equiv of xylylisocyanide, at room temperature, to yield the corresponding azatantalacyclopropane complex Cp*Ta($\eta^2$-Me$_2$CNxylyl)(OCH$_2$)$_2$py (**6**) (Scheme 6). Complex **6** has been isolated as a yellow, air-sensitive solid in 85% yield. On the other hand, complex **3** reacts readily with *tert*-butyl isocyanide in C$_6$D$_6$ in a 1:1 molar ratio in a NMR tube-scale to yield the azatantalacyclopropane complex Cp*Ta($\eta^2$-Me$_2$CN$^t$-Bu)(OCH$_2$)$_2$py (**7**) in an almost quantitative yield. All

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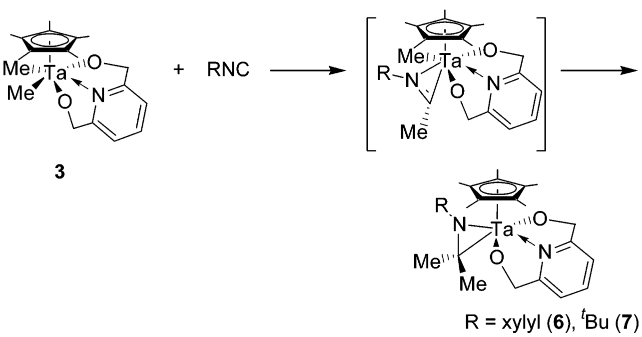
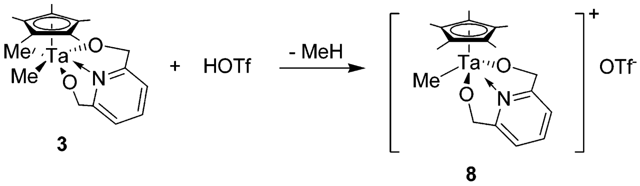
**Scheme 6**



**Scheme 7**



attempts to prepare and isolate complex **7** in a preparative scale were unsuccessful, and it has been characterized solely by $^{1}$H and $^{13}$C NMR.

The $^{1}$H and $^{13}$C NMR spectra of both complexes are in agreement with the proposed structure (see Scheme 6). As an example the $^{1}$H NMR spectrum of **6** shows a singlet signal at 1.84 ppm, which is assigned to the Cp* ligand protons, and two singlet signals at 1.64 and 2.42 ppm with a relative integral of six protons each, which correspond to methyl groups of the imine moiety. In addition, the spectrum shows two doublet signals attributable to the methylene protons of the alkoxide moiety and several multiplet signals due to the aromatic protons. Furthermore, the $^{13}$C NMR spectrum shows, among others, a singlet signal at 79.7 ppm, which we tentatively assign to the carbon atom of imine ligand. The chemical shift is in agreement with that expected for an azametallacycle ring, and it is consistent with values reported for early-d-block $\eta^{2}$-imine compounds. On the other hand, according to the NMR data, the imine ligand would be coordinated to the metallic center in a symmetric $\eta^{2}$-fashion.[21] Presumably, the formation of **6** and **7** arises via a pathway analogous to that proposed for complex **4** involving initial insertion of an isocyanide moiety into one Ta−Me bond to form the corresponding mono($\eta^{2}$-iminoacyl) complex, followed by a second methyl migration, rendering a $\eta^{2}$-imine derivative (Scheme 6).[22]

Finally, reaction of **3** with triflic acid occurs, in acetonitrile at room temperature, in a rather selective way to yield, through protonolysis of only one of the two tantalum−methyl bonds, the corresponding alkyl cationic complex [Cp*TaMe(OCH$_2$)$_2$py]OTf (**8**) (Scheme 7). In the same way, complex **2** reacts with triflic acid in CD$_3$CN and in a 1:1 molar ratio to yield also complex **8**.

Complex **8** was isolated in a moderate yield (53%) as a white solid. It is insoluble in toluene or pentane and rather soluble in THF or acetonitrile. Its $^{1}$H and $^{13}$C NMR spectra show that, at room temperature, both methylene groups in the dialkoxide ligand are equivalent and therefore that the ligand is coordinated to the metal in a symmetric fashion with a pseudo-tetragonal pyramidal coordination environment for the metal center, as depicted in Scheme 7. The $^{1}$H NMR shows singlet signals at −0.23 and 2.22 ppm attributable to the methyl groups bonded to the metal center and to the Cp* ligand, respectively, while the methylene groups give rise to two doublet signals at 5.11 and 5.97 ppm and the aromatic protons are shown by two multiplet signals at 7.65 and 8.20 ppm.

In summary, in this paper we report here the synthesis of several monocyclopentadienyl complexes of tantalum with an assisted dialkoxide ligand, which exhibits a tridentate mer-coordination. Therefore it is bonded to the metal center in a “pincer” fashion. We have been able to synthesize in a very selective way two different isomers of Cp*TaMe$_2$(OCH$_2$)$_2$py, and we have studied the reactivity of both with unsaturated organic molecules such as carbon monoxide or isocyanides, finding that it depends on the coordination mode; while the cis derivative yields through a double methyl migration ketone or imine complexes, respectively, the trans complex does not react under the same reaction conditions. We have also explored the synthesis of cationic alkyl derivatives. We would like to call attention to the potential role that pincer dialkoxide ligands can play in modulating the structure as well as the reactivity of early transition metal complexes.

## Experimental Details

**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 reagents were prepared by literature procedures: Cp*TaMe$_4$,[20] Cp*TaCl$_4$.[21] The commercially available compounds, (HOCH$_2$)$_2$py, LiMe in diethyl ether, and HOTf, were used as received from Aldrich.

$^{1}$H and $^{13}$C NMR spectra were recorded on a 200 Mercury Varian Fourier transform 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 Cp*TaCl$_2$(OCH$_2$)$_2$py (1).** To a mixture of Cp*TaCl$_4$ (0.521 g, 1.13 mmol) and (HOCH$_2$)$_2$py (0.158 g, 1.13 mmol) were added toluene (5 mL) and NEt$_3$ (0.32 mL, 2.26 mL). The mixture was stirred at 70 °C for 3 h, and after that the suspension was filtered and the solvent was evaporated under vacuum. The residue was washed with pentane to yield 0.458 g (77%) of complex **1**. IR (Nujol/PET, cm$^{-1}$): 1614 (m), 1577 (m), 1382 (s), 1335 (s), 1256 (m), 1162 (m) 1110 (m), 1067 (vs), 788 (s), 647 (m), 536 (vs). $^{1}$H NMR (C$_6$D$_6$, rt, 200 MHz): 2.31 (s, 15H, Cp*), 5.77, (s, 4H, CH$_2$), 6.03 (m, 2H, Ar), 6.63 (m, 1H, Ar). $^{13}$C{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ 12.4 (s, Cp*), 80.7 (s, CH$_2$), 116.4 (s, Ar), 125.1 (s, Cp*), 138.5 (s, Ar), 162.8 (s, Ar$_{\mathrm{ipso}}$). Anal. Calcd for C$_{17}$H$_{22}$Cl$_2$O$_2$NTa: C, 38.95; H, 4.23; N, 2.67. Found: C, 38.58; H, 4.20; N, 2.60.

**Synthesis of *trans*-Cp*TaMe$_2$(OCH$_2$)$_2$py (2).** To a suspension of complex **1** (0.339 g, 0.65 mmol) in Et$_2$O (10 mL), at −68 °C, was added a solution 1.6 M of LiMe in Et$_2$O (0.80 mL). The mixture was allowed to reach room temperature and then stirred for 3 h. After that, the solvent was removed under

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**Table 4. Crystal Data and Structure Refinement for 1, 2, and 4**

| | **1** | **2** | **4** |
|---|---|---|---|
| empirical formula | $C_{17}H_{22}Cl_2NO_2Ta$ | $C_{19}H_{24}NO_2Ta$ | $C_{20}H_{28}NO_3Ta$ |
| fw | 524.21 | 479.34 | 511.38 |
| temperature | 293(2) K | 293(2) K | 200(2) K |
| wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| cryst syst, space group | triclinic, $P\bar{1}$ | monoclinic, $P2_1/a$ | orthorhombic, $P2_12_12_1$ |
| unit cell dimens | $a = 8.030(3)$ Å, $\alpha = 80.22(2)$ deg.<br>$b = 8.597(2)$ Å, $\beta = 81.24(3)°$<br>$c = 14.587(2)$ Å, $\gamma = 64.67(2)°$ | $a = 14.888(3)$ Å<br>$b = 8.022(4)$ Å, $\beta = 113.51(3)°$<br>$c = 16.723(3)$ Å | $a = 8.200(2)$ Å<br>$b = 14.023(7)$ Å<br>$c = 17.074(4)$ Å |
| volume | 893.4(4) Å$^3$ | 1831.6(10) Å$^3$ | 1963.3(12) Å$^3$ |
| $Z$, calcd density | 2, 1.949 g/cm$^3$ | 4, 1.738 g/cm$^3$ | 4, 1.730 g/cm$^3$ |
| abs coeff | 64.59 cm$^{-1}$ | 60.10 cm$^{-1}$ | 56.16 cm$^{-1}$ |
| $F(000)$ | 508 | 936 | 1008 |
| cryst size | 0.4 × 0.2 × 0.1 mm | 0.3 × 0.2 × 0.2 mm | 0.3 × 0.3 × 0.1 mm |
| $\theta$ range for data collection | 2.64 to 27.97° | 2.66 to 27.98° | 2.39 to 27.97° |
| limiting indices | $-10 \leq h \leq 10$<br>$-11 \leq k \leq 11$<br>$0 \leq l \leq 19$ | $-19 \leq h \leq 18$<br>$0 \leq k \leq 10$<br>$0 \leq l \leq 22$ | $-10 \leq h \leq 10$<br>$-18 \leq k \leq 18$<br>$-22 \leq l \leq 22$ |
| no. of reflns collected/unique | 4484/4315 [$R$(int) = 0.0324] | 4397/4258 [$R$(int) = 0.0442] | 5396/4745 [$R$(int) = 0.0172] |
| completeness to $\theta = 27.97$ | 100.0% | 96.2% | 100.0% |
| no. of data/restraints/params | 4315/0/213 | 4258/0/208 | 4745/0/231 |
| goodness-of-fit on $F^2$ | 1.130 | 0.929 | 0.873 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0247, wR2 = 0.0669 | R1 = 0.0432, wR2 = 0.0615 | R1 = 0.0202, wR2 = 0.0524 |
| $R$ indices (all data) | R1 = 0.0279, wR2 = 0.0798 | R1 = 0.1444, wR2 = 0.0778 | R1 = 0.0226, wR2 = 0.0535 |
| absolute structure param | | | −0.011(10) |
| largest diff peak and hole | 1.054 and −1.614 e Å$^{-3}$ | 0.735 and −1.172 e Å$^{-3}$ | 1.167 and −1.152 e Å$^{-3}$ |

vacuum and the residue extracted with toluene. Slow diffusion of pentane into the toluene solution yielded 0.235 g (75%) of complex **2**. IR (Nujol/PET, cm$^{-1}$): 1693 (m), 1607 (m), 1577 (m), 1382 (s), 1303 (m), 1256 (m), 1157 (m) 1104 (s), 1067 (vs), 773 (s), 647 (m), 505 (vs). $^1$H NMR ($C_6D_6$, rt, 200 MHz): −0.13 (s, 6H, Ta-Me), 2.06 (s, 15H, Cp*), 5.43 (s, 4H, $CH_2$), 6.06 (m, 2H, Ar), 6.67 (m, 1H, Ar). $^{13}$C NMR: 11.1 (s, Cp*), 29.7 (s, Ta-Me), 78.6 (s, $CH_2$), 116.2 (s, Ar), 118.5 (s, Cp*), 136.5 (s, Ar), 161.1 (s, Ar$_{ipso}$). Anal. Calcd for $C_{19}H_{28}O_2NTa$: C, 47.21; H, 5.83; N, 2.89. Found: C, 47.10; H, 5.98; N, 2.80.

**Synthesis of *cis*-Cp*TaMe$_2$(OCH$_2$)$_2$py (3).** To a mixture of Cp*TaMe$_4$ (0.439 g, 1.16 mmol) and (HOCH$_2$)$_2$py (0.162 g, 1.16 mmol) were added toluene (5 mL) and THF (10 mL) at room temperature, and the mixture was stirred for 3 h. After that the solvent was evaporated and the residue washed with pentane to yield 0.410 g (72%) of complex **3**. IR (Nujol/PET, cm$^{-1}$): 1603 (m), 1330 (s), 1256 (m), 1167 (m) 1110 (m), 1067 (s), 778 (s), 641 (m), 489 (m). $^1$H NMR ($C_6D_6$, rt, 200 MHz): 0.00 (s, 6H, Ta-Me), 2.00 (s, 15H, Cp*), 5.44, (d, $^2J_{H-H} = 17.5$ Hz, $CH_2$), 5.60 (d, $^2J_{H-H} = 17.5$ Hz, $CH_2$), 6.13 (m, 2H, Ar), 6.58 (m, 1H, Ar). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 11.4 (s, Cp*), 38.0 (s, Ta-Me), 75.8 (s, $CH_2$), 115.9 (s, Ar), 116.2 (s, Cp*), 137.5 (s, Ar), 168.9 (s, Ar$_{ipso}$). Anal. Calcd for $C_{19}H_{28}O_2NTa$: C, 47.21; H, 5.83; N, 2.89. Found: C, 46.59; H, 5.95; N, 2.95.

**Synthesis of Cp*Ta($\eta^2$-Me$_2$CO)(OCH$_2$)$_2$py (4).** A solution of Cp*TaMe$_2$(OCH$_2$)$_2$py (0.175 g, 0.36 mmol) in toluene at −20 °C was left to react with an excess of carbon monoxide, under atmospheric pressure, for 1 h. After that, the mixture was filtered and the solvent partially evaporated under vacuum. Slow diffusion of pentane into the toluene solution at −30 °C affords orange crystals of complex **4** (0.150 g, 74%). IR (Nujol/PET, cm$^{-1}$): 1603 (m), 1330 (s), 1257 (m), 1167 (m) 1110 (s), 1067 (s), 778 (s), 642 (m), 500 (m). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 1.91 (s, 6H, $CH_3$), 2.03 (s, 15H, Cp*), 5.20 (d, $^2J_{HH} = 17.97$ Hz, 2H, $CH_2$), 5.37 (d, $^2J_{HH} = 17.97$ Hz, 2H, $CH_2$), 6.10 (m, 2H, Ar), 6.73 (m, 1 H, Ar). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 10.7 (s, Cp*), 28.5 (s, $CH_3$), 77.8 (s, $CH_2$), 115.4 (s, Ar), 118.3 (s, Me$_2$CO), 128.4 (s, Cp*), 138.8 (s, Ar), 166.3 (s, Ar$_{ipso}$). Anal. Calcd for $C_{20}H_{28}NO_3Ta$: C, 46.96; H, 5.51; N, 2.73. Found: C, 46.55; H, 5.37; N, 2.70.

**Synthesis of Cp*Ta(O)(OCH$_2$)$_2$py (5).** A solution of complex **4** in toluene (0.100 g, 0.19 mmol) and water (3.4 $\mu$L, 0.19 mmol) was left at room temperature for 4 days. Slow diffusion of pentane into the resulting solution yields colorless crystals of complex **5** (0.053 g, 58%). IR (Nujol/PET, cm$^{-1}$): 1687 (w), 1608 (m), 1572 (m), 1335 (m), 1157 (m), 1120 (s), 1072 (s), 788 (m), 783 (m), 526 (m), 489 (s). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 2.05 (s, 15H, Cp*), 5.74 (d, $^2J_{HH} = 21.99$ Hz, 2H, $CH_2$), 5.84 (d, $^2J_{HH} = 21.99$ Hz, 2H, $CH_2$), 7.26 (m, 2H, Ar), 7.81 (m, 1H, Ar). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 11.3 (s, Cp*), 77.7 (s, $CH_2$), 117.1 (s, Ar), 118.7 (s, Cp*), 140.3 (s, Ar), 167.2 (s, Ar$_{ipso}$). Anal. Calcd for $C_{17}H_{22}O_3NTa$: C, 43.50; H, 4.72; N, 2.98. Found: C, 42.90; H, 4.54; N, 2.74.

**Synthesis of Cp*Ta($\eta^2$-Me$_2$CNxylyl)(OCH$_2$)$_2$py (6).** To a mixture of Cp*TaMe$_2$(OCH$_2$)$_2$py (0.092 g, 0.19 mmol) and xylylN≡C (0.025 g, 0.19 mmol) was added toluene (3 mL). The solution was stirred at room temperature for 30 min. After that, the mixture was filtered and the solvent eliminated. The oil obtained was washed with 5 mL of cool pentane to afford a yellow solid (0.098 g, 84%), which was characterized as **6**. IR (Nujol/PET, cm$^{-1}$): 1683 (m), 1614 (m), 1580 (m), 1271 (s), 1236 (s) 1157 (m), 1120 (s), 1107 (s), 1096 (s), 1080 (s), 494 (s). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 1.64 (s, 6H, $CH_3$), 1.84 (s, 15H, Cp*), 2.42 (s, 6H, $CH_3$), 5.40 (d, $^2J_{HH} = 17.96$ Hz, 2H, $CH_2$), 5.56 (d, $^2J_{HH} = 17.96$ Hz, 2H, $CH_2$), 6.21 (m, 2H, Ar), 6.79−7.15 (m, 4H, Ar). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 10.7 (s, Cp*), 20.8, 26.5 (s, $CH_3$), 78.0 (s, $CH_2$), 79.7 (s, C=N), 115.5 (s, Cp*), 117.7 (s, Ar), 123.5 (s, Ar), 128.4 (s, Ar), 136.9 (s, Ar$_{ipso}$), 138.7 (s, Ar), 150.9 (s, Ar$_{ipso}$), 166.8 (s, Ar$_{ipso}$). Anal. Calcd for $C_{28}H_{37}N_2O_2Ta$: C, 54.72; H, 6.07; N, 4.56. Found: C, 54.06; H, 6.00; N, 4.48.

**Synthesis of Cp*Ta($\eta^2$-Me$_2$CN$^t$Bu)(OCH$_2$)$_2$py (7).** To a solution of Cp*TaMe$_2$(OCH$_2$)$_2$py (0.045 g, 0.09 mmol) in $C_6D_6$ was added $^t$BuN≡C (10 $\mu$L, 0.09 mmol). After 30 min at room temperature the solution was bright orange, and the $^1$H and $^{13}$C NMR spectra showed **7** as the only detectable compound. $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 1.18 (s, 9H, $CH_3$), 1.99 (s, 15H, Cp*), 2.05 (s, 6H, $CH_3$), 5.28 (d, $^2J_{HH} = 17.60$ Hz, 2H, $CH_2$), 5.45 (d, $^2J_{HH} = 17.60$ Hz, 2H, $CH_2$), 6.18 (m, 2H, Ar), 6.79 (m, 1H, Ar). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 11.43 (s, Cp*), 29.8 (s, Me$_2$C), 30.6 (s, CMe$_3$), 33.8 (s, CMe$_3$), 63.3 (s, C=N), 78.4 (s, $CH_2$), 115.5 (s, Cp*), 117.6 (s, Ar), 139.1 (s, Ar), 167.4 (Ar$_{ipso}$).

**Synthesis of [Cp*TaMe(OCH$_2$)$_2$py]OTf (8).** To a suspension of complex **3** (0.111 g, 0.23 mmol) in 5 mL of acetonitrile was slowly added triflic acid (0.020 mL), and the solution was stirred for 1 h at room temperature. The solvent was removed under vacuum and the residue washed with 5 mL of pentane to yield 0.078 g (53%) of complex **8**. IR (Nujol/PET, cm$^{-1}$): 1637 (m), 1609 (m), 1603 (m), 1579 (m), 1371 (s), 1345 (m), 1285 (vs), 1243 (vs), 1168 (vs), 1105 (s), 1068 (vs), 1035 (vs), 792 (s), 638 (vs), 544 (vs). $^1$H NMR ($CD_3CN$, rt, 200 MHz): −0.23

(s, 3H, Ta-Me), 2.22 (s, 15H, Cp*), 5.97, (d, $^2J_{H-H}$ = 14.66 Hz, $CH_2$), 5.11 (d, $^2J_{H-H}$ = 14.66 Hz, $CH_2$), 7.65 (m, 2H, Ar), 8.20 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR ($CD_3CN$): $\delta$ 10.1 (s, Cp*), 36.5 (s, Ta-Me), 79.8 (s, $CH_2$), 117.8 (s, Ar), 121.8 (s, Cp*), 140.4 (s, Ar), 163.1 (s, $Ar_{ipso}$). Anal. Calcd for $C_{19}H_{25}O_5F_3SNTa$: C, 36.95; H, 4.08; N, 2.27. Found: C, 36.51; H, 4.24; N, 2.17.

**X-ray Data Collection and Structure Determination.** Single crystals of **1**, **2**, and **4** were obtained by slow diffusion of pentane into a saturated solution of the complexes in toluene. Intensity data were collected for all three compounds using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) on a Nonius-Mach3 diffractometer. The structures were solved by direct methods employing the SHELXS-97 program.[25] All atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using the program SHELXL-97.[26]The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated by the program. The positions of hydrogen atoms are calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that the associated carbon atoms and participated in the calculation of final *R*-indices. For disordered carbon atoms of the Cp ligand of complex **2** occupancies were refined initially and then fixed. Crystallographic data are collected in Table 4.

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**Supporting Information Available:** Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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