DALTON
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New tantalum compounds supported by 3,3′-disubstituted-1,1′-bi-2-naphthoxide ligation†

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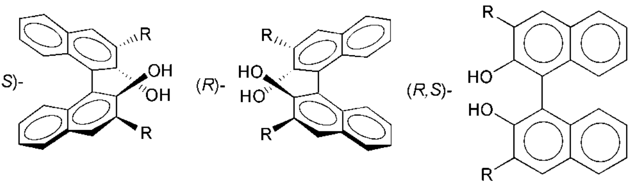
Several tantalum compounds supported by 3,3′-disubstituted-1,1′-bi-2-naphthol derived ligands have been prepared and initial aspects of their reactivity studied.

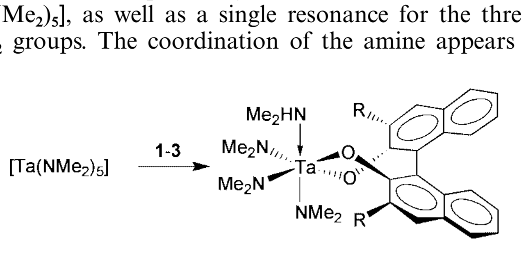
The use of *ortho*-substituted phenoxide ligands (ArO) to support organometallics at niobium and tantalum metal centers has proven very successful.[1] However, to date few examples of asymmetric versions of this $[(ArO)_2M]$ (M = Nb, Ta) based chemistry have been reported although we[2] and others[3] have recently reported on the use of chiral *ortho*-(1-naphthyl)-phenoxides as ancillary ligands. However, while the important chiral auxiliary 1,1′-bi-2-naphthol has found applications in many areas of asymmetric transition metal chemistry,[4] the niobium and tantalum chemistry of this ligand appears to be underdeveloped. We report here, some of our initial results on the chemistry of 3,3′-disubstituted derivatives of this ligand system with tantalum.

We have prepared a number of parent 3,3′-disubstituted ligands **1**–**3** (Scheme 1) *via* straightforward literature methods using either resolved or racemic versions of 2,2′-dihydroxy-1,1′-binaphthol.[5] Reaction of $[Ta_2Cl_{10}]$ with **1**–**3** or their dilithium or dipotassium salts lead to an as yet unidentified mixture (NMR) of products. However, reaction of $[Ta(NMe_2)_5]$[6] with **1**–**3** afforded compounds **4**–**7** as yellow solids in high yields (Scheme 2).‡ The solution NMR spectroscopic properties of **4**–**7** indicate the presence of coordinated Me_2NH, formed from the protonolysis reaction between **1**–**3** and $[Ta(NMe_2)_5]$, as well as a single resonance for the three $Ta–NMe_2$ groups. The coordination of the amine appears to be insensitive to the bulk of the 3,3′-substituents in these compounds. The solid state structures of (*S*)-**4** (Fig. 1), (*R*)-**6** and (*R*,*S*)-**7**,§ confirm the presence of coordinated Me_2NH. All three compounds possess a pseudo-octahedral geometry about the metal center with the amine group *cis* to both aryloxide oxygen atoms. The structural parameters are essentially identical for all three compounds although the solid-state structure of (*R*)-**6** contained a disorder of the Ta atom along the amide–amine axis.



1: R = $SiMe_3$ **2a**: R = $SiMe_2Ph$ **2b**: R = $SiMePh_2$ **3**: R = $SiPh_3$

Scheme 1



(*S*)-**4**: R = $SiMe_3$ shown; (*R*)-**5**: R = $SiMe_2Ph$
(*R*)-**6**: R = $SiMePh_2$ (*R*,*S*)-**7**: R = $SiPh_3$

Scheme 2

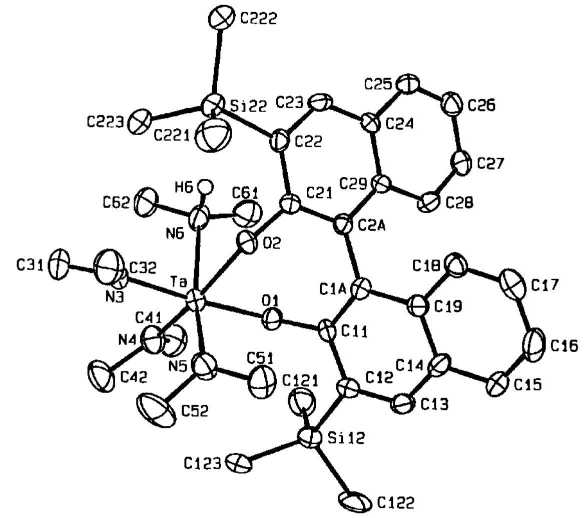


Fig. 1 Molecular structure of (*S*)-**4** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ta–O(1) 2.036(4), Ta–O(2) 2.039(3), Ta–N(3) 2.006(5), Ta–N(4) 2.009(5), Ta–N(5) 2.000(5), Ta–N(6) 2.465(5); O(1)–Ta–O(2) 84.9(2), O(1)–Ta–N(3) 175.1(2), O(1)–Ta–N(4) 89.2(2), O(1)–Ta–N(5) 94.9(2), O(1)–Ta–N(6) 91.9(2), O(2)–Ta–N(3) 94.1(2), O(2)–Ta–N(4) 164.7(2), O(2)–Ta–N(5) 91.5(2), O(2)–Ta–N(6) 79.2(2), N(3)–Ta–N(4) 90.5(3), N(3)–Ta–N(5) 89.9(3), N(3)–Ta–N(6) 93.2(2), N(4)–Ta–N(5) 103.1(2), N(4)–Ta–N(6) 86.0(2), N(5)–Ta–N(6) 170.3(2), Ta–O(1)–C(11) 130.3(4), Ta–O(2)–C(21) 132.5(3).

Addition of $SiCl_4$ to a hydrocarbon solution of (*S*)-**4** leads to the formation of a mixture of (*S*)-**9** and (*S*)-**10** (Scheme 3, Fig. 2).§ The formation of (*S*)-**10** appears to result from (*S*)-**9** reacting with excess HCl that is generated in the Me_2NH-catalyzed amide/chloride replacement reaction. It has proven difficult to physically separate and characterize (*S*)-**9** and (*S*)-**10**, although a few crystals of (*S*)-**10** were obtained from benzene–pentane solutions. Both compounds also have essentially the same NMR spectroscopic properties. Treatment of a C_6D_6 solution of the (*S*)-**9**, (*S*)-**10** mixture with Bu_3SnH in the presence of PMe_3 leads to a species which we formulate as the monohydride (*S*)-**11** (Scheme 3). The ^1H NMR spectrum of (*S*)-**11** contains a Ta–H resonance as a doublet of doublets at δ 22.0 ($^2J_{H\text{-}P}$ = 92 and 95 Hz). Two $SiMe_3$ resonances for the binaphthoxide ligand are also present. The ^{31}P NMR spectrum of (*S*)-**11** also shows non-equivalent phosphine ligands. Previous work with monodentate aryloxide

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† Electronic supplementary information (ESI) available: preparation and spectroscopic data for compounds **4**–**11**. See http://www.rsc.org/suppdata/dt/b0/b005681m/

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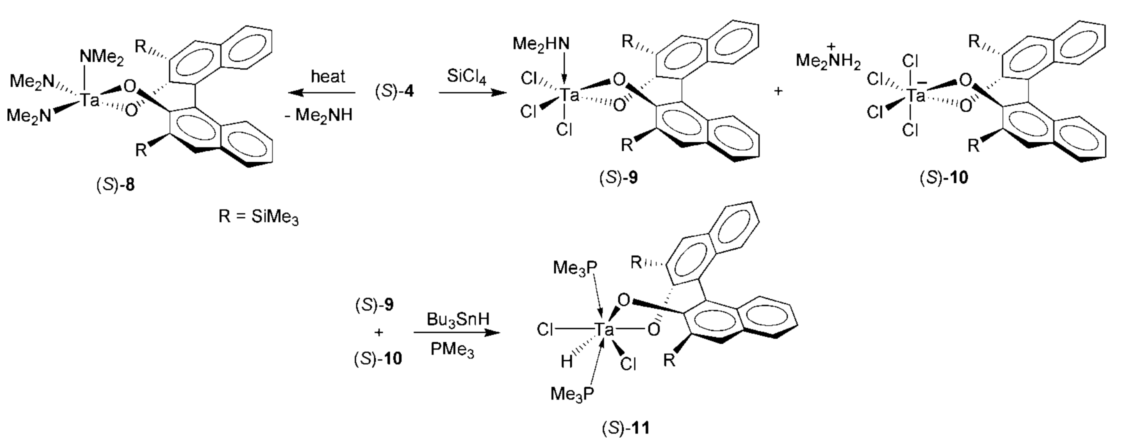

Scheme 3

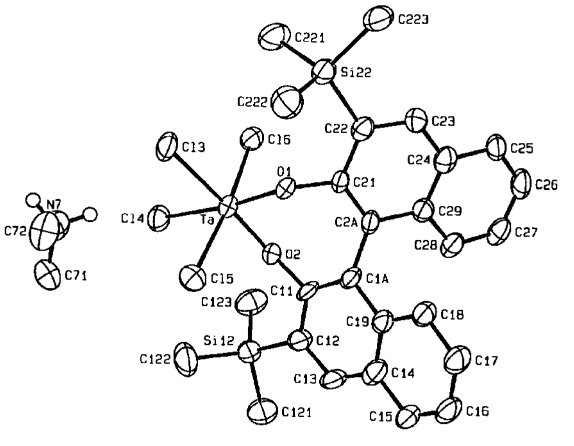

Fig. 2 Molecular structure of (*S*)-**10** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ta–O(1) 1.889(6), Ta–O(2) 1.893(7), Ta–Cl(3) 2.420(3), Ta–Cl(4) 2.431(3), Ta–Cl(5) 2.362(2), Ta–Cl(6) 2.379(2); O(1)–Ta–O(2) 89.8(3), O(1)–Ta–Cl(3) 89.8(2), O(1)–Ta–Cl(4) 173.4(2), O(1)–Ta–Cl(5) 96.0(2), O(1)–Ta–Cl(6) 90.0(2), O(2)–Ta–Cl(3) 176.3(2), O(2)–Ta–Cl(4) 93.2(2), O(2)–Ta–Cl(5) 89.5(2), O(2)–Ta–Cl(6) 93.0(2), Cl(3)–Ta–Cl(4) 87.6(1), Cl(3)–Ta–Cl(5) 86.9(1), Cl(3)–Ta–Cl(6) 90.7(1), Cl(4)–Ta–Cl(5) 89.9(1), Cl(4)–Ta–Cl(6) 84.0(1), Cl(5)–Ta–Cl(6) 173.5(1), Ta–O(1)–C(21) 135.7(6), Ta–O(2)–C(11) 134.7(6).

ligands has shown that seven-coordinate mono-, di- and trihydrides adopt a pentagonal bipyramidal structure with *trans*-axial aryloxide oxygen atoms. The assigned structure for (*S*)-**11** (axial O and Cl) is, therefore, based upon these previous results and the spectroscopic data.

In an attempt to avoid the formation of (*S*)-**10**, solid (*S*)-**4** was gently heated under vacuum to remove $\mathrm{Me_2NH}$ leading to the amine-free (*S*)-**8**. Unfortunately treatment of (*S*)-**8** with $\mathrm{SiCl_4}$ generated a complex mixture resulting from incomplete amide replacement. Apparently for (*S*)-**8** the lack of coordinated $\mathrm{Me_2NH}$ leads to poor catalysis of the chloride replacement reaction.

Acknowledgements

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Notes and references

‡ Selected spectroscopic data: NMR ($\mathrm{C_6D_6}$, 30 °C) aromatic signals unless indicated: ^{1}H: (*S*)-**4**: δ 8.12 (s), 7.77 (d), 6.82–7.20; 3.19 (s, $\mathrm{NMe_2}$); 1.87 (br, $\mathrm{NH}Me_2$); 0.47 (s, $\mathrm{SiMe_3}$). **5**: δ 8.09 (s), 7.63–7.76 (m), 6.86–7.25; 3.14 (s, $\mathrm{NMe_2}$); 1.98 (s, $\mathrm{NH}Me_2$); 0.70 (s), 0.69 (s, $\mathrm{Si}Me_2\mathrm{Ph}$). (*R*)-**6**: δ 7.88 (s), 7.72 (m), 7.40 (d), 6.81–7.30; 2.89 (s, $\mathrm{NMe_2}$); 1.81 (s, $\mathrm{NH}Me_2$); 1.00 (s, $\mathrm{Si}Me\mathrm{Ph_2}$). (*R*,S)-**7**: δ 8.12 (s), 7.85–8.12 (m), 7.44 (d), 7.29 (d), 7.10–7.16 (m), 6.86–6.97; 2.70 (s, $\mathrm{NMe_2}$); 1.79 (s, $\mathrm{NH}Me_2$). (*R*)-**8**: δ 8.14 (s), 7.78 (d), 7.28 (d), 7.08 (t), 6.89 (t); 3.07 (s, $\mathrm{NMe_2}$); 0.48 (s, $\mathrm{SiMe_3}$). (*S*)-**9** and (*S*)-**10**: δ 8.23 (s), 7.65 (d), 6.65–7.16; 6.77 (br, NH); 2.07 (br, $\mathrm{NMe_2}$); 0.77 (s, $\mathrm{SiMe_3}$). (*S*)-**11**: δ 22.0 (dd, $^2J_{\mathrm{H-P}} = 92$, 95 Hz, Ta–H); 8.24 (s), 6.67–8.41; 1.74 (br, $\mathrm{NMe_2}$); 1.36 (d), 1.00 (d, $^2J_{\mathrm{H-P}} = 9.2$ Hz, $\mathrm{PMe_3}$); 0.81 (s), 0.39 (s, $\mathrm{SiMe_3}$). ^{13}C: (*S*)-**4**: δ 164.9 (Ta–O–C); 46.7 ($\mathrm{NMe_2}$); 40.5 ($\mathrm{NHMe_2}$); −0.1 ($\mathrm{SiMe_3}$). (*R*)-**5**: δ 165.0 (Ta–O–C); 47.1 ($\mathrm{NMe_2}$); 39.6 ($\mathrm{NHMe_2}$); −0.8, −1.4 ($\mathrm{SiMe_2Ph}$). (*R*)-**6**: δ 165.8 (Ta–O–C); 46.9 ($\mathrm{NMe_2}$); 40.9 ($\mathrm{NHMe_2}$); −2.1 ($\mathrm{SiMePh_2}$). (*R*,S)-**7**: δ 165.7 (Ta–O–C); 46.1 ($\mathrm{NMe_2}$); 40.0 ($\mathrm{NHMe_2}$). (*S*)-**8**: δ 164.9 (Ta–O–C); 45.6 ($\mathrm{NMe_2}$); −0.1 ($\mathrm{SiMe_3}$). (*S*)-**9** and (*S*)-**10**: δ 163.0 (Ta–O–C); 35.8 ($\mathrm{NMe_2}$); 0.4 ($\mathrm{SiMe_3}$). ^{31}P **11**: δ 10.9 (d, $^2J_{\mathrm{PP}} = 42.0$ Hz, $\mathrm{PMe_3}$); 3.7 (d, $^2J_{\mathrm{PP}} = 42$ Hz, $\mathrm{PMe_3}$).

§ *Crystal data*: For (*S*)-**4** at 193 K: $\mathrm{TaN_4O_2Si_2C_{34}H_{53}}$, $M = 786.95$, space group $P2_12_12_1$ (no. 19), $a = 11.0515(3)$, $b = 15.2435(4)$, $c = 21.8989(5)$ Å, $V = 3689.2(3)$ Å^3, $D_c = 1.417$ g cm^{-3}, $Z = 4$. Of the 8380 unique reflections collected ($8.00 \leqslant 2\theta \leqslant 55.00°$) with Mo-Kα radiation ($\lambda = 0.71073$ Å), the 8380 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o) = 0.045$ and $R_w(F_o^2) = 0.088$. For (*R*)-**6** at 173 K: $\mathrm{TaN_4O_2Si_2C_{72}H_{79}}$, $M = 1269.58$, space group $C222_1$ (no. 20), $a = 11.4866(2)$, $b = 20.5325(4)$, $c = 26.7517(5)$ Å, $V = 6309.4(4)$ Å^3, $D_c = 1.336$ g cm^{-3}, $Z = 4$. Of the 7930 unique reflections collected ($8.00 \leqslant 2\theta \leqslant 57.42°$) with Mo-Kα radiation ($\lambda = 0.71073$ Å), the 7930 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o) = 0.040$ and $R_w(F_o^2) = 0.073$. For (*R*,S)-**7** at 173 K: $\mathrm{TaN_4O_2Si_2C_{70}H_{71}}$, $M = 1237.49$, space group $P2_1/c$ (no. 14), $a = 11.6987(2)$, $b = 18.2575(4)$, $c = 28.1025(5)$ Å, $\beta = 94.759(1)°$, $V = 5981.7(4)$ Å^3, $D_c = 1.374$ g cm^{-3}, $Z = 4$. Of the 14457 unique reflections collected ($8.00 \leqslant 2\theta \leqslant 55.70°$) with Mo-Kα radiation ($\lambda = 0.71073$ Å), the 14457 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o) = 0.048$ and $R_w(F_o^2) = 0.077$. For (*S*)-**10** at 173 K: $\mathrm{TaCl_4NO_2Si_2C_{31}H_{39}}$, $M = 836.59$, space group $C2$ (no. 5), $a = 27.604(2)$, $b = 12.7559(7)$, $c = 11.549(1)$ Å, $\beta = 100.591(3)°$, $V = 3997.4(9)$ Å^3, $D_c = 1.390$ g cm^{-3}, $Z = 4$. Of the 8683 unique reflections collected ($8.00 \leqslant 2\theta \leqslant 55.85°$) with Mo-Kα radiation ($\lambda = 0.71073$ Å), the 8683 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o) = 0.054$ and $R_w(F_o^2) = 0.130$. CCDC reference number 186/2089.

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