

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

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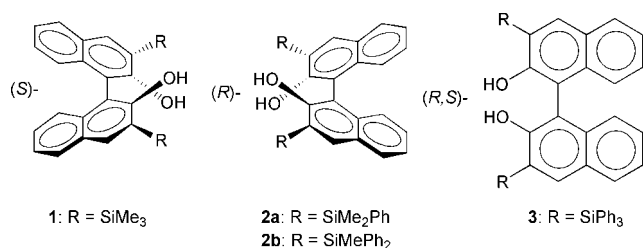
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Several tantalum compounds supported by 3,3'-disubstituted-1,1'-bi-2-naphthol derived ligands have been prepared and initial aspects of their reactivity studied.

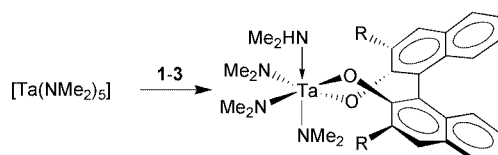
The use of *ortho*-substituted phenoxide ligands (ArO) to support organometallics at niobium and tantalum metal centers has proven very successful.¹ However, to date few examples of asymmetric versions of this [(ArO)₂M] (M = Nb, Ta) based chemistry have been reported although we² and others³ have recently 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



Scheme 1

using either resolved or racemic versions of 2,2'-dihydroxy-1,1'-binaphthol.⁵ Reaction of [Ta₂Cl₁₀] with 1–3 or their dilithium or dipotassium salts lead to an as yet unidentified mixture (NMR) of products. However, reaction of [Ta(NMe₂)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 Me₂NH, formed from the protonolysis reaction between 1–3 and [Ta(NMe₂)₅], as well as a single resonance for the three Ta–NMe₂ groups. The coordination of the amine appears to be



(S)-4: R = SiMe₃ shown; (R)-5: R = SiMe₂Ph
(R)-6: R = SiMePh₂ (R,S)-7: R = SiPh₃

Scheme 2

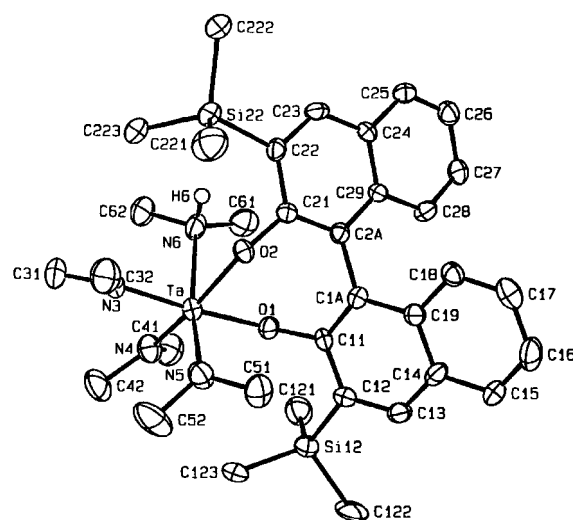
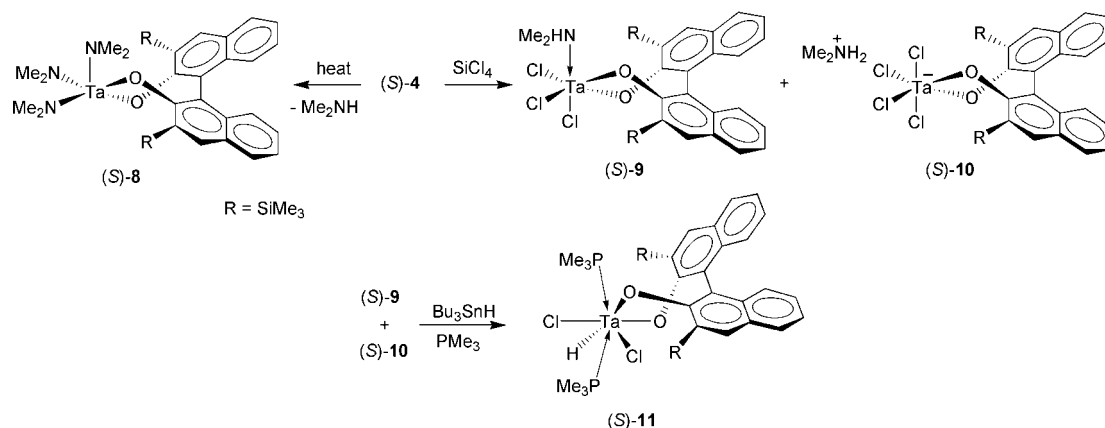


Fig. 1 Molecular structure of (*S*)-4 showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ta–O(1) 2.036(4), Ta–O(2) 2.039(3), Ta–N(3) 2.006(5), Ta–N(4) 2.009(5), Ta–N(5) 2.000(5), Ta–N(6) 2.465(5); O(1)–Ta–O(2) 84.9(2), O(1)–Ta–N(3) 175.1(2), O(1)–Ta–N(4) 89.2(2), 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).

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 Me₂NH. All three compounds possess a pseudo-octahedral geometry about the metal center with the amine group *cis* to both aryloxy 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.

Addition of SiCl₄ 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 Me₂NH-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 C₆D₆ solution of the (*S*)-9, (*S*)-10 mixture with Bu₃SnH in the presence of PMe₃ 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–P} = 92 and 95 Hz). Two SiMe₃ resonances for the binaphthoxide ligand are also present. The ³¹P NMR spectrum of (*S*)-11 also shows non-equivalent phosphine ligands. Previous work with monodentate aryloxy

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



Scheme 3

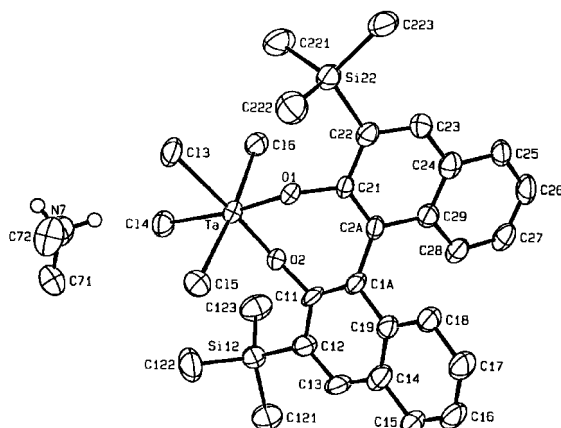


Fig. 2 Molecular structure of (S)-10 showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ta–O(1) 1.889(6), Ta–O(2) 1.893(7), Ta–Cl(3) 2.420(3), Ta–Cl(4) 2.431(3), Ta–Cl(5) 2.362(2), Ta–Cl(6) 2.379(2); O(1)–Ta–O(2) 89.8(3), O(1)–Ta–Cl(3) 89.8(2), O(1)–Ta–Cl(4) 173.4(2), 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 aryloxy 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 Me₂NH leading to the amine-free (S)-8. Unfortunately treatment of (S)-8 with SiCl₄ generated a complex mixture resulting from incomplete amide replacement. Apparently for (S)-8 the lack of coordinated Me₂NH leads to poor catalysis of the chloride replacement reaction.

Acknowledgements

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Notes and references

† Selected spectroscopic data: NMR (C₆D₆, 30 °C) aromatic signals unless indicated: ¹H: (S)-4: δ 8.12 (s), 7.77 (d), 6.82–7.20; 3.19 (s, NMe₂); 1.87 (br, NHMe₂); 0.47 (s, SiMe₃). 5: δ 8.09 (s), 7.63–7.76 (m), 6.86–7.25; 3.14 (s, NMe₂); 1.98 (s, NHMe₂); 0.70 (s), 0.69 (s, SiMe₂Ph). (R)-6: δ 7.88 (s), 7.72 (m), 7.40 (d), 6.81–7.30; 2.89 (s, NMe₂); 1.81 (s, NHMe₂); 1.00 (s, SiMePh₂). (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, NMe₂); 1.79 (s, NHMe₂). (R)-8: δ 8.14 (s), 7.78 (d), 7.28 (d), 7.08 (t), 6.89 (t); 3.07 (s, NMe₂); 0.48 (s, SiMe₃). (S)-9 and (S)-10: δ 8.23 (s), 7.65 (d), 6.65–7.16; 6.77 (br, NH);

2.07 (br, NMe₂); 0.77 (s, SiMe₃). (S)-11: δ 22.0 (dd, ²J_{H-P} = 92, 95 Hz, Ta–H); 8.24 (s), 6.67–8.41; 1.74 (br, NMe₂); 1.36 (d), 1.00 (d, ²J_{H-P} = 9.2 Hz, PMe₃); 0.81 (s), 0.39 (s, SiMe₃). ¹³C: (S)-4: δ 164.9 (Ta–O–C); 46.7 (NMe₂); 40.5 (NHMe₂); –0.1 (SiMe₃). (R)-5: δ 165.0 (Ta–O–C); 47.1 (NMe₂); 39.6 (NHMe₂); –0.8, –1.4 (SiMe₂Ph). (R)-6: δ 165.8 (Ta–O–C); 46.9 (NMe₂); 40.9 (NHMe₂); –2.1 (SiMePh₂). (R,S)-7: δ 165.7 (Ta–O–C); 46.1 (NMe₂); 40.0 (NHMe₂). (S)-8: δ 164.9 (Ta–O–C); 45.6 (NMe₂); –0.1 (SiMe₃). (S)-9 and (S)-10: δ 163.0 (Ta–O–C); 35.8 (NMe₂); 0.4 (SiMe₃). ³¹P 11: δ 10.9 (d, ²J_{PP} = 42.0 Hz, PMe₃); 3.7 (d, ²J_{PP} = 42 Hz, PMe₃).

§ *Crystal data*: For (S)-4 at 193 K: TaN₄O₂Si₂C₃₄H₅₃, *M* = 786.95, space group *P*2₁2₁ (no. 19), *a* = 11.0515(3), *b* = 15.2435(4), *c* = 21.8989(5) Å, *V* = 3689.2(3) Å³, *D*_c = 1.417 g cm^{–3}, *Z* = 4. Of the 8380 unique reflections collected (8.00 ≤ 2θ ≤ 55.00°) with Mo-Kα radiation (λ = 0.71073 Å), the 8380 with *F*_o² > 2σ(*F*_o²) were used in the final least-squares refinement to yield *R*(*F*_o) = 0.045 and *R*_w(*F*_o²) = 0.088. For (R)-6 at 173 K: TaN₄O₂Si₂C₇₂H₇₉, *M* = 1269.58, space group *C*222₁ (no. 20), *a* = 11.4866(2), *b* = 20.5325(4), *c* = 26.7517(5) Å, *V* = 6309.4(4) Å³, *D*_c = 1.336 g cm^{–3}, *Z* = 4. Of the 7930 unique reflections collected (8.00 ≤ 2θ ≤ 57.42°) with Mo-Kα radiation (λ = 0.71073 Å), the 7930 with *F*_o² > 2σ(*F*_o²) were used in the final least-squares refinement to yield *R*(*F*_o) = 0.040 and *R*_w(*F*_o²) = 0.073. For (R,S)-7 at 173 K: TaN₄O₂Si₂C₇₀H₇₁, *M* = 1237.49, space group *P*2₁/c (no. 14), *a* = 11.6987(2), *b* = 18.2575(4), *c* = 28.1025(5) Å, β = 94.759(1)°, *V* = 5981.7(4) Å³, *D*_c = 1.374 g cm^{–3}, *Z* = 4. Of the 14457 unique reflections collected (8.00 ≤ 2θ ≤ 55.70°) with Mo-Kα radiation (λ = 0.71073 Å), the 14457 with *F*_o² > 2σ(*F*_o²) were used in the final least-squares refinement to yield *R*(*F*_o) = 0.048 and *R*_w(*F*_o²) = 0.077. For (S)-10 at 173 K: TaCl₄NO₂Si₂C₃₁H₃₉, *M* = 836.59, space group *C*2 (no. 5), *a* = 27.604(2), *b* = 12.7559(7), *c* = 11.549(1) Å, β = 100.591(3)°, *V* = 3997.4(9) Å³, *D*_c = 1.390 g cm^{–3}, *Z* = 4. Of the 8683 unique reflections collected (8.00 ≤ 2θ ≤ 55.85°) with Mo-Kα radiation (λ = 0.71073 Å), the 8683 with *F*_o² > 2σ(*F*_o²) were used in the final least-squares refinement to yield *R*(*F*_o) = 0.054 and *R*_w(*F*_o²) = 0.130. CCDC reference number 186/2089.

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