

## C–H Bond Cleavage and Regioselective C–C Coupling on a Tantalum-Bound Pincer Ligand

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The design of new ligands is an important issue in both inorganic and organometallic chemistry. Because ligands are able to affect and control the chemical properties of metals, chemists are continually searching for new ligand systems to synthesise complexes with the required properties.<sup>[1]</sup> This approach normally implies the synthesis of the ligand precursors, which must then be coordinated to the corresponding metal. A different procedure is to modify the ligand once it is in the coordination sphere of the metal and take the advantage of its ability to mediate some organic processes.

In recent years we have studied a series of early transition-metal complexes with a dialkoxide pincer ligand and have discovered that the bonding of the ONO ligand to the metal centre is remarkably stable, which allows the synthesis of water-soluble tantalum organometallic complexes.<sup>[2]</sup> In order to explore further the role of the ligand, we thought that it would be interesting to modify it by introducing different functionalities.

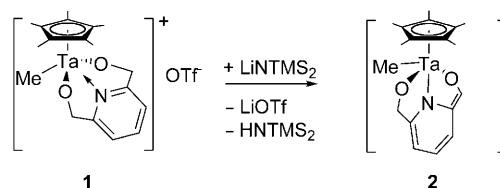
To this end, reactions involving C–H bond-activation processes allow a clean method for the functionalization of C–H moieties.<sup>[3]</sup> In this field, early transition-metal compounds have been studied because of their ability to mediate a wide range of processes. In particular, tantalum derivatives supported by bulky alkoxide, siloxide or aryloxy ligands are known to mediate coupling reactions and C–O activation,<sup>[4]</sup> C–N activation<sup>[5]</sup> and C–H activation.<sup>[6–7]</sup> This ability is especially attractive when two of these reactions can be sequentially assisted by the same metal complex.

We herein report a versatile protocol for the functionalization of a dialkoxide pincer ligand through sequential C–H activation/C–C coupling processes to give a variety of tetradentate ligands.

Given the high reactivity of the pyridyl side chains,<sup>[8–9]</sup> we envisaged that bringing in a strong nucleophile in the coordination sphere of the tantalum centre in [TaCp\*Me(OCH<sub>2</sub>)<sub>2</sub>py]OTf (**1**; Cp\* = pentamethylcyclopentadienyl, py = pyridine)<sup>[2a]</sup> could lead to the cleavage of a C–H bond in the methylene moiety.

In this way, the tantalum complex **1** reacts with Li(NTMS<sub>2</sub>) in a 1:1 molar ratio to yield a deep-red complex that has been characterised by the usual spectroscopic techniques as complex **2** (Scheme 1). Complex **2** is air and moisture sensitive, soluble in toluene or THF and less soluble in pentane or Et<sub>2</sub>O. The <sup>1</sup>H and the <sup>13</sup>C NMR spectra of complex **2** can be fully assigned on the basis of the structure shown in Scheme 1.

Note that the <sup>1</sup>H NMR spectrum of **2** shows that one of the pyridinic ring protons is shifted to very high field ( $\delta =$



Scheme 1. Synthesis of the tantalum complex **2**.

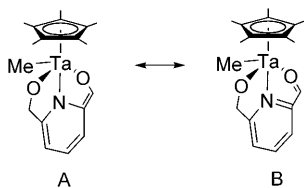
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4.83 ppm). Besides, the integral of the two doublets assigned to the methylene protons ( $\delta=4.77$  and 4.94 ppm) indicates that only one methylene group is present in the complex. In accordance with all of the spectroscopic features, the bonding mode of the pincer ligand can be described as intermediate between forms A and B (Scheme 2). Form A is formally a Ta<sup>V</sup> complex whereas in B the formal oxidation state of the tantalum is III. The new ligand is quite interesting and worth studying; the proposed bonding mode for the activated moiety can be somehow compared to that of redox-active ligands such as *o*-iminobenzoquinones<sup>[10]</sup> or *N,N*-bis-(phenoxide)amides.<sup>[11]</sup>



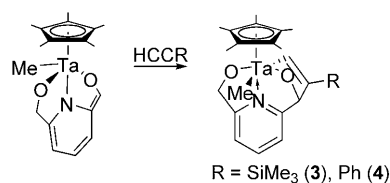
Scheme 2.

When the reaction of **1** with Li(NTMS)<sub>2</sub> is conducted in C<sub>6</sub>D<sub>6</sub> in an NMR tube and monitored by <sup>1</sup>H NMR spectroscopy, it can be seen that the formation of **2** is quantitative. In addition, a resonance for HNTMS<sub>2</sub> is observed at  $\delta=0.04$  ppm. From this experiment we can also see that the tantalum methyl bond in **2** is kinetically inert toward HN(TMS)<sub>2</sub>. This fact is in agreement with the inertness of the methyl group in **1**, which reacts with water to give the corresponding water-soluble alkyl complex [TaCp\*Me(H<sub>2</sub>O)(OCH<sub>2</sub>)<sub>2</sub>py]OTf.<sup>[26]</sup>

To evaluate the use of **2** as a synthon for the functionalization of the pincer fragment through C–C formation processes we have carried out reactions with diverse unsaturated organic molecules such as terminal alkynes or ketones.

Complex **2** reacts, at room temperature, with trimethylsilyl or phenyl acetylene in a regioselective way to yield, respectively, the alkenyl tantalum derivatives **3** or **4** (Scheme 3), which are isolated as yellow crystals and have been characterised by the usual analytical and spectroscopic techniques as well as by X-ray diffraction methods. Complexes **3** and **4** are air sensitive, soluble in toluene or THF and are less soluble in pentane.

The molecular structures of **3** and **4** have been determined by an X-ray diffraction study.<sup>[12]</sup> ORTEP drawings of **3** and **4** are shown in Figure 1. Complexes **3** and **4** show compar-



Scheme 3. Synthesis of the tantalum complexes **3** and **4**.

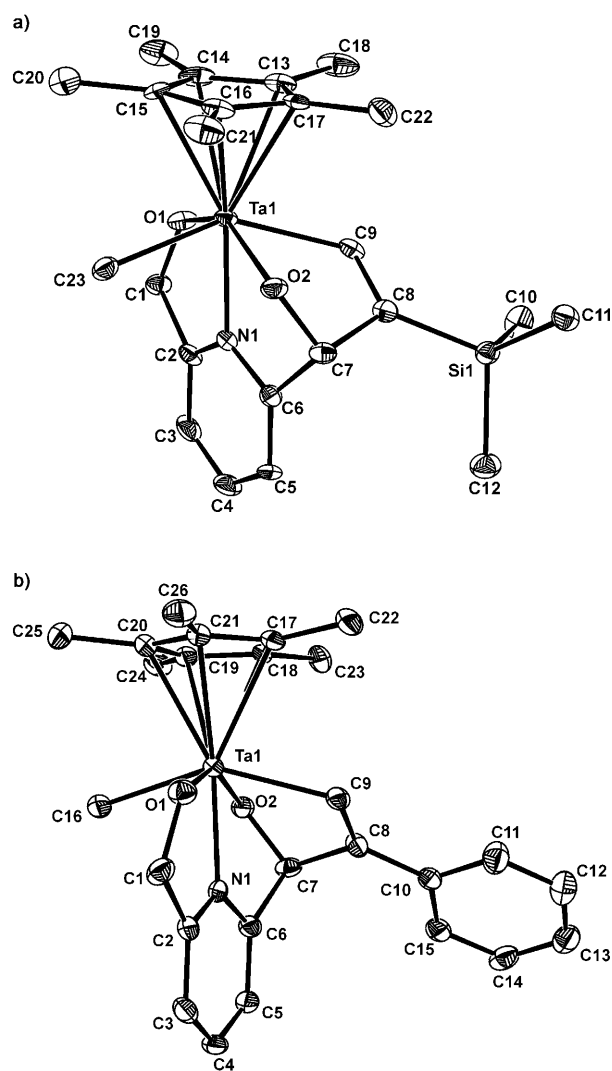


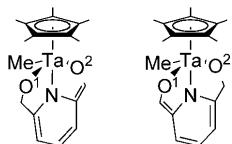
Figure 1. ORTEP diagram (30% probability ellipsoids) of a) **3** and b) **4**. Selected bond lengths [Å]: **3**, Ta1–O1=1.962(6), Ta1–O2=2.017(6), Ta1–N1=2.193(7), Ta1–C9=2.281(9); Ta1–C23=2.269(9); **4**, Ta1–O1=1.961(4), Ta1–O2=2.011(4), Ta1–N1=2.187(5), Ta1–C9=2.264(6); Ta1–C16=2.267(7).

able geometrical parameters. The coordination geometry around the metal can be described as pseudo-octahedral. The tantalum atom is bound to the cyclopentadienyl ring in an  $\eta^5$  mode. On the other hand, the alkoxide ligand is bound to the metal in a tetradentate fashion, through both oxygen atoms that are placed in the equatorial plane, to the nitrogen of the pyridinic moiety that is in the *trans* position to the Cp\* group and to the unsubstituted carbon atom of the coupled alkyne that placed in the equatorial plane in the *trans* position to the methyl group.

The Ta1–O1 bond length in **3** (1.962(6) Å) is in the normal range for tantalum–alkoxide complexes.<sup>[13]</sup> The Ta1–O2 bond length (2.017(6) Å) is longer, probably to allow coordination of C9. The Ta1–N1 bond length (2.193(7) Å) is rather short and comparable to that found in anionic nitrogen ligands.<sup>[14]</sup>

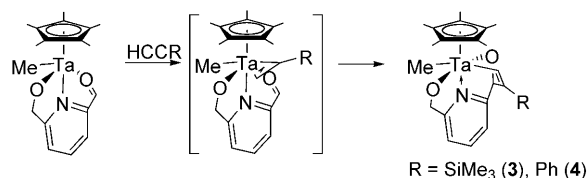
On the other hand, the Ta1–C9 (2.281(9) Å) and Ta1–C23 (2.269(9) Å) bond lengths are within the expected range for tantalum–alkyl complexes.<sup>[15]</sup>

Complexes **3** and **4** contain a chiral centre, C7, but they are obtained and crystallised as a racemic mixture of both enantiomers as it would be expected because, according to the symmetric disposition of the pincer ligand in **1**, C–H bond activation can occur at any of the two methylene groups in the starting material (Scheme 4) and therefore the coupling reaction would render different isomers.



Scheme 4.

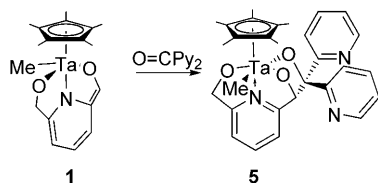
Formation of complexes **3** and **4** can be proposed to proceed through a pathway involving the initial coordination of the alkyne moiety to the tantalum centre followed by the insertion of the carbonyl group of the pincer ligand (form B of Scheme 2) into the Ta–C bond of the substituted carbon of the alkyne moiety (Scheme 5).<sup>[16]</sup> The reactions of **2** with



Scheme 5.

trimethylsilyl or phenyl acetylene in C<sub>6</sub>D<sub>6</sub> were monitored by <sup>1</sup>H NMR spectroscopy. In both instances the reaction takes place in C<sub>6</sub>D<sub>6</sub> at room temperature to yield **3** or **4** as the only detectable products, indicating that formation of the alkyne complex is the rate-determining step. It is interesting to point out that **1** does not react with diphenylacetylene under the same experimental conditions.

Moreover, **2** reacts with dipyridylketone in a 1:1 molar ratio, to yield **5** in which a new trialkoxide ligand is bound to the tantalum centre in a tetradentate fashion (Scheme 6).



Scheme 6. Synthesis of the tantalum derivative **5**.

The <sup>1</sup>H NMR spectrum of **5** displays two doublet signals at  $\delta = 5.50$  and  $6.39$  ppm for the ligand methylene protons (OCH<sub>2</sub>), again indicating asymmetry about the O<sub>2</sub>N plane of the ligand. The shifts of the oxygen-bound carbon atoms

( $\delta = 80.2, 90.6$  and  $91.4$  ppm) are in agreement with the proposed C–C coupling of the ketone fragment and the pincer ligand in **2**. Besides, the <sup>1</sup>H and <sup>13</sup>C NMR spectra indicate that the pyridinic rings are in different chemical environments as would be expected for the structure proposed for **5**.

The molecular structure of **5** was established by X-ray diffraction methods.<sup>[12]</sup> An ORTEP view of **5** is shown in Figure 2. The study shows **5** to be mononuclear with a pseudo-octahedral geometry around the tantalum atom. The metal centre is bound to the Cp\* and Me ligands and to a new trialkoxide ligand in a tetradentate fashion.

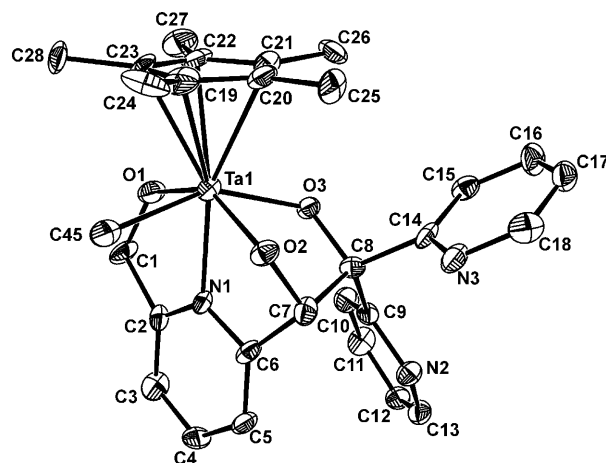


Figure 2. ORTEP drawing of **5** (30% probability ellipsoids). Selected bond lengths [Å]: Ta1–O1 = 1.954(9), Ta1–O2 = 2.031(8), Ta1–N1 = 2.173(11), Ta1–O3 = 2.044(8); Ta1–C45 = 2.239(13).

Note that, as in the case of **3** and **4**, the rigid nature of the ligand imposes some specific structural parameters. In this way, the Ta1–O2 bond length (2.031(8) Å) is comparable to the Ta1–O3 2.044(8) bond length but, as in **2** and **3**, it is longer than the Ta1–O1 bond length (1.954(9) Å).

In summary, we have seen that although the ligand is quite reactive and is involved in the C–H bond activation processes, the original  $\kappa^3$ -O,N,O bonding to the tantalum centre is robust and remains throughout. Complex **2** has been shown to be an interesting starting material because it allows the modification of the coordination environment of the metal centre by introducing a variety of different functions. Studies aimed at further disclosing this reactivity are going on in our laboratory.

## Experimental Section

**General methods:** All manipulations of air sensitive complexes were carried out with rigorous exclusion of oxygen and moisture.

**Complex 2:** A solution of LiNTMS<sub>2</sub>·Et<sub>2</sub>O (0.047 g, 0.19 mmol) in toluene was added to a suspension of [TaCp\*Me(OCH<sub>2</sub>)<sub>2</sub>py]OTf (0.120 g, 0.19 mmol) in toluene at room temperature. Upon addition, the white suspension became dark red and it was stirred at room temperature for 1 h. After filtration, the toluene solution was dried and the residue was

washed with pentane to yield a dark-red solid characterised as **2** (yield = 0.065 g, 71%).  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]$ benzene, 25°C, TMS):  $\delta$  = -0.15 (s, 3H; Me), 1.75 (s, 15H; Cp\*), 4.77 (d,  $^2J(\text{H,H})$  = 17.20 Hz, 1H; CH<sub>2</sub>), 4.83 (d,  $^3J(\text{H,H})$  = 5.92 Hz, 1H; Ar), 4.94 (d,  $^2J(\text{H,H})$  = 17.20 Hz, 1H; CH<sub>2</sub>), 6.11 (dd,  $^3J(\text{H,H})$  = 5.92, 9.16 Hz, 1H; Ar), 6.46 (d,  $^3J(\text{H,H})$  = 9.16 Hz, 1H; Ar), 7.69 ppm (s, 1H; CHO);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $[\text{D}_6]$ benzene, 25°C):  $\delta$  = 10.1 (Cp\*), 32.3 (Ta–Me), 79.0 (CH<sub>2</sub>), 94.8 (Ar), 117.1 (Cp\*), 117.2 (CHO), 122.7 (Ar), 135.2 (Ar), 138.0 (C<sub>ipso</sub>), 156.6 ppm (C<sub>ipso</sub>); IR (Nujol/PET):  $\tilde{\nu}$  = 1604 (m), 1580 (m), 1464 (vs), 1377 (s), 1296 (s), 1258 (s), 1168 (m), 1155 (m), 1101 (m), 1075 (s), 1041 (s), 961 (w), 889 (w), 840 (w), 776 (m), 729 (vs), 721 (vs), 641 cm<sup>-1</sup> (m); elemental analysis calcd (%) for C<sub>18</sub>H<sub>24</sub>NO<sub>2</sub>Ta: C 46.26, H 5.18, N 3.00; found: C 45.75, H 5.12, N 2.91.

**Complex 3:** To a solution of **2** in toluene (0.236 g, 0.51 mmol) was added HCCSiMe<sub>3</sub> (71  $\mu\text{L}$ , 0.51 mmol) and the solution was stirred at room temperature for 3 h. The solvent was removed under vacuum and the residue was extracted with pentane. Cooling the pentane solution at -25°C overnight afforded yellow crystals characterised as **3** (yield = 0.160 g, 56%).  $^1\text{H NMR}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -0.63 (s, 3H; Me), -0.02 (s, 9H; SiMe<sub>3</sub>), 1.96 (s, 15H; Cp\*), 5.36 (d,  $^2J(\text{H,H})$  = 17.97 Hz, 1H; CH<sub>2</sub>), 5.67 (d,  $^3J(\text{H,H})$  = 17.97 Hz, 1H; CH<sub>2</sub>), 6.46 (s, 1H; CH), 6.96 (m, 1H; Ar), 7.06 (m, 1H; Ar), 7.64 (m, 1H; Ar), 9.28 ppm (s, 1H; CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C):  $\delta$  = -1.1 (SiMe<sub>3</sub>), 10.6 (Cp\*), 33.1 (Ta–Me), 80.0 (CH<sub>2</sub>O), 91.5 (CHO), 114.2 (Ar), 115.3 (Ar), 118.6 (Cp\*), 137.5 (Ar), 157.0 (CSiMe<sub>3</sub>), 162.4 (C<sub>ipso</sub>), 164.3 (C<sub>ipso</sub>), 213.6 ppm (C–Ta); IR (Nujol/PET):  $\tilde{\nu}$  = 1600 (m), 1574 (m), 1464 (vs), 1377 (s), 1295 (s), 1251 (vs), 1163 (s), 1143 (s), 1060 (s), 1046 (vs), 993 (m), 864 (s), 830 (vs), 781 (s), 729 (vs), 721 (vs), 644 (m), 615 cm<sup>-1</sup> (m); elemental analysis calcd (%) for C<sub>23</sub>H<sub>34</sub>NO<sub>2</sub>SiTa: C 48.84, H 6.05, N 2.47; found: C 48.34, H 5.88, N 2.43.

**Complex 4:** HCCPh (61  $\mu\text{L}$ , 0.56 mmol) was added to a solution of **2** in toluene (0.261 g, 0.56 mmol) and the solution was stirred at room temperature for 3 h. Slow diffusion of Et<sub>2</sub>O into the toluene solution yielded yellow crystals of **4** (yield = 0.247 g, 77%).  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]$ benzene, 25°C, TMS):  $\delta$  = -0.01 (s, 3H; Me), 2.02 (s, 15H; Cp\*), 5.16 (d,  $^2J(\text{H,H})$  = 17.88 Hz, 1H; CH<sub>2</sub>), 5.34 (d,  $^3J(\text{H,H})$  = 17.88 Hz, 1H; CH<sub>2</sub>), 5.91 (m, 1H; Ar), 6.53 (m, 1H; Ar), 6.62 (m, 1H; Ar), 6.97 (m, 1H; Ph), 7.03 (s, 1H; CH), 7.13 (m, 2H; Ph), 7.40 (m, 2H; Ph), 9.18 ppm (s, 1H; CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $[\text{D}_6]$ benzene, 25°C):  $\delta$  = 10.8 (Cp\*), 35.8 (Ta–Me), 79.9 (CH<sub>2</sub>O), 91.1 (CHO), 113.9 (Ar), 114.8 (Ar), 118.5 (Cp\*), 124.4 (Ph), 125.6, (Ph), 128.3 (Ph), 137.0 (Ar), 139.4 (C<sub>ipso</sub>), 154.9 (CPh), 161.8 (C<sub>ipso</sub>), 164.3 (C<sub>ipso</sub>), 194.58 ppm (C–Ta); IR (Nujol/PET): 1593 (m), 1580 (m), 1573 (w), 1464 (vs), 1377 (vs), 1303 (m), 1151 (m), 1082 (m), 1064 (s), 1053 (s), 1025 (m), 776 (s), 770 (s), 747 (vs), 729 (vs), 721 (vs), 692 (m), 647 cm<sup>-1</sup> (m); elemental analysis calcd (%) for C<sub>26</sub>H<sub>30</sub>NO<sub>2</sub>Ta: C 54.83, H 5.30, N 2.45; found: C 54.64, H 5.42, N 2.54.

**Complex 5:** Di-2-pyridylketone (0.113 g, 0.61 mmol) was added to a solution of **2** in toluene (0.287 g, 0.61 mmol) and the solution was stirred at room temperature for 1 h. The solvent was removed under vacuum and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> before the solution was evaporated and the residue was washed with pentane to yield a white compound that was characterised as **5**. (yield = 0.293 g, 73%).  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]$ benzene, 25°C, TMS):  $\delta$  = -0.34 (s, 3H; Me), 1.87 (s, 15H; Cp\*), 5.50 (d,  $^2J(\text{H,H})$  = 18.09 Hz, 1H; CH<sub>2</sub>), 6.39 (d,  $^3J(\text{H,H})$  = 18.09 Hz, 1H; CH<sub>2</sub>), 6.48 (m, 1H; Ar), 6.89 (m, 1H; Ar), 6.93 (m, 1H; Ar), 7.02 (m, 1H; Ar), 7.30 (m, 1H; Ar), 7.44 (m, 1H; Ar), 7.54 (s, 1H; CH), 7.60 (m, 1H; Ar), 7.81 (m, 1H; Ar), 7.81 (m, 1H; Ar), 8.02 (m, 1H; Ar), 8.60 ppm (m, 1H; Ar);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 10.7 (Cp\*), 37.7 (Ta–Me), 80.2 (CH<sub>2</sub>O), 90.6 (CHO), 91.4 (CO), 116.5 (Ar), 117.3 (Ar), 121.4 (Cp\*), 121.5 (Ar), 122.2 (Ar), 126.8 (Ar), 136.3 (Ar), 136.5 (Ar), 137.8 (Ar), 137.9 (Ar), 147.4, (Ar), 147.7 (Ar), 149.2 (C<sub>ipso</sub>), 162.3 (C<sub>ipso</sub>), 164.2 (C<sub>ipso</sub>), 164.4 ppm (C<sub>ipso</sub>); IR (Nujol/PET): 1681 (m), 1634 (m), 1607 (m), 1591 (m), 1464 (vs), 1377 (s), 1296 (s), 1258 (vs), 1226 (m), 1166 (m), 1101 (m), 1029 (m), 954 (m), 889 (w), 771 (m), 729 (vs), 721 (vs), 639 cm<sup>-1</sup> (m); elemental analysis calcd (%) for C<sub>29</sub>H<sub>32</sub>N<sub>3</sub>O<sub>3</sub>Ta: C 53.45, H 4.95, N 6.45; found: C 52.98, H 5.11, N 6.28.

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**Keywords:** C–C coupling • C–H activation • organometallic complexes • pincer ligands • tantalum

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- [12] Crystal data for complex **3**: C<sub>23</sub>H<sub>34</sub>NO<sub>2</sub>SiTa; size: 0.43 × 0.32 × 0.14 mm<sup>3</sup>; M<sub>r</sub> = 565.55; T = 180(2) K; Mo<sub>Kα</sub>; triclinic; space group P $\bar{1}$ ; a = 9.4543(3), b = 13.3076(4), c = 20.0032(9) Å; α = 105.950(2), β = 93.695(2), γ = 106.078(1)°; V = 2298.08(14) Å<sup>3</sup>; Z = 4; ρ = 1.635 mgm<sup>-3</sup>; μ = 4.853 mm<sup>-1</sup>; F(000) = 1128; 20186 reflections were measured of which 11326 are unique (R<sub>int</sub> = 0.0985) and 6867 are observed [I > 2σ(I)]; final R<sub>1</sub> = 0.0578 and wR<sub>2</sub> = 0.1278 for reflections with [I > 2σ(I)] and R<sub>1</sub> = 0.0872, wR<sub>2</sub> = 0.1493 for all data; GOF = 0.870; final largest diffraction peak and hole: 3.183 and -4.270 e Å<sup>-3</sup>. Complex **4**: C<sub>26</sub>H<sub>30</sub>NO<sub>2</sub>Ta; size: 0.25 × 0.23 × 0.22 mm<sup>3</sup>; M<sub>r</sub> = 569.46; T = 180(2) K; Mo<sub>Kα</sub>; monoclinic; space group P2<sub>1</sub>/c; a = 8.628(1), b = 14.457(2), c = 17.454(3) Å; β = 95.656(3)°; V = 2166.6(6) Å<sup>3</sup>; Z = 4; ρ = 1.746 mg m<sup>-3</sup>; μ = 5.096 mm<sup>-1</sup>; F(000) = 1128; 12110 reflections were measured of which 4363 are unique (R<sub>int</sub> = 0.0535) and 2665 are observed [I > 2σ(I)]; final R<sub>1</sub> = 0.0339 and wR<sub>2</sub> = 0.0769 for reflections with [I > 2σ(I)] and R<sub>1</sub> = 0.0634, wR<sub>2</sub> = 0.0888 for all data; GOF = 0.963; final largest diffraction peak and hole: 0.950 and -1.047 e Å<sup>-3</sup>. Complex **5**: C<sub>29</sub>H<sub>32</sub>N<sub>3</sub>O<sub>3</sub>Ta; size: 0.30 × 0.13 × 0.11 mm<sup>3</sup>; M<sub>r</sub> = 651.53; T = 290(2) K; Mo<sub>Kα</sub>; monoclinic; space group P2<sub>1</sub>/c; a = 18.235(2), b = 9.358(1), c = 15.270(3) Å; β = 93.482(6)°; V = 2600.9(6) Å<sup>3</sup>; Z = 4; ρ = 1.664 Mg m<sup>-3</sup>; μ = 4.262 mm<sup>-1</sup>M; F(000) = 1296; 20770 reflections were measured of which 5326 are unique (R<sub>int</sub> = 0.0858) and 2347 are observed [I > 2σ(I)]. Final R<sub>1</sub> = 0.0651 and wR<sub>2</sub> = 0.1323 for reflections with [I > 2σ(I)] and R<sub>1</sub> = 0.1667, wR<sub>2</sub> = 0.1792 for all data; GOF = 0.914; final largest diffraction peak and hole: 1.466 and -1.373 e Å<sup>-3</sup>. CCDC-777121 (**3**), 777122 (**4**), and 777123 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.
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