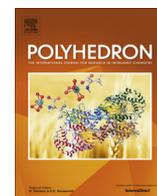




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## Dearomatization and functionalization of tantalum bonded dialkoxide pincer ligands

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### ABSTRACT

New tantalum derivatives with dearomatized pincer ligands have been prepared:  $[\text{TaCp}^*\text{Cl}\{\kappa^3\text{-N,O,O}-(\text{OCH}_2)(\text{OCH})\text{py}\}]$  (**2**) has been synthesized by deprotonation of  $[\text{TaCp}^*\text{Cl}_2\{\kappa^3\text{-N,O,O}-(\text{OCH}_2)_2\text{py}\}]$  with  $\text{LiNTMS}_2$  and  $[\text{Cp}^*\text{Ta}\{\kappa^3\text{-N,O,O}-(\text{OCH}_2)_2\text{pyH}\}]_2(\mu\text{-O})$  (**3**) has been obtained by reaction of  $[\text{TaCp}^*(\text{OTf})_2\{\kappa^3\text{-N,O,O}-(\text{OCH}_2)_2\text{py}\}]$  with  $\text{Li}[\text{HB}(\text{Et})_3]$ . The reaction of complex **2** or the analogous methyl derivative  $[\text{TaCp}^*\text{Cl}\{\kappa^3\text{-N,O,O}-(\text{OCH}_2)(\text{OCH})\text{py}\}]$  with methyl methacrylate (MMA) render the corresponding tantalum enolates  $[\text{TaCp}^*\text{X}\{\kappa^4\text{-O,N,O,C}-(\text{OCH}_2)(\text{OCHMMA})\text{py}\}]$  ( $\text{X} = \text{Cl}$  (**5**),  $\text{Me}$  (**6**)). The Ta–O bond of the enolate fragment reacts selectively with water or with triflic acid to render the corresponding tantalum hydroxide (**7**) or triflate (**8**), respectively. The structure of **3** has been determined by X-ray diffraction.

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### 3. Introduction

When first introduced by Moulton and Shaw in 1976 [1] the term pincer ligand designate a monoanionic terdentate ligand. However, nowadays the concept has been used to define a great variety of ligands that compel three donor atoms to the metal in a *mer*-fashion [2–4].

The burgeoning interest in the chemistry of pincer complexes can be attributed to their robust nature and to the accessible modifications that allow a fine tuning of complexes electronic and steric properties. These characteristics make their complexes interesting in different areas of chemistry such as catalysis [5], sensors [6,7], and material science [8,9]. Among these, redox-active pincer ligands are especially relevant because they can expand metal reactivity acting as an electron reservoir giving rise to a variety of spectacular chemical transformations [10–16].

In previous works, we have studied the chemistry of early transition metal complexes stabilized by ONO dianionic pincer ligands [17–22] that have shown to be versatile enough to allow us the preparation of water soluble organometallic complexes. Moreover, we have reported a simple synthetic strategy for the construction of new ligands that can incorporate a variety of functions into the pincer ligand through a redox active moiety [23]. Given the

important role of ligands in modulating the reactivity of metal complexes [24–26] we decided to explore if this functionalization procedure would allow the incorporation of polar and reactive moieties into the pincer ligand structure. Here, we report the synthesis of new of tantalum complexes with dearomatized pincer ligands and their reactivity with a conjugated unsaturated molecule, methyl methacrylate.

### 4. Experimental details

#### 4.1. Materials and methods

The preparation and handling of described compounds was performed, unless otherwise stated, with rigorous exclusion of air and moisture under argon atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under argon atmosphere. Commercially available compounds were used as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE 400 Fourier Transform spectrometers. Trace amounts of protonated solvents were used as reference, and chemical shifts are reported in units of parts per million relative to  $\text{SiMe}_4$ .

#### 4.2. Synthesis

$[\text{TaCp}^*\text{Cl}\{\kappa^3\text{-N,O,O}-(\text{OCH}_2)(\text{OCH})\text{py}\}]$  (**2**)

To a solution of  $[\text{TaCp}^*\text{Cl}_2\{\kappa^3\text{-N,O,O}-(\text{OCH}_2)_2\text{py}\}]$  (0.425 g, 0.81 mmol) in toluene, at room temperature was added a solution of

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LiNTMS<sub>2</sub>.Et<sub>2</sub>O (0.197 g, 0.81 mmol) in toluene. The dark purple solution formed was stirred at room temperature for 1 h. After filtration, the toluene solution was dried under vacuum and the residue washed with pentane yielding a purple solid that was characterized as **2** (Yield, 0.311 g, 79%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.84 (s, 15 H, Cp\*), 4.61 (d, <sup>2</sup>J<sub>HH</sub> = 17.77 Hz, 1H, CH<sub>2</sub>), 4.64 (m, 1 H, Ar), 4.78 (d, <sup>2</sup>J<sub>HH</sub> = 17.20 Hz, 1 H, CH<sub>2</sub>), 6.05 (m, 1 H, Ar), 6.25 (m, 1 H, Ar), 7.35 (s, 1 H, CHO); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 10.2 (Cp\*), 79.7 (CH<sub>2</sub>), 99.2 (CH), 119. (Ar), 120.8 (Cp\*), 122.4 (CHO), 143.4 (CH), 154.3 (C–CH<sub>2</sub>O). Anal. Calcd. for C<sub>17</sub>H<sub>21</sub>ClNO<sub>2</sub>Ta: C, 41.85; H, 4.33; N, 2.87. Found: C, 41.62; H, 4.38; N, 2.65%.

[TaCp\*{κ<sup>3</sup>-N,O,O-(OCH<sub>2</sub>)<sub>2</sub>pyH}]<sub>2</sub>(μ-O) (**3**)

To a suspension of [TaCp\*(OTf)<sub>2</sub>{κ<sup>3</sup>-N,O,O-(OCH<sub>2</sub>)<sub>2</sub>py}] (0.348 g, 0.46 mmol) in pentane was added Li[HBtEt<sub>3</sub>] (0.93 mL, 1 M in THF). The solution was stirred at room temperature for 1 h. After that, the solvent was removed under vacuum and the residue extracted with Et<sub>2</sub>O. Crystals of compound **3** were obtained by cooling the ether solution to –20 °C (Yield: 0.136 g, 63%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.93 (s, 15H, Cp\*), 3.45 (d, <sup>2</sup>J<sub>HH</sub> = 19.81 Hz, 1H, CH<sub>2</sub>), 3.67 (d, <sup>2</sup>J<sub>HH</sub> = 19.81 Hz, 1H, CH<sub>2</sub>), 4.12 (s, 2 H, CH), 5.23 (d, <sup>2</sup>J<sub>HH</sub> = 14.60 Hz, 2H, CH<sub>2</sub>), 5.55 (d, <sup>2</sup>J<sub>HH</sub> = 14.60 Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 10.1 (Cp\*), 77.5 (CH<sub>2</sub>), 88.3 (CH), 120.3 (Cp\*), 154.9 (C–CH<sub>2</sub>O). Anal. Calcd. for C<sub>34</sub>H<sub>46</sub>N<sub>2</sub>O<sub>5</sub>Ta<sub>2</sub>: C, 44.16; H, 5.01; N, 3.03. Found: C, 43.70; H, 5.03; N, 2.83%.

[TaCp\*Cl{κ<sup>3</sup>-O,N,O,C-(OCH<sub>2</sub>)(OCHMMA)py}] (**5**)

To a solution of [TaCp\*Cl{κ<sup>3</sup>-N,O,O-(OCH<sub>2</sub>)(OCH)py}] (**2**) (0.133 g, 0.27 mmol) in toluene at room temperature was added MMA (29 μL, 0.27 mmol) and the mixture was stirred at room temperature for 1 h. The residue formed upon evaporation of the toluene was washed with pentane to yield a yellow compound that characterized as **5** (0.101 g, 63%): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.45 (s, 3H, Me), 1.88 (dd, *J* = 5.7, 15.5 Hz, 1H, CH<sub>2</sub>), 2.21 (s, 15H, Cp\*), 2.76 (d, <sup>3</sup>J<sub>HH</sub> = 15.5 Hz, 1H, CH<sub>2</sub>), 3.11 (s, 3 H, Me), 5.63 (d, <sup>2</sup>J<sub>HH</sub> = 18.0 Hz, 1H, CH<sub>2</sub>), 5.70 (d, <sup>2</sup>J<sub>HH</sub> = 18.0 Hz, 1H, CH<sub>2</sub>), 6.14 (s, 1H, CHMMA), 6.12 (m, 1H, Ar), 6.20 (m, 1H, Ar), 7.74 (m 1 H, Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 11.6 (Cp\*), 19.8 (Me), 40.1.8 (CH<sub>2</sub>), 52.8 (MeO), 79.1 (C=CO(OMe)), 79.3 (CH<sub>2</sub>O), 89.1 (CHMMA), 115.5 (Ar), 115.7 (Ar), 123.9 (Cp\*), 138.6 (Ar), 156.8 (C=CO(OMe)), 162.9 (C<sub>ipso</sub>), 165.8 (C<sub>ipso</sub>). C<sub>22</sub>H<sub>29</sub>ClNO<sub>4</sub>Ta: C, 44.95; H, 4.97; N, 2.38. Found: C, 44.54; H, 4.88; N, 2.31.

[TaCp\*Me{κ<sup>4</sup>-O,N,O,C-(OCH<sub>2</sub>)(OCHMMA)py}] (**6**)

To a solution of [TaCp\*Me{κ<sup>3</sup>-N,O,O-(OCH<sub>2</sub>)(OCH)py}] (0.386 g, 0.82 mmol) in toluene was added MMA (89 μL, 0.82 mmol) and the mixture was left at room temperature for 1 h. After filtration, the solvent was evaporated and the residue washed with pentane to yield a yellow solid that was characterized as compound **6** (0.251 g, 53%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ –0.16 (s, 3H, Me), 1.59 (s, 3H, Me), 1.98 (dd, *J* = 5.9, 15.4 Hz, 1H, CH<sub>2</sub>), 2.07 (s, 15H, Cp\*), 2.87 (d, <sup>3</sup>J<sub>HH</sub> = 15.4 Hz, 1H, CH<sub>2</sub>), 3.21 (s, 3 H, Me), 5.39 (d, <sup>2</sup>J<sub>HH</sub> = 18.2 Hz, 1H, CH<sub>2</sub>), 5.50 (d, <sup>2</sup>J<sub>HH</sub> = 18.4 Hz, 1H, CH<sub>2</sub>), 6.05 (d, <sup>2</sup>J<sub>HH</sub> = 5.9 Hz, 1H, CHMMA), 6.12 (m, 1H, Ar), 6.26 (m, 1H, Ar), 7.76 (m 1 H, Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 10.3 (Cp\*), 20.0 (Me), 34.8 (CH<sub>2</sub>), 41.2 (TaMe), 52.0 (MeO), 75.7 (C=CO(OMe)), 78.4 (CH<sub>2</sub>O), 88.4 (CHMMA), 115.5 (Ar), 115.8 (Ar), 120.5 (Cp\*), 137.7 (Ar), 157.2 (C=CO(OMe)), 161.7 (C<sub>ipso</sub>), 165.5 (C<sub>ipso</sub>). C<sub>23</sub>H<sub>32</sub>NO<sub>4</sub>Ta: C, 48.67; H, 5.68; N, 2.46. Found: C, 48.58; H, 5.65; N, 2.24.

[TaCp\*Me{κ<sup>3</sup>-O,N,O-(OCH<sub>2</sub>)(OCHMMAH)py}(OH)] (**7**)

To a solution of **6** (0.198 g, 0.35 mmol) in Et<sub>2</sub>O at room temperature was added water (15 μL, 0.83 mmol) and the mixture was left at –25 °C for 1 day. The pale yellow crystals formed were characterized as **7** (0.151 g, 74%). <sup>1</sup>H NMR: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ –0.73 (s, 3H, Me), 1.25 (d, <sup>3</sup>J<sub>HH</sub> = 6.84 Hz, 3H, Me), 1.64 (s, OH), 1.89 (m, 1H, CH<sub>2</sub>), 2.05 (s, 15H, Cp\*), 2.22 (m, 1H, CH<sub>2</sub>), 2.91 (m, 1H, CH), 3.54 (s, 3H, Me), 5.59 (m, 1 H, CH), 5.63 (d, <sup>2</sup>J<sub>HH</sub> = 18.21 Hz, 1H, CH<sub>2</sub>), 5.78 (d, <sup>2</sup>J<sub>HH</sub> = 18.21 Hz, 1H, CH<sub>2</sub>), 7.11 (m, 1 H, Ar), 7.16

(m, 1H, Ar), 7.76 (m, 1H, Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 10.7 (Cp\*), 16.3 (Me), 30.2 (CH<sub>2</sub>), 35.1 (Me), 39.7 (TaMe), 51.6 (MeO), 78.0 (CH<sub>2</sub>O), 84.6 (CH), 117.1 (Ar), 117.8 (Ar), 120.3 (Cp\*), 138.4 (Ar), 163.0 (C<sub>ipso</sub>), 164.6 (C<sub>ipso</sub>), 177.6 (C=O). C<sub>23</sub>H<sub>34</sub>NO<sub>5</sub>Ta: C, 47.18; H, 5.85; N, 2.39. Found: C, 47.51; H, 5.63; N, 2.28.

[TaCp\*Me{κ<sup>3</sup>-O,N,O-(OCH<sub>2</sub>)(OCHMMAH)py}(OTf)] (**8**)

To a solution of **6** (0.282 g, 0.50 mmol) in toluene was added triflic acid (44 μL, 0.50 mmol) and the solution was stirred for 1 h at room temperature. The solvent was evaporated under vacuum and the residue washed with Et<sub>2</sub>O yielding a white solid that was identified as **8** (0.294, 82%). NMR: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ –0.37 (s, 3H, Me), 1.29 (d, <sup>3</sup>J<sub>HH</sub> = 6.72 Hz, 3H, Me), 1.73 (m, 1H, CH<sub>2</sub>), 1.94 (m, 1H, CH<sub>2</sub>), 2.13 (s, 15H, Cp\*), 2.89 (m, 1H, CH), 3.69 (s, 3H, Me), 5.80 (m, 1H, CH), 5.85 (d, 1 H, <sup>2</sup>J<sub>HH</sub> = 18.61 Hz, CH<sub>2</sub>), 6.23 (d, 1 H, <sup>2</sup>J<sub>HH</sub> = 18.61 Hz, CH<sub>2</sub>), 7.33 (m, 1 H, Ar), 7.41 (m, 1H, Ar), 7.93 (m, 1H, Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 10.5 (Cp\*), 15.0 (Me), 35.7 (CH<sub>2</sub>), 36.7 (Me), 38.8 (TaMe), 51.0 (MeO), 80.2 (CH<sub>2</sub>O), 87.1 (CH), 117.6 (Ar), 117.8 (Ar), 122.3 (Cp\*), 139.8 (Ar), 164.1 (C<sub>ipso</sub>), 165.5 (C<sub>ipso</sub>), 176.0 (C=O). C<sub>24</sub>H<sub>33</sub>F<sub>3</sub>NO<sub>7</sub>STa.0.25C<sub>6</sub>H<sub>7</sub>: C, 41.76; H, 4.76; N, 1.89; S, 4.32. Found: C, 41.51; H, 4.78; N, 1.77; S, 4.16.

#### 4.3. X-ray crystallography

A summary of crystal data collection and refinement parameters for **3** compound are given in Table 1. Single crystal for **3** was mounted on a glass fiber and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite monochromated Mo K $\alpha$  radiation source ( $\lambda$  = 0.71073 Å). Data were integrated using SAINT [27] and an absorption correction was performed with the programme SADABS [28]. The software package WINGX [29,30] was used for space group determination, structure solution and refinement by full-matrix least-squares methods based on *F*<sup>2</sup>. All non-hydrogen atoms were refined with anisotropic displacement coefficients and the hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic

**Table 1**  
Crystal data and structure refinement for **3**.

Empirical formula	C <sub>34</sub> H <sub>46</sub> N <sub>2</sub> O <sub>5</sub> Ta <sub>2</sub>
Formula weight	924.63
<i>T</i> (K)	180(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.6173(9)
<i>b</i> (Å)	11.4131(11)
<i>c</i> (Å)	17.4581(17)
$\alpha$ (°)	90.200(2)
$\beta$ (°)	98.484(2)
$\gamma$ (°)	105.803(2)
<i>V</i> (Å <sup>3</sup> )	1632.3(3)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.881
Absorption coefficient (mm <sup>–1</sup> )	6.742
<i>F</i> (0 0 0)	900
Crystal size (mm)	0.15 × 0.14 × 0.12
Index ranges	–10 ≤ <i>h</i> ≤ 10, –14 ≤ <i>k</i> ≤ 14, –21 ≤ <i>l</i> ≤ 20
Reflections collected	11378
Independent reflections ( <i>R</i> <sub>int</sub> )	6429 [0.0467]
Data/restraints/parameters	6429/1197/483
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.012 <sup>c</sup>
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0418, <sup>a</sup> <i>wR</i> <sub>2</sub> = 0.0837 <sup>b</sup>
Largest difference peak/hole, (e Å <sup>–3</sup> )	0.996 and –1.442

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2) \}^{1/2}$ .

<sup>c</sup>  $GOF = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}$ , where *n* = number of reflections and *p* = total number of parameters refined.

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