

# Regioselective insertion of 2-vinylpyridine in niobium and tantalum aryloxy complexes: an alternate route to pyridylalkyl metallacycles†‡

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A series of niobium and tantalum aryloxy complexes containing pyridylethyl ligation have been synthesized via 2-vinylpyridine insertion to metal hydride complexes.

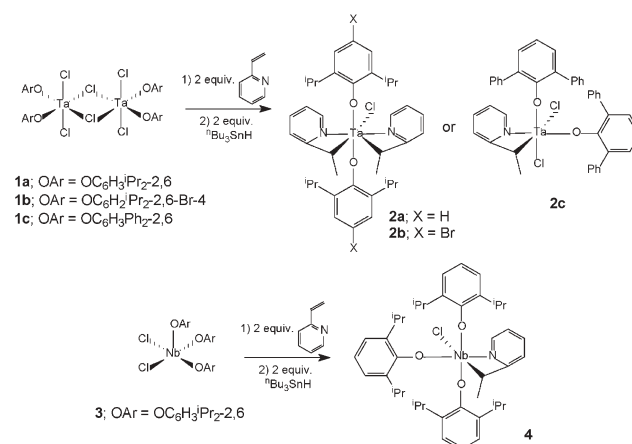
Hydride derivatives of niobium and tantalum containing aryloxy ligands have been demonstrated to catalyze the hydrogenation of a variety of arene substrates.<sup>1</sup> From many strategies available for the synthesis of transition metal hydrides, two successful procedures have been reported for the synthesis of niobium and tantalum hydride complexes involving high-pressure hydrogenolysis<sup>2</sup> and treatment of the corresponding chloro aryloxides with <sup>n</sup>Bu<sub>3</sub>SnH in the presence of a donor phosphine.<sup>3</sup> By using the second method, a series of aryloxy complexes [M(OC<sub>6</sub>H<sub>3</sub>R<sub>2-2,6</sub>)<sub>2</sub>(Cl)<sub>3-n</sub>(H)<sub>n</sub>L<sub>2</sub>] (M = Nb, Ta; R = <sup>i</sup>Pr, <sup>t</sup>Bu, Ph; n = 1–3; L = donor ligand) have been prepared.<sup>3</sup> A study of the reactions of these hydride complexes with olefins and alkynes has provided a better understanding of mechanistic details of the catalytic hydrogenation reaction.<sup>4</sup> We have shown that the reaction of [Ta(OC<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr<sub>2-2,6</sub>)<sub>2</sub>(H)<sub>2</sub>(Cl)(PMe<sub>2</sub>Ph)<sub>2</sub>] with styrene produces 1 equiv of PhEt, H<sub>2</sub>, and the dehydrogenation product [Ta(OC<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr-η<sup>2</sup>-CMe=CH<sub>2</sub>)(OC<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr<sub>2-2,6</sub>)(Cl)(PMe<sub>2</sub>Ph)<sub>2</sub>].<sup>4</sup> In this work we report the reaction of Group 5 metal hydride aryloxy complexes with 2-vinylpyridine.

The reactions of a series of four mixed chloro bis/tris aryloxy complexes **1a–c** and **3** with <sup>n</sup>Bu<sub>3</sub>SnH in the presence of 2-vinylpyridine were investigated. In all cases, the products were obtained by reacting a suspension of complexes **1a–c** or **3** in hydrocarbon solvent with 2 equiv of 2-vinylpyridine (Scheme 1). To this solution, 2 equiv of <sup>n</sup>Bu<sub>3</sub>SnH was added. The reaction proceeds first with H/Cl exchange giving [M(OAr)<sub>n</sub>HCl<sub>4-n</sub>(C<sub>7</sub>H<sub>7</sub>N)<sub>x</sub>] (where n = 2 for M = Ta and n = 3 for M = Nb) and <sup>n</sup>Bu<sub>3</sub>SnCl.<sup>3</sup> Attempts to use other sources of hydride such as LiBH<sub>4</sub> and NaBH<sub>4</sub> were not successful. The 2-vinylpyridine olefin then inserts into the metal–hydride bond. Depending on the steric hindrance of aryloxy, a second H/Cl exchange may occur followed by a second 2-vinylpyridine insertion into the Ta–H bond. After stirring for 15 hours at room temperature the products were isolated in powder form as follows: yellow [Ta(OC<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr<sub>2-2,6</sub>)<sub>2</sub>(η<sup>2</sup>-C<sub>7</sub>H<sub>8</sub>N)<sub>2</sub>Cl] (**2a**); yellow [Ta(OC<sub>6</sub>H<sub>2</sub><sup>i</sup>Pr<sub>2-2,6</sub>-Br-4)<sub>2</sub>(η<sup>2</sup>-C<sub>7</sub>H<sub>8</sub>N)<sub>2</sub>Cl] (**2b**); tan [Ta(OC<sub>6</sub>H<sub>3</sub>Ph<sub>2-2,6</sub>)<sub>2</sub>(η<sup>2</sup>-C<sub>7</sub>H<sub>8</sub>N)<sub>2</sub>Cl<sub>2</sub>] (**2c**); or golden orange

[Nb(OC<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr<sub>2-2,6</sub>)<sub>3</sub>(η<sup>2</sup>-C<sub>7</sub>H<sub>8</sub>N)Cl] (**4**) (Scheme 1). In all cases the products reflect a regioselective insertion with hydride migration to the β-carbon resulting in a 4-membered pyridylalkyl metallacycle. Regioselective insertion is believed to result from a kinetic effect dependant upon the electronic and steric nature of the olefin substrate and metal complex.<sup>5</sup> These products are strikingly different from that obtained when Group 5 metal hydride aryloxy complexes are reacted with styrene, despite similarity with 2-vinylpyridine, signifying the importance of the nitrogen heteroatom.

Compounds **2a** and **2b** contain two pyridylethyl ligands. This suggests that the second H/Cl exchange occurred along with the second 2-vinylpyridine insertion into the Ta–H bond. It seems that increased stability arising from pyridine chelation after the first 2-vinylpyridine insertion prevents σ-bond metathesis between the pyridylethyl ligand and a second hydride ligand. Attempts to react more than 2 equiv of 2-vinylpyridine/<sup>n</sup>Bu<sub>3</sub>SnH failed to replace the third chloride atom.

An ORTEP drawing of the tantalum complex **2a** is given in Fig. 1. Compound **2a** has a pseudo pentagonal bipyramidal geometry with a seven-coordinate Ta center. The two aryloxides are axial with an average Ta–O distance of 1.925 Å. The chloride and two η<sup>2</sup>-C<sub>7</sub>H<sub>8</sub>N ligands are equatorial with Ta–Cl, Ta–C<sub>ave</sub>, and Ta–N<sub>ave</sub> distances of 2.493(1), 2.275, and 2.245 Å, respectively. The bite angle of the pyridylethyl ligand N31–Ta–C321 is 60.10(2)°. The *cis* C–Ta–C pyridylethyl ligand geometry present in the solid state seems to be maintained in solution as indicated by NMR. Spectra from VT NMR experiments recorded between 25 and 100 °C indicate a structure consistent with the geometry of the solid. The crystal structure and NMR spectra indicate that

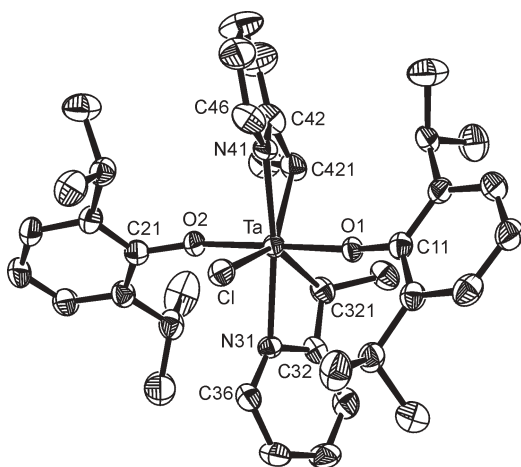


Scheme 1 Preparation of compounds **2a–c** and **4**.

† Electronic supplementary information (ESI) available: synthesis, and characterization, for compounds **2a–c** and **4**. See <http://www.rsc.org/suppdata/cc/b4/b416536e/>

‡ This paper is dedicated with the most sincere gratitude to the memory of our mentor and friend Ian P. Rothwell, Richard B. Moore Distinguished Professor of Chemistry.

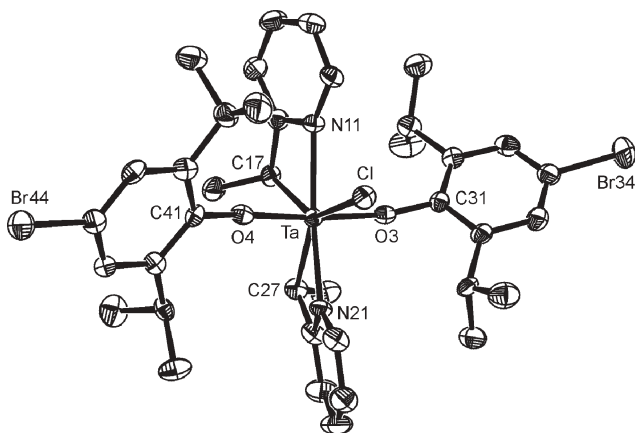
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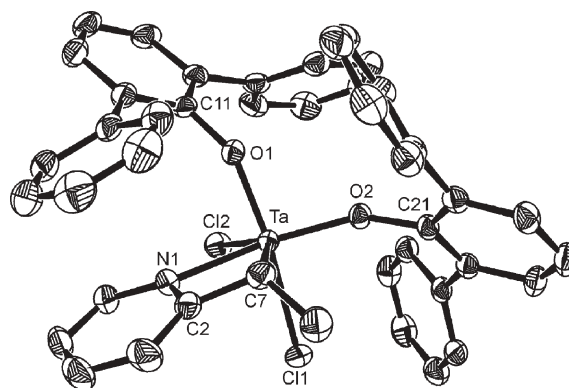
**Fig. 1** An ORTEP drawing of  $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}_2\text{-2,6})_2(\text{C}_7\text{H}_8\text{N})_2\text{Cl}]$ , **2a**, with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Ta–O1 1.923(3), Ta–O2 1.927(3), Ta–Cl 2.4934(1), Ta–N31 2.237(4), Ta–N41 2.253(4), Ta–C321 2.284(5), Ta–C421 2.266(5); C321–Ta–C421 79.1(2), N31–Ta–C321 60.10(2), N41–Ta–C421 60.48(2), O1–Ta–O2 174.26(1), N31–Ta–N41 162.55(1), O1–Ta–Cl 87.07(9), O2–Ta–Cl 87.22(1).

hydride, presumably originating from  ${}^n\text{Bu}_3\text{SnH}$ , ends up on the terminal carbon atom. To further confirm the source of hydride the reaction was carried out using **1a**, 2-vinylpyridine, and  ${}^n\text{Bu}_3\text{SnD}$ . The isolated product was  $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}_2\text{-2,6})_2(\text{CH}(\text{py})\text{-}(\text{CH}_2\text{D}))_2\text{Cl}]$  confirming that  ${}^n\text{Bu}_3\text{SnH}$  is the source of hydrogen at the  $\beta$ -carbon.

The seven-coordinate compound **2b** adopts a pseudo pentagonal bipyrimidal arrangement of ligands about the tantalum metal center. An ORTEP drawing of complex **2b** is given in Fig. 2. Compound **2b** also contains two pyridylethyl ligands featuring a structure similar to that of **2a**. The presence of the Br atom only shortens the Ta–O bond length slightly by 0.026 Å compared to **2a**.



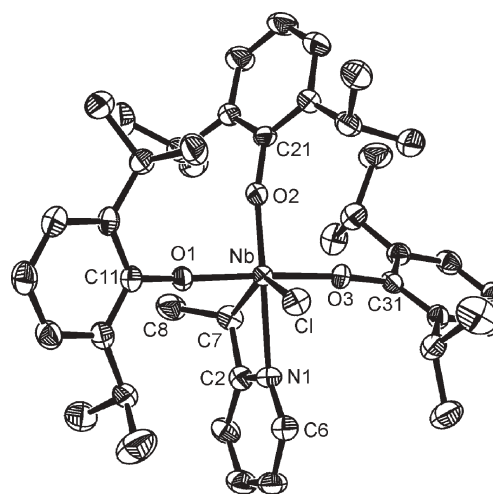
**Fig. 2** An ORTEP drawing of  $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}_2\text{-2,6-Br-4})_2(\text{C}_7\text{H}_8\text{N})_2\text{Cl}]$ , **2b**, with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Ta–O3 1.904(3), Ta–O4 1.894(3), Ta–Cl 2.5064(1), Ta–N11 2.240(4), Ta–N21 2.258(4), Ta–C17 2.283(5), Ta–C27 2.278(5); C17–Ta–C27 77.77(2), N11–Ta–C17 60.56(2), N21–Ta–C27 60.58(2), O3–Ta–O4 173.78(2), N11–Ta–N21 162.59(2), O3–Ta–Cl 86.35(1), O4–Ta–Cl 88.34(1).



**Fig. 3** An ORTEP drawing of  $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\text{C}_7\text{H}_8\text{N})\text{Cl}]_2$ , **2c**, with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Ta–O1 1.8891(2), Ta–O2 1.8705(2), Ta–Cl1 2.3900(7), Ta–Cl2 2.3976(7), Ta–N1 2.215(2), Ta–C7 2.229(3); O1–Ta–O2 95.57(8), N1–Ta–C7 61.91(1), Cl1–Ta–Cl2 85.48(3), O1–Ta–Cl1 172.63(6), O2–Ta–N1 156.15(9), O1–Ta–C7 97.33(9), C7–Ta–Cl1 85.05(8).

For compound **2c**, it seems that steric hindrance of 2,6-diphenylphenoxide ligands prevent a second H/Cl exchange. Hence, only one 2-vinylpyridine inserts. The use of excess 2-vinylpyridine/ ${}^n\text{Bu}_3\text{SnH}$  failed to initiate replacement of an additional chloride ligand. An ORTEP drawing of complex **2c** is given in Fig. 3. Compound **2c** has a pseudo octahedral geometry with a six-coordinate tantalum center. The two aryloxides are *cis* with a O1–Ta–O2 angle of  $95.57(8)^\circ$ . The *trans* influence is observed where the Ta–O1 (*trans* to Cl) bond is longer than the Ta–O2 (*trans* to py) bond by 0.018 Å.

The niobium complex, **4** with one pyridylethyl ligand was isolated. The use of excess 2-vinylpyridine/ ${}^n\text{Bu}_3\text{SnH}$  failed to replace the second chloride atom. An ORTEP drawing of complex **4** is given in Fig. 4. Compound **4** adopts a pseudo octahedral geometry with a six-coordinate Nb center. The three aryloxides are



**Fig. 4** An ORTEP drawing of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}_2\text{-2,6})_3(\text{C}_7\text{H}_8\text{N})\text{Cl}]$ , **4**, with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Nb–N1 2.293(3), Nb–C7 2.266(4), Nb–Cl 2.4003(1), Nb–O1 1.910(2), Nb–O2 1.874(3), Nb–O3 1.907(2); N1–Nb–C7 60.86(1), N1–Nb–Cl 80.63(8), O1–Nb–O2 91.80(1), O2–Nb–O3 90.58(1), O1–Nb–O3 177.45(1), N1–C2–C7 109.1(3), O1–Nb–N1 93.10(1).

in a *mer* arrangement with two sets of Nb–O distances. The Nb–O2 distance is slightly shorter than Nb–O1 and Nb–O3 by 0.035 Å.

While many metal complexes containing  $\eta^2$ -pyridylalkyl ligands have been reported,<sup>6</sup> to our knowledge, compounds **2a–c** and **4** are the third example of Group 5 pyridylalkyl compounds.<sup>7</sup> A series of related  $\eta^2$ -(*N,C*)-pyridine tantalum complexes have also been reported.<sup>8</sup> Furthermore, this work represents the third synthetic methodology for preparing pyridylalkyl derivatives. The other two are C–H bond activation and organolithium/Grignard-reagent metathesis.<sup>6b</sup>

The presence of chelating pyridine ligands has allowed the isolation of compounds **2a–c** and **4** by preventing  $\sigma$ -bond metathesis that was seen in reactions with styrene. These compounds present a rare example of Group 5 pyridylalkyl complexes and the first to be characterized crystallographically. §

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## Notes and references

§ *Crystal data.* **2a:** C<sub>38</sub>H<sub>50</sub>ClN<sub>2</sub>O<sub>2</sub>Ta, *M* = 783.24, triclinic, *a* = 12.1330(3), *b* = 12.3876(3), *c* = 13.9642(4) Å,  $\alpha$  = 98.8630(10),  $\beta$  = 115.4240(10),  $\gamma$  = 101.1690(10)°, *U* = 1791.75(18) Å<sup>3</sup>, *T* = 150 K, space group *P* $\bar{1}$  (no. 2), *Z* = 2,  $\rho_{\text{calcd}}$  = 1.45 g cm<sup>-3</sup>, Mo–K $\alpha$  ( $\lambda$  = 0.71073 Å),  $\mu$ (Mo–K $\alpha$ ) = 3.139 mm<sup>-1</sup>, 17886 data collected, 8312 unique data (*R*<sub>int</sub> = 0.057), *R*(*F*<sub>o</sub>) = 0.042, *R*<sub>w</sub>(*F*<sub>o</sub><sup>2</sup>) = 0.102. **2b:** C<sub>38</sub>H<sub>48</sub>Br<sub>2</sub>ClN<sub>2</sub>O<sub>2</sub>Ta, *M* = 941.04,

triclinic, *a* = 12.2625(7), *b* = 12.7572(8), *c* = 14.0939(11) Å,  $\alpha$  = 111.989(3),  $\beta$  = 101.730(4),  $\gamma$  = 102.100(3)°, *U* = 1900.0(2) Å<sup>3</sup>, *T* = 150 K, space group *P* $\bar{1}$  (no. 2), *Z* = 2,  $\rho_{\text{calcd}}$  = 1.64 g cm<sup>-3</sup>, Mo–K $\alpha$  ( $\lambda$  = 0.71073 Å),  $\mu$ (Mo–K $\alpha$ ) = 5.046 mm<sup>-1</sup>, 12828 data collected, 8833 unique data (*R*<sub>int</sub> = 0.050), *R*(*F*<sub>o</sub>) = 0.042, *R*<sub>w</sub>(*F*<sub>o</sub><sup>2</sup>) = 0.084. **2c:** 2C<sub>6</sub>H<sub>6</sub>·C<sub>43</sub>H<sub>34</sub>Cl<sub>2</sub>NO<sub>2</sub>Ta, *M* = 1004.84, triclinic, *a* = 11.4442(4), *b* = 11.7997(4), *c* = 17.5214(5) Å,  $\alpha$  = 82.0975(19),  $\beta$  = 84.3171(18),  $\gamma$  = 75.1193(17)°, *U* = 2259.97(13) Å<sup>3</sup>, *T* = 150 K, space group *P* $\bar{1}$  (no. 2), *Z* = 2,  $\rho_{\text{calcd}}$  = 1.48 g cm<sup>-3</sup>, Mo–K $\alpha$  ( $\lambda$  = 0.71073 Å),  $\mu$ (Mo–K $\alpha$ ) = 2.563 mm<sup>-1</sup>, 22282 data collected, 10513 unique data (*R*<sub>int</sub> = 0.035), *R*(*F*<sub>o</sub>) = 0.030, *R*<sub>w</sub>(*F*<sub>o</sub><sup>2</sup>) = 0.063. **4:** C<sub>43</sub>H<sub>59</sub>ClNNbO<sub>3</sub>, *M* = 766.31, monoclinic, *a* = 16.4650(10), *b* = 13.6886(7), *c* = 18.7548(9) Å,  $\alpha$  = 90,  $\beta$  = 107.69(3),  $\gamma$  = 90°, *U* = 4026.9(4) Å<sup>3</sup>, *T* = 150 K, space group *P*2<sub>1</sub>/*n* (no. 14), *Z* = 4,  $\rho_{\text{calcd}}$  = 1.26 g cm<sup>-3</sup>, Mo–K $\alpha$  ( $\lambda$  = 0.71073 Å),  $\mu$ (Mo–K $\alpha$ ) = 0.388 mm<sup>-1</sup>, 37822 data collected, 9506 unique data (*R*<sub>int</sub> = 0.095), *R*(*F*<sub>o</sub>) = 0.064, *R*<sub>w</sub>(*F*<sub>o</sub><sup>2</sup>) = 0.162. CCDC 255067–255070. See <http://www.rsc.org/suppdata/cc/b4/b416536e/> for crystallographic data in .cif or other electronic format.

- 1 I. P. Rothwell, *Chem. Commun.*, 1997, **15**, 1331.
- 2 J. M. Mayer, P. T. Wolczanski, B. D. Santarsiero, W. A. Olson and J. E. Bercaw, *Inorg. Chem.*, 1983, **22**, 1149.
- 3 B. C. Parkin, J. R. Clark, V. M. Visciglio, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1995, **14**, 3002.
- 4 D. R. Mulford, J. R. Clark, S. W. Schweiger, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1999, **18**, 4448.
- 5 (a) G. Alagona, C. Ghio, R. Lazzaroni and R. Settambolo, *Organometallics*, 2001, **20**, 5394; (b) N. M. Doherty and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107**, 2670.
- 6 (a) T. R. van den Ancker and C. L. Raston, *J. Organomet. Chem.*, 1995, **500**, 289; (b) R. Duchateau, E. A. C. Brussee, A. Meetsma and J. H. Teuben, *Organometallics*, 1997, **16**, 5506; (c) W. P. Leung, H. K. Lee, L. H. Weng, Z. Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1997, 779.
- 7 (a) D. A. Lemenovskii, T. V. Baukova, G. Zyzik, V. A. Knizhnikov, V. P. Fedin and E. G. Perevalova, *Koord. Khim.*, 1978, **4**, 1033; (b) D. A. Lemenovskii, T. V. Baukova, V. A. Knizhnikov, E. G. Perevalova and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 1976, **226**, 585.
- 8 P. A. Fox, M. A. Bruck, S. D. Gray, N. E. Gruhn, C. Grittini and D. E. Wigley, *Organometallics*, 1998, **17**, 2720.