Interconversion of CN and CNH₂ Ligands: Electrosynthesis and X-ray Crystallographic Structures of *trans*-[W(CNH₂)Cl(dppe)₂] and *trans*-[W(CNH₂)Cl(dppe)₂][BF₄] (dppe = Ph₂PCH₂CH₂PPh₂): Aminocarbyne (≡C–NH₂) or Iminomethylenium (=C=NH₂⁺) Ligands?

David L. Hughes, Saad K. Ibrahim, Hapipah Moh'd Ali and Christopher J. Pickett*

The Nitrogen Fixation Laboratory, AFRC Institute of Plant Science Research, University of Sussex, Brighton, UK BN1 9RQ

Electrochemical reduction of *trans*-[W(CN)Cl(dppe)₂] in the presence of phenol gives *trans*-[W(CNH₂)Cl(dppe)₂] **3**, which can be oxidised electrochemically or chemically to the paramagnetic cation *trans*-[W(CNH₂)Cl(dppe)₂] **4**; X-ray crystallographic analyses of **3** and **4** [BF₄] suggest that the CNH₂ group at both the 18 and 17e W-centres is best described as iminomethylenium (=C=NH₂⁺); **3** and the deutero-complex *trans*-[W(CND₂)Cl(dppe)₂] reduce azobenzene with regeneration of the parent cyanide, the former giving hydrazobenzene and latter PhNDNDPh, suggesting that the CNH(D)₂ complexes can behave as 2H(D) atom transfer reagents.

Compounds possessing the aminocarbyne ligand CNH₂ are rare. Hitherto only two examples of this ligand bound at a single metal centre were known, *trans*-[Re(CNH₂)-Cl(dppe)₂]⁺ **1** and *trans*-[Mo(CNH₂)Cl(dppe)₂] **2**.[1,2] Complex **1** was obtained by protonolysis of a trimethylsilylisocyanide precursor and its structure determined by X-ray crystallography.[1] Complex **2** was electrosynthesised from *trans*-[Mo(CN)Cl(dppe)₂] and provided the first example of the reduction of coordinated cyanide to the CNH₂ group.[2] We now report the electrosynthesis of two new aminocarbyne complexes: the tungsten analogue of **2**, *trans*-[W(CNH₂)Cl(dppe)₂] **3**, and its paramagnetic 17-electron derivative *trans*-[W(CNH₂)Cl(dppe)₂]⁺ **4**. Whereas crystals of the molybdenum complex **2** were found to be unsuitable for X-ray structural analysis, those of **3** and **4** diffracted well: molecular dimensions have been determined for both these compounds and the hydrogen atoms on the CNH₂ ligand located crystallographically for **4**[BF₄].

The reduction of the Wᴵᴵ cyanide[3] *trans*-[W(CN)Cl(dppe)₂] **5** is illustrated by the cyclic voltammograms of Fig. 1, which were recorded at a vitreous carbon electrode in CH₂Cl₂–0.2 mol dm⁻³ [NBu₄][BF₄] (*a*) in the absence of a proton source (*b*) in the presence of phenol and (*c*) after bulk electrolysis at −1.9 V *vs.* ferrocenium–ferrocene. The reversible one-electron reduction of **5** in the absence of phenol becomes an irreversible two-electron process in its presence

and a new peak is observed which corresponds to the oxidation of the product **3**. Controlled potential electrolysis of the cyanide in the presence of phenol consumes 2 F mol⁻¹ and generates **3** as a stable product, which could be isolated from the catholyte and recrystallised as bright yellow needles from CH₂Cl₂–Et₂O (44% yield). It was characterised as *trans*-[W(CNH₂)Cl(dppe)₂] spectroscopically and by microanaly-sis.† Complex **3** undergoes a reversible one-electron oxidation (*E⁰* = −0.76 V; conditions as for **5**) to give the 17-electron cation **4**: in the presence of the base, Et₃N or PhO⁻, a two-electron irreversible oxidation to the parent cyanide **5** is observed, *cf.* Fig. 1(*c*). Treatment of **3** with HBF₄–Et₂O in CH₂Cl₂ also leads to the formation of paramagnetic **4**, which was isolated as orange crystals of **4**[BF₄] in 40% yield.† These reactions are summarised by Scheme 1.

X-ray crystal structures of **3** and **4** are shown in Figs. 2 and 3.‡ Pertinent molecular dimensions are summarised in Table 1 together with those previously determined for [Re(CNH₂)Cl-(dppe)₂][BF₄] **1**. There is a surprising difference in the dimensions of the CNH₂ ligand at the tungsten centres compared with those at rhenium. The metal (M) bound CNH₂ group can be considered as possessing a character lying between that of the two canonical forms {M⁻=C=NH₂⁺} and {M≡C–NH₂}, which formally represent iminomethylenium and aminocarbyne arrangements, respectively. The structural parameters for the 17e and 18e tungsten centres indicate there
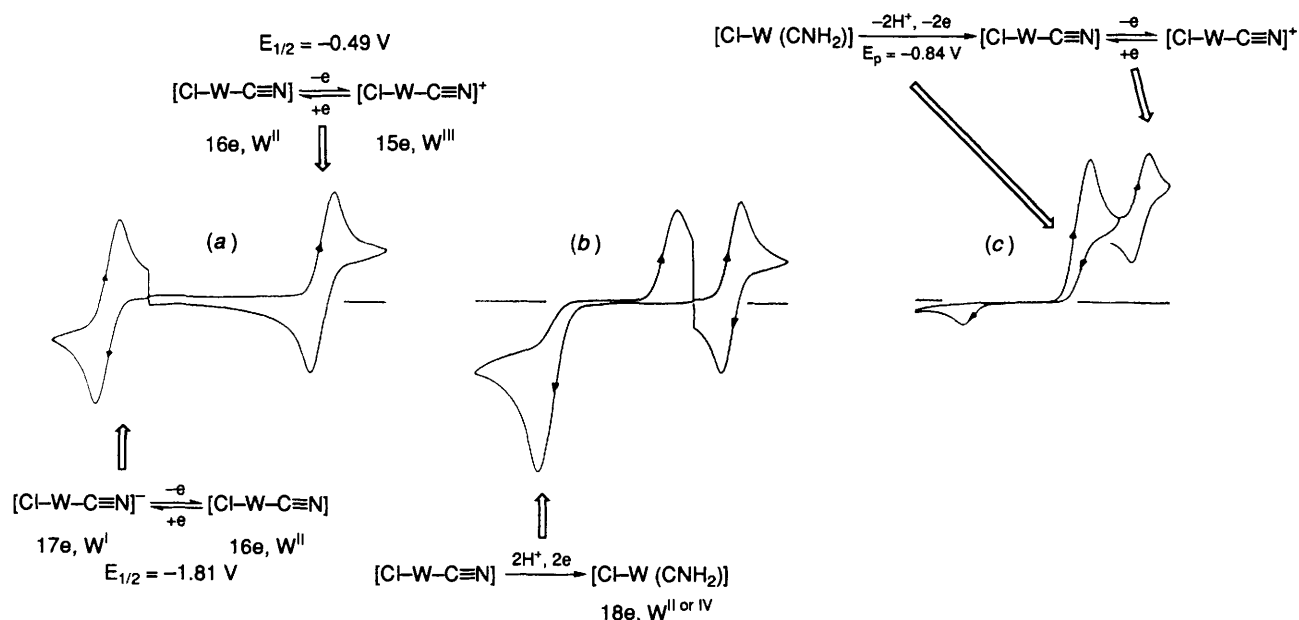
Scheme 1

Fig. 1 Cyclic voltammetry of **5**. Scan-rate 100 mV s⁻¹ (*a*) before and (*b*) after addition of phenol; (*c*) shows the response after exhaustive reduction which converts **5** to **3**; note that the anodic peak for reduction of **5** is absent unless the scan encompasses the oxidation of the product (inset).

is a greater iminomethylenium character than on rhenium where the ligand tends more to the aminocarbyne form.

Metal–chlorine bond lengths (M–Cl, Table 1) are in accord with this interpretation. In the 17e cation **4** the W–Cl bond length is significantly longer (*ca.* 0.04 Å) than in the 18e cation **1**, as is consistent with {Cl–W=C=NH₂⁺} (W^{III}) rather than {Cl–W$^+$≡C–NH₂} (W^V) character. The difference in M–Cl bond lengths between the 18e compounds **3** and **1** is even more pronounced (*ca.* 0.10 Å), concordant with the former tending to the canonical limit {Cl–W⁻=C=NH₂⁺} (W^{II}).

Comparison of bond length data for the redox pair **3** and **4** shows that whereas the W–Cl bond is shorter in **4**, the W–P bond distances, on average, are longer than those of **3**. This

follows the normal trend established for 15e/16e and 16e/17e redox pairs possessing axial Cl ligands at the square planar *trans*-[M(dppe)₂] unit: the more electron-deficient the metal centre the longer the average M–P bond length (back-bonding is weaker) and the shorter the M–Cl distance (s and p donation from Cl to M is enhanced).[4] The average M–P distance for the 18e species **1** and **3** are very similar.

Hydrazides such as *trans*-[W(NNH₂)Cl(dppe)₂]⁺, isoelectronic with **3**, condense with aldehydes and ketones to give diazoalkane complexes [W(NNCR₂)Cl(dppe)₂]⁺ (R = H, alkyl or aryl).[5] However reactions of **3** with a range of more or less activated aldehydes or ketones failed to give *trans*-[W(CNCR₂)Cl(dppe)₂]. *Trans*-[W(CN)Cl(dppe)₂] **5** was formed instead, possibly by 2H atom-transfer to the organic substrate.

The propensity of **3** to behave as a 2H atom-transfer reagent was probed by examining its reaction, and that of its deutero-derivative *trans*-[W(CND₂)Cl(dppe)₂], with azobenzene. Stirring a solution of **3** in THF at 50 °C with PhNNPh for 1 h affords hydrazobenzene and the parent cyanide complex **5**, which precipitates on cooling to room temp Yields of the

Table 1

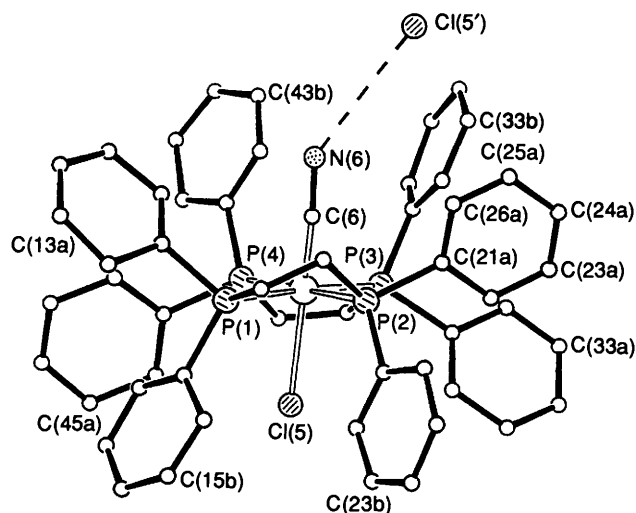| Compound	Bond lengths/Å			
	M–P$_{(mean)}$	M–Cl	C–N	M–C
1	2.456(2)	2.485(1)	1.309(5)	1.802(4)
4	2.54(2)	2.527(2)	1.200(12)	1.872(8)
3	2.455(5)	2.592(5)	1.156(24)	1.868(17)

Fig. 2 View of **3**, showing a proposed hydrogen bond, which links molecules in long chains
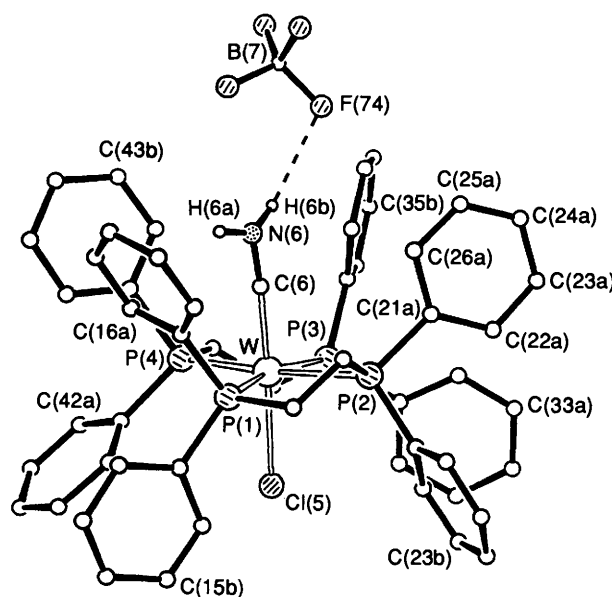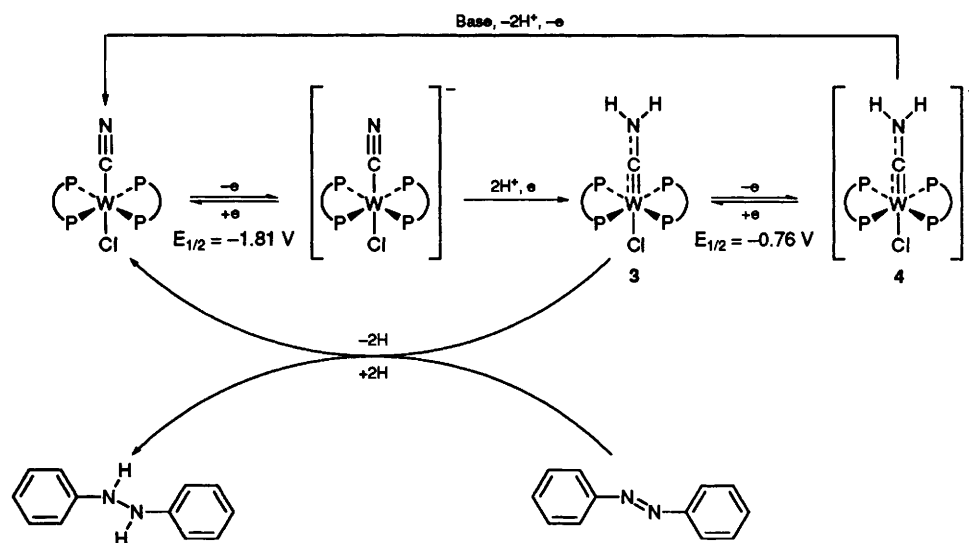

Fig. 3 View of the cation and anion in the BF₄⁻ salt of **4**. A hydrogen bond links the two ions.

Scheme 1 Summary of reactions of the tungsten(ii) cyanide

isolated products were in the range 40–50%. The deuterium labelled compound PhNDNDPh is correspondingly produced on reacting trans-[W(CND$_2$)Cl(dppe)$_2$] with azobenzene under the same conditions, Scheme 1.

Hydrogen atom transfer reactions from coordinated ligands to organic substrates are rare: Rakowski-Dubois has illustrated 2H atom transfer via hydrosulfido–sulfido ligand interconversion at bridging Mo centres.[6] In our case, it is probably the formation of the stable C–N triple bond which provides the driving force for the substrate reduction reaction.

Footnotes

† Selected spectroscopic data for 3: ^{1}H NMR (CD$_2$Cl$_2$) δ 2.2 (s, 2 H, NH$_2$), 2.4–2.7 (br m, 8 H, PCH$_2$CH$_2$P), 7.0–7.3 (m, 40 H, Ph); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ −94.4 (s), ref. Me$_3$PO; ^{13}C{^{1}H}) NMR (CD$_2$Cl$_2$) δ 217.2 (quintet, J_{PC} 11.8 Hz, WC NH$_2$); FTIR v/cm^{-1} (Nujol mull) 3297m and 3385w (NH), deuterio complex, trans-[W(CND$_2$)Cl(dppe)$_2$], 2412 (ND).

For 4: EPR (CH$_2$Cl$_2$, frozen solution, 9.373 GHz, 9.34 mW, 120 K) g_1 = 1.97, g_2 = 2.05, g_3 = 2.18; rhombic signal $g_{average}$ = 2.07; poorly resolved hyperfine on g_2 consistent with 1:4:6:4:1 coupling to ^{31}P <A> ca. 3 mT; FTIR v/cm^{-1} (Nujol mull) 3286m and 3375w (NH), 1050s (BF); NMR silent; satisfactory C, H, N microanalyses were obtained for the new compounds 3, 4 and 5.

‡ Crystal data for 3: C$_{53}$H$_{50}$ClNP$_4$W, M = 1044.2. Monoclinic, space group Pn, a = 23.095(5), b = 8.951(1), c = 11.114(2) Å, β = 99.069(5)°, V = 2268.8 Å^3. Z = 2, D$_c$ = 1.528 g cm^{-3}, F(000) = 1052, μ(Mo-Kα) = 28.4 cm^{-1}. A yellow, rectangular prism, dimensions ca. 0.10 × 0.14 × 0.19 mm, mounted on a glass fibre and coated with epoxy resin, was photographed. Data were collected on a CAD4 diffractometer (monochromated radiation) for accurate cell parameters (from centred settings of 25 reflections, θ ca. 12.5°, each in four orientations) and intensity measurements (θ$_{max}$ 25°). 4076 Unique intensities were corrected for Lorentz-polarisation effects, slight deterioration and absorption. The structure determination was by the heavy atom method, refinement by large-block-matrix least-squares methods to R = 0.062, R$_g$ = 0.073^7 for 3698 reflections (with I > σ$_1$),

w = (σ$_F^2$ + 0.0025F^2)$^{-1}$. All non-hydrogen atoms, except C(6) in the aminocarbyne ligand, were refined anisotropically. H atoms of dppe ligands were included in idealised positions. Noted that dimensions in CNH$_2$ ligand varied considerably with the weighting scheme used; H-atoms in this ligand were not fully characterised.

For 4: C$_{53}$H$_{50}$ClNP$_4$W·BF$_4$·CH$_2$Cl$_2$, M = 1215.9. Monoclinic, space group P2$_1$/a, a = 26.182(3), b = 13.371(1), c = 15.034(2) Å, β = 95.255(10)°, V = 5240.8 Å^3. Z = 4, D$_c$ = 1.541 g cm^{-3}, F(000) = 2436, μ(Mo-Kα) = 25.8 cm^{-1}. A yellow plate crystal, dimensions ca. 0.07 × 0.30 × 0.40, mounted on a glass fibre, was examined as for 3. Cell parameters were from 25 reflections, θ ca. 10.5°; intensities measured to θ$_{max}$ 22.5°. There was no deterioration of the crystal; other corrections were applied to 6841 reflections as for 3. Structure determination and refinement in SHELX^7 as for 3. Final R = 0.045, R$_g$ = 0.055^7 for 6036 reflections (I > σ$_1$), w = (σ$_F^2$ + 0.00127F^2)$^{-1}$. H-atoms of CNH$_2$ group were located and refined; all other H-atoms were included in idealised positions. The anion is disordered. All non-hydrogen atoms of cation and solvent refined anisotropically. For both analyses, scattering factor curves for neutral atoms were from ref. 8. Computer programs (refs. 7 and 9) were run on a MicroVAX II in NFL. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 D. L. Hughes, C. J. Pickett, A. J. L. Pombeiro and R. L. Richards, J. Chem. Soc., Chem. Commun., 1986, 246.
2 D. L. Hughes, M. Y. Mohammed and C. J. Pickett, J. Chem. Soc., Chem. Commun., 1989, 1399.
3 The cyanide was prepared from the anion [W(CN)(N$_2$)(dppe)$_2$]$^-$ by a method analogous to that used for the preparation of [MoCl(CN)(dppe)$_2$]; A. Hills, D. L. Hughes, C. J. Macdonald, M. Y. Mohammed and C. J. Pickett, J. Chem. Soc., Dalton Trans., 1991, 121.
4 T. I. Al-Salih, M. T. Duarte, J. J. R. Frausta da Silva, A. M. Galvao, M. C. Guedes da Silva, P. B. Hitchcock, D. L. Hughes, C. J. Pickett, A. J. L. Pombeiro and R. L. Richards, J. Chem. Soc., Dalton Trans., 1993, 3015.
5 W. Hussain, G. J. Leigh, H. Mohd. Ali and C. J. Pickett, J. Chem. Soc., Dalton Trans., 1988, 553, and references therein.
6 M. McKenna, L. L. Wright, D. J. Miller, L. Tanner, R. C. Haltiwanger, and M. Rakowski-Dubois, J. Am. Chem. Soc., 1983, 105, 5329.
7 G. M. Sheldrick, SHELX-76, Program for crystal structure analysis, University of Cambridge, 1976.
8 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974.
9 S. N. Anderson, R. L. Richards and D. L. Hughes, J. Chem. Soc., Dalton Trans., 1986, 245.