

## Synthesis and Structure of a Perpendicular Bridging Alkylidyneamine Ligand in $[W_2(\eta-C_5H_4Pr^i)_2Cl_4(\mu-Cl)(\mu-EtCNH)]$

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Treatment of the  $W\equiv W$  triply-bonded dimers  $[W_2(\eta-C_5H_4R)_2Cl_4]$  ( $R = Pr^i$  or Me) with  $R'CN$  ( $R' = Me, Et, \text{ or } Ph$ ) followed by HCl gas affords the complexes  $[W_2(\eta-C_5H_4R)_2Cl_4(\mu-Cl)(\mu-Cl)(\mu-R'CNH)]$  in quantitative yield; the X-ray crystal structure for  $R = Pr^i, R' = Et$  reveals a perpendicular bridging EtCNH ligand.

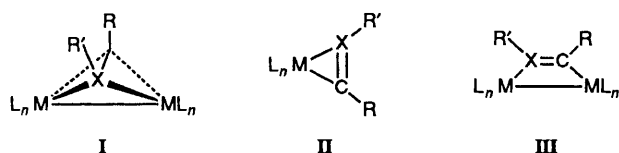
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Alkyne complexes of the general types **I–III** ( $X = C$ ) are well established in organo-transition metal chemistry.<sup>1</sup> However, although the closely-related alkylidyneamine ligand ( $RCNR'$ ) has been found to coordinate to metal centres in terminal<sup>2</sup> (**II**,  $X = N$ ) and parallel bridging<sup>3</sup> (**III**,  $X = N$ ) modes,

perpendicular bridge  $\mu$ -alkylidyneamine complexes (**I**,  $X = N$ ) have not been described. Here we report the synthesis and characterisation of the perpendicular bridge  $\mu$ -alkylidyneamine derivatives  $[W_2(\eta-C_5H_4R)_2Cl_4(\mu-Cl)(\mu-R'CNH)]$  ( $R = Pr^i$  or Me;  $R' = Me, Et, \text{ or } Ph$ ).

Treatment of toluene solutions of the  $W\equiv W$  triply-bonded compounds  $[W_2(\eta-C_5H_4R)_2Cl_4]$  (**1**  $R = Pr^i$  **a**, or  $Me$  **b**)<sup>4</sup> with nitriles ( $R'CN$ ) affords brown compounds, the analytical and spectroscopic data† for which are consistent with compounds containing a  $\mu-(\sigma + \pi)$ -bound nitrile ligand,  $[W_2(\eta-C_5H_4R)_2Cl_4\{\mu-(\sigma + \pi)-R'CN\}](R' = Me$  **2**,  $Et$  **3** or  $Ph$  **4**;  $R = Pr^i$  **a** or  $Me$  **b**).

Thus, the  $^1H$  and  $^{13}C$  NMR spectra of **2–4** show resonances assignable to two diastereotopic  $\eta-C_5H_4R$  ligands and to a coordinated  $R'CN$  ligand. In the  $^{13}C$  NMR spectra the resonances for the internal carbon atoms of the  $R'CN$  ligand appear at  $\delta$  ca. 240 and possess  $^{183}W$  satellites (where observed) of the proper intensity for a carbon atom bonded to one tungsten atom [ $^1J(^{13}C-^{183}W)$  ca. 95 Hz; satellite intensity ca. 14% by area]. There is no evidence for a  $\nu(C\equiv N)$  absorption in the IR spectra of **2–4**, and since submission of our manuscript we have obtained preliminary results of an X-ray crystal structure determination of **3b** that confirm the  $\mu-(\sigma + \pi)$  mode of coordination of the nitrile ligand illustrated. Complexes containing a  $\mu-(\sigma + \pi)$ -nitrile moiety have been reported previously.<sup>5</sup>



† Satisfactory analyses have been obtained for all the new compounds except **5a** which could only be obtained as an oily solid contaminated by varying quantities of solvent.

**Selected spectroscopic data:** IR data,  $cm^{-1}$ , KBr. NMR data,  $^1H$  300 MHz,  $^{13}C$ - $\{^1H\}$  75.5 MHz, as  $\delta$  relative to  $SiMe_4$ ,<sup>a</sup> in  $[^2H_6]$ benzene,<sup>b</sup> in  $[^2H_2]$ dichloromethane,<sup>c</sup> in  $[^2H_6]$ dimethyl sulphoxide, relative intensity, coupling constant ( $J$ , in Hz) and assignment; for virtual multiplets the apparent coupling constant is not given;  $J$  refers to the  $^1H$ - $^1H$  coupling constant unless stated otherwise. **2a:**  $^1H$  NMR:<sup>a</sup> 6.33, 5.60 (2  $\times$  virtual q, 2  $\times$  1H, 2  $\times$   $\eta-C_5H_4Pr^i$ ), 5.42 (overlapping 2  $\times$  virtual q, 2H, 2  $\times$   $\eta-C_5H_4Pr^i$ ), 5.33, 5.28, 5.20, 4.99 (4  $\times$  virtual q, 4  $\times$  1H, 4  $\times$   $\eta-C_5H_4Pr^i$ ), 3.42 [s, 3H,  $\mu-(\sigma + \pi)$ -MeCN], 3.22, 2.91 (2  $\times$  sept, 2  $\times$  1H,  $J$  6.9, 2  $\times$  CHMe<sub>2</sub>), 1.30–1.0 (4  $\times$  d, 4  $\times$  3H,  $J$  6.9, 4  $\times$  CHMe<sub>2</sub>).  $^{13}C$ - $\{^1H\}$  NMR:<sup>a</sup> 240.7 ( $^1J(^{13}C-^{183}W)$  98 [ca. 14.1% by area],  $\mu-(\sigma + \pi)$ -MeCN], 130.8, 130.4 (2  $\times$  CPr<sup>i</sup>), 105.4, 105.0, 103.4, 101.8, 100.8, 97.8, 90.7 [8  $\times$  CH ( $\eta-C_5H_4Pr^i$ ); two signals overlapping], 29.2, 28.8 (2  $\times$  CHMe<sub>2</sub>), 26.3 [ $\mu-(\sigma + \pi)$ -MeCN], 23.8, 23.0, 22.7, 22.4 (4  $\times$  CHMe<sub>2</sub>).

**2b:**  $^1H$  NMR:<sup>a</sup> 5.88, 5.65, 5.40 (3  $\times$  virtual q, 3  $\times$  1H, 3  $\times$   $\eta-C_5H_4Me$ ), 5.35 (overlapping 2  $\times$  virtual q, 2H, 2  $\times$   $\eta-C_5H_4Me$ ), 5.20, 5.05, 4.67 (3  $\times$  virtual q, 3  $\times$  1H, 3  $\times$   $\eta-C_5H_4Me$ ), 3.35 [s, 3H,  $\mu-(\sigma + \pi)$ -MeCN], 2.15, 2.07 (2  $\times$  s, 2  $\times$  3H, 2  $\times$   $\eta-C_5H_4Me$ ).

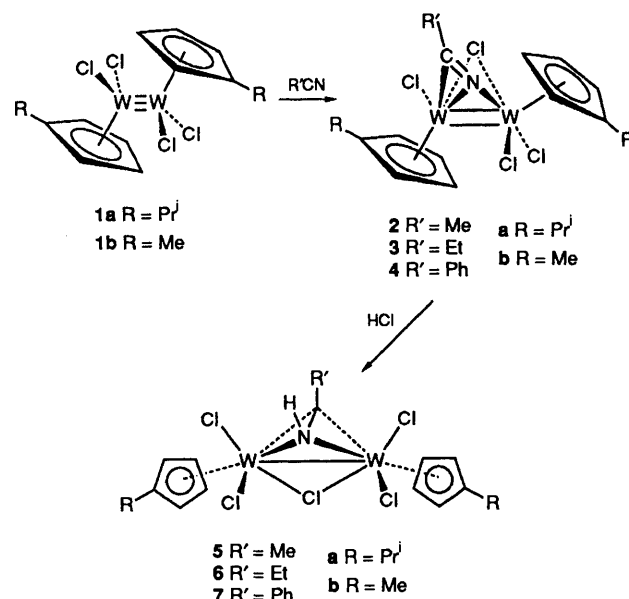
**5a:**  $^1H$  NMR:<sup>b</sup> 6.20 (br m, 2H, 2  $\times$   $\eta-C_5H_4Pr^i$ ), 5.89 (br s, 1H,  $\mu$ -MeCNH), 5.73, 5.17, 4.78 (3  $\times$  br m, 3  $\times$  2H, 3  $\times$   $\eta-C_5H_4Pr^i$ ), 3.91 (s, 3H,  $\mu$ -MeCNH), 3.52 (sept, 2H,  $J$  6.9, CHMe<sub>2</sub>), 1.45, 1.38 (2  $\times$  d, 2  $\times$  6H,  $J$  6.9, 2  $\times$  CHMe<sub>2</sub>).  $^{13}C$ - $\{^1H\}$  NMR:<sup>b</sup> 141 [ $^1J(^{13}C-^{183}W)$  34 (ca. 26% by area),  $\mu$ -MeCNH], 134.8 (CPr<sup>i</sup>), 114.6, 105.7, 100.4, 98.8 [4  $\times$  CH ( $\eta-C_5H_4Pr^i$ )], 28.1 (CHMe<sub>2</sub>), 27.2 ( $\mu$ -MeCNH), 22.5, 21.5 (2  $\times$  CHMe<sub>2</sub>). IR:  $\nu(N-H)$  3342.

**5b:**  $^1H$  NMR:<sup>c</sup> 9.54 (br s, 1H,  $\mu$ -MeCNH), 5.99, 5.95, 5.50, 5.47 (4  $\times$  br m, 4  $\times$  2H, 4  $\times$   $\eta-C_5H_4Me$ ), 3.71 (s, 3H,  $\mu$ -MeCNH), 2.53 (s, 6H,  $\eta-C_5H_4Me$ ).

**8:**  $^1H$  NMR:<sup>b</sup> 6.99, 5.79, 5.74 (3  $\times$  virtual q, 3  $\times$  1H, 3  $\times$   $\eta-C_5H_4Pr^i$ ), 5.67 (2  $\times$  overlapping virtual q, 2H, 2  $\times$   $\eta-C_5H_4Pr^i$ ), 5.59 (virtual q, 1H,  $\eta-C_5H_4Pr^i$ ), 5.53 [d of virtual q, 1H,  $^3J(^1H-^{31}P)$  7.5,  $\eta-C_5H_4Pr^i$ ], 4.46 (d of q, 1H,  $^2J$  16.1,  $^3J$  7.3, CH<sub>2</sub>Me), 4.36 (virtual q, 1H,  $\eta-C_5H_4Pr^i$ ), 4.07 (d of q, 1H,  $^2J$  15.1,  $^3J$  7.3, CH<sub>2</sub>Me), 3.84 (d of q, 1H,  $^2J$  15.1,  $^3J$  7.3, CH<sub>2</sub>Me), 3.39 (d of q, 1H,  $^2J$  16.1,  $^3J$  7.3, CH<sub>2</sub>Me), 2.95 (sept, 1H,  $J$  7.3, CHMe<sub>2</sub>), 2.35 (sept, 1H,  $J$  7.3, CHMe<sub>2</sub>), 1.68 [d, 9H,  $^2J(^1H-^{31}P)$  8.8, PMe<sub>3</sub>], 1.27 (d, 3H,  $J$  7.3, CHMe<sub>2</sub>), 1.21 (overlapping 2  $\times$  d and t, 9H, CHMe<sub>2</sub> and CH<sub>2</sub>Me), 1.10 (t, 3H,  $J$  7.3, CH<sub>2</sub>Me), 1.00 (d, 3H,  $J$  7.3, CHMe<sub>2</sub>).  $^{13}C$ - $\{^1H\}$  NMR:<sup>b</sup> 141.4 [d,  $^2J(^{13}C-^{31}P)$  7,  $\mu-C_2Et_2$ ], 138.4, 132.6 (2  $\times$  CPr<sup>i</sup>), 121.3 [d,  $^2J(^{13}C-^{31}P)$  7,  $\mu-C_2Et_2$ ], 106.2, 103.3, 102.2, 98.3, 95.6, 91.5, 89.9, 89.6 [8  $\times$  CH ( $\eta-C_5H_4Pr^i$ )], 31.4 [d,  $^3J(^{13}C-^{31}P)$  7, CH<sub>2</sub>Me], 29.9 (CH<sub>2</sub>Me), 28.7, 28.2 (2  $\times$  CHMe<sub>2</sub>), 23.1, 22.9, 22.4, 21.6 (4  $\times$  CHMe<sub>2</sub>), 18.8, 17.7 (2  $\times$  CH<sub>2</sub>Me), 15.7 [d  $^1J(^{13}C-^{31}P)$  28, PMe<sub>3</sub>].

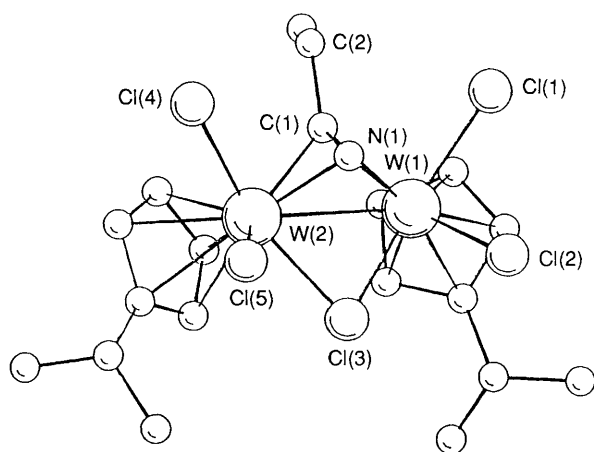
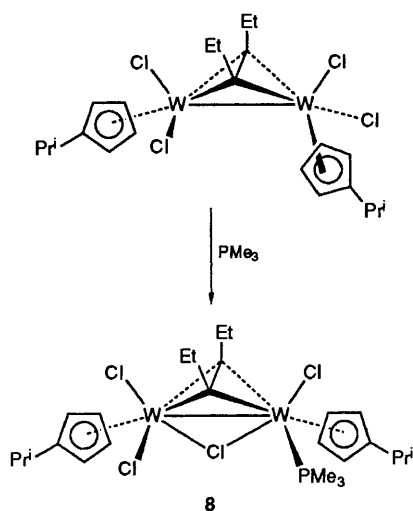
Treatment of toluene solutions of **2–4** with HCl gas affords the purple complexes  $[W_2(\eta-C_5H_4R)_2Cl_4(\mu-Cl)(\mu-R'CNH)](R' = Me$  **5**,  $Et$  **6**, or  $Ph$  **7**;  $R = Pr^i$  **a** or  $Me$  **b**) in near-quantitative yields. The molecular structure of  $[W_2(\eta-C_5H_4Pr^i)_2Cl_4(\mu-Cl)(\mu-EtCNH)]$  **6a**‡ as determined by single crystal X-ray diffraction is shown in Fig. 1. The compound **6a** consists of two mutually eclipsed  $W(\eta-C_5H_4Pr^i)Cl_2$  fragments linked by bridging Cl and EtCNH groups.§ If the  $\eta-C_5H_4Pr^i$  rings are considered to occupy single coordination sites and any metal-metal bond is ignored then **6a** may be described as a confacial bioctahedron. The W–W bond length [2.9359(4) Å] in **6a** is substantially lengthened from that of the precursor  $[W_2(\eta-C_5H_4Pr^i)_2Cl_4]$  [**1a**,  $W\equiv W = 2.3678(6)$  Å], and the C–N bond length [1.405(8) Å] is notably longer than those observed for  $\eta^2$ -RCNR' complexes (1.22–1.30 Å).<sup>2</sup> These observations suggest extensive donation of electron density from the ditungsten centre to vacant  $\pi^*$  orbitals of the  $\mu$ -EtCNH ligand in a manner analogous to that proposed to occur for dinuclear  $\mu$ -alkyne complexes (**I**,  $X = CR'$ ).<sup>1a</sup>

The solution  $^1H$  and  $^{13}C$  NMR data for **5–7** are consistent with the maintenance of structures analogous to that of **6a**. Thus, the  $^1H$  NMR spectra show resonances assignable to a diastereotopic  $\eta-C_5H_4R$  ring and to a  $R'CNH$  ligand, the N–H resonance appearing as a broad signal at  $\delta$  ca. 6 (in  $[^2H_2]$ dichloromethane) or  $\delta$  ca. 10 (in  $[^2H_6]$ dimethyl sulphoxide). The  $^{13}C$  NMR spectra also show resonances assignable to  $\eta-C_5H_4R$  and  $R'$  moieties. An additional singlet at  $\delta$  ca. 145



‡ Crystal data for **6a**:  $C_{19}H_{28}Cl_5NW_2$ ,  $M = 815.41$ , crystal size = ca.  $0.15 \times 0.25 \times 0.30$  mm, monoclinic, space group  $P2_1/c$ ,  $a = 7.347(1)$ ,  $b = 13.840(2)$ ,  $c = 22.767(4)$  Å,  $\beta = 94.41(2)^\circ$ ,  $V = 2300.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.354$  g  $cm^{-3}$ ,  $\mu(Mo-K\alpha) = 108.05$   $cm^{-1}$ ,  $F(000) = 1528$ , scan mode  $\omega-2\theta$ ,  $T = 293$  K,  $2 < 2\theta < 50^\circ$ , total unique data 4044, number of observations [ $I > 3\sigma(I)$ ] 3164, number of variables 245, observations/variables 12.9,  $R_{merge} = 0.041$ ,  $R = 0.028$ ,  $R_w = 0.033$  (Chebyshev; parameters 21.4, -16.7, 16.2, -0.580). Data were collected on an Enraf-Nonius CAD4-F diffractometer. The structure was solved using Patterson and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms attached to C were placed in calculated positions. Crystallographic calculations were carried out using the CRYSTALS suite of programs<sup>7</sup> on a Micro VAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The N–H atom could not be located from a Fourier difference synthesis, but its position may be inferred from the IR and NMR data.



**Fig. 1** Molecular structure of  $[\text{W}_2(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_4(\mu\text{-Cl})(\mu\text{-EtCNH})]$  **6a**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) as follows:  $\text{W}(1)\text{-W}(2)$  2.9359(4),  $\text{W}(1)\text{-Cl}(1)$  2.462(2),  $\text{W}(1)\text{-Cl}(2)$  2.454(2),  $\text{W}(1)\text{-Cl}(3)$  2.434(2),  $\text{W}(1)\text{-N}(1)$  2.064(6),  $\text{W}(1)\text{-C}(1)$  2.100(7),  $\text{W}(1)\text{-Cp}_{\text{cent}(1)}$  2.03,  $\text{W}(2)\text{-Cl}(3)$  2.443(2),  $\text{W}(2)\text{-Cl}(4)$  2.479(2),  $\text{W}(2)\text{-Cl}(5)$  2.420(2),  $\text{W}(2)\text{-N}(1)$  2.049(6),  $\text{W}(2)\text{-C}(1)$  2.106(7),  $\text{W}(2)\text{-Cp}_{\text{cent}(2)}$  2.04;  $\text{W}(1)\text{-Cl}(3)\text{-W}(2)$  74.02(5),  $\text{C}(2)\text{-C}(1)\text{-N}(1)$  126.6(6),  $\text{Cp}_{\text{cent}(1)}\text{-W}(1)\text{-W}(2)$  121.1,  $\text{Cp}_{\text{cent}(2)}\text{-W}(2)\text{-W}(1)$  121.9, where  $\text{Cp}_{\text{cent}(1)}$  and  $\text{Cp}_{\text{cent}(2)}$  refer to the computed  $\eta\text{-C}_5\text{H}_4\text{Pr}^i$  centroids for  $\text{W}(1)$  and  $\text{W}(2)$  respectively.

which (where observed) shows  $^{183}\text{W}$  satellites of the proper intensity for a carbon atom bonded to two tungsten atoms is assigned to the internal carbon atom of the  $\mu\text{-R}'\text{CNH}$  ligand. A sharp band at *ca.*  $3340\text{ cm}^{-1}$  in the IR spectra of **5**–**7** is assigned as  $\nu(\text{N-H})$ ; the isotopomer  $[\text{W}_2(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_4(\mu\text{-Cl})(\mu\text{-MeCND})]$  **5a**–**d**, prepared from **1a** and MeCN followed by treatment with DCl, shows a band assignable to  $\nu(\text{N-D})$  at  $2486\text{ cm}^{-1}$ .

We have also prepared the related perpendicular bridge  $\mu$ -alkyne complex  $[\text{W}_2(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_3(\mu\text{-Cl})(\mu\text{-C}_2\text{Et}_2)(\text{PMe}_3)]$  **8** from  $[\text{W}_2(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2\text{Cl}_4(\mu\text{-C}_2\text{Et}_2)]^6$  and  $\text{PMe}_3$ . The analytical and spectroscopic data for **8** strongly support a structure analogous to those **5**–**7**. Thus, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **8** show resonances assignable to two types of

diastereotopic  $\eta\text{-C}_5\text{H}_4\text{Pr}^i$  and Et groups, and an additional doublet at  $\delta$  1.68 is assigned to a  $\text{PMe}_3$  ligand. Resonances assignable to the internal carbon atoms of the  $\mu\text{-C}_2\text{Et}_2$  ligand are observed as doublets at  $\delta$  141.4 and 121.3 [ $^2J(^{13}\text{C}\text{-}^{31}\text{P})$  7 Hz], the low field shift being in the range observed for the internal C atoms of the  $\mu\text{-R}'\text{CNH}$  ligands in **5**–**7**. The compounds **5**–**8** are valence isoelectronic and further highlight the close relationship between the  $\text{R}'\text{CNH}$  and  $\text{RCCR}'$  ligands.

In conclusion we have shown for the first time that the  $\text{RCNH}$  ligand can coordinate in a perpendicular bridging manner analogous to that well-established for alkynes.

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