Aminocarbyne Coupling Reactions at $M(Ph_2PCH_2CH_2PPh_2)_2$ (M = Mo or W) Sites. Synthesis and Properties of the Diaminoacetylene Complexes *trans*-$[MX(\eta^2\text{-}MeHNC{\equiv}CNHMe)(Ph_2PCH_2CH_2PPh_2)_2]A$ (X = F, Cl or ClO_4; A = BF_4, PF_6, HCl_2 or ClO_4) and of their Di(aminocarbyne)-type Precursors†

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Treatment of *trans*-$[M(CNMe)_2(dppe)_2]$ **1** (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) in CH_2Cl_2 with HA (A = BF_4, PF_6, Cl or ClO_4) gives the diaminoacetylene complexes *trans*-$[MX(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2]A$ **2** (X = F, Cl or ClO_4; A = BF_4, PF_6, HCl_2 or ClO_4). The crystal structure of *trans*-$[MoF(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2][BF_4]$ has been determined. A key intermediate in the reaction, *trans*-$[M(CNHMe)_2(dppe)_2]A_2$ **3** (A = HCl_2 or ClO_4), has also been isolated and shown to be best viewed as a 'iminomethylenium' species =C=NHMe. The acetylenic C≡C triple bond in **2** undergoes base-induced cleavage (*e.g.*, by $LiBu^n$) to form the parent complex **1**.

Activation, by a transition-metal centre, towards reductive coupling of isocyanides,[1–8] carbon monoxide[2,3,5,9] or other small unsaturated C_1 molecules is a subject of growing interest, with particular relevance to the development of strategies for carbon–carbon bond formation. These reactions have potential implications in the synthesis of organic compounds.

Reductive coupling of isocyanide ligands was recognized for the first time in 1976,[10] in a system involving $[MoI(CNBu^t)_6]I$, a reducing agent (Zn) and a proton source. Under refluxing conditions, the η^2-diaminoacetylene complex $[MoI(\eta^2\text{-}Bu^tHNC{\equiv}CNHBu^t)(CNBu^t)_4]I$ is formed.

Similar studies[1–9] on related systems and on carbon monoxide showed that electrophilic attack at activated alkyl isocyanide or carbon monoxide ligands forms aminocarbyne $M{\equiv}CNER$ (M = Mo or W centre, E = H or R, R = alkyl) or, *e.g.*, siloxycarbyne $M{\equiv}COSiR_3$ (M = V, Nb or Ta centre) intermediates which are precursors to the formation of diaminoacetylenes (RENC≡CNER) or acetylene diether ($R_3SiOC{\equiv}COSiR_3$) ligands, respectively. Cross-coupling reactions have also been accomplished.

Induction of coupling by nucleophilic reagents has been observed[7] recently in the conversion of $[W(\eta^5\text{-}C_5Me_5)(CNEt_2)_2(CNEt)][BF_4]$, with two *cis*-aminocarbyne-type ligands, into the alkyne species $[W(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)(CNEt)_2][BF_4]$ or $[WBr_2(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)(CNEt)][BF_4]$, upon reaction with CNEt or Br_2, respectively. In addition, electrophile- or nucleophile-induced coupling reactions of carbyne ligands (or with isocyanide or carbon monoxide) have also been described recently,[11] mainly for some tungsten systems. However, the factors which drive the C–C coupling step have not yet been clearly defined.

The diisocyanide complexes *trans*-$[M(CNR)_2(dppe)_2]$ **1** (M = Mo or W, R = alkyl, dppe = $Ph_2PCH_2CH_2PPh_2$) which we have previously prepared[12,13] could be promising candidates to undergo the reductive coupling process. We showed previously[13–15] that in these complexes the isocyanide ligands, activated by the very electron-rich d^6 metal centre $M(dppe)_2$, readily undergo protonation (with a variety of mineral acids) to give the monocarbyne complexes *trans*-$[M(CNHMe)(CNMe)(dppe)_2]^+$ which are susceptible to further protonation to give the compounds formulated, on the basis of the then available data, as the 'di(aminocarbyne)'-type species *trans*-$[M(CNHMe)_2(dppe)_2]^{2+}$. Hydride and hydrido-carbyne complexes are also products of these reactions depending upon the conditions.[16] We have re-examined these results and, following a preliminary report,[1] now show that, when using $HBF_4{\cdot}Et_2O$ as the proton source, the 'di(aminocarbyne)' complexes *trans*-$[M(CNHMe)_2(dppe)_2][BF_4]_2$ undergo readily fluorination and carbyne–carbyne coupling to give the η^2-di(methylamino)acetylene fluoro complexes *trans*-$[MF(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2][BF_4]$ which were previously formulated[14] as their parent 'dicarbyne' complexes.

However, by using other acids with conjugate bases which have weaker nucleophilicity than BF_4^- towards our metal centres ($HClO_4$ or HCl), we have succeeded in isolating the corresponding 'di(aminocarbyne)'-type intermediates and demonstrated their conversion into the final η^2-diaminoacetylene products.

In the following paper[17] we report the first detailed mechanistic study on the reductive coupling of isocyanides, which is focussed on the protonation reactions of the above-mentioned diisocyanide complexes **1** and their $CNBu^t$ analogues.

Results and Discussion

Treatment of a CH_2Cl_2 solution of *trans*-$[M(CNMe)_2(dppe)_2]$ **1** (M = Mo or W) with $[Et_2OH][BF_4]$ (in Et_2O) or HPF_6 (in

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

$$\begin{tikzcd}
trans\text{-}[M(CNMe)_2(dppe)_2] \arrow[r, "HA"] & trans\text{-}[M(CNHMe)(CNMe)(dppe)_2]A \ \mathbf{4} \arrow[d, "HA"] \\
trans\text{-}[MX(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2]A \ \mathbf{2} & trans\text{-}[M(CNHMe)_2(dppe)_2]A_2 \ \mathbf{3} \arrow[l, "X^-"']
\end{tikzcd}$$

Scheme 1 For **2**: X = F, A = BF_4 or PF_6; X = Cl, A = HCl_2; X = A = ClO_4. For **3**: A = HCl_2 or ClO_4

methanol) (HA, rapidly added, in *ca.* 2 s, in a two-fold molar ratio) leads to the ready formation of *trans*-[MX(η^2-MeHNC≡CNHMe)(dppe)$_2$]A **2** (X = F, A = BF_4 or PF_6) in which the diaminoacetylene ligand is rapidly derived from the proton-induced coupling of the isocyanide ligands, and the fluoride ligand is derived from BF_4^- or PF_6^- [equation (1)].

$$trans\text{-}[M(CNMe)_2(dppe)_2] \xrightarrow{HA} \underset{\mathbf{1}}{} trans\text{-}[MX(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2]A \quad \mathbf{2}\ (X = F, A = BF_4 \text{ or } PF_6) \quad (1)$$

The reaction with HPF_6 is somewhat slower than with HBF_4, possibly in accord with the expected higher metal fluorinating ability of BF_4^-. The propensity of BF_4^- to fluorinate metals readily has been observed before, for example in the formation of *trans*-[MoF(η^2-PhC≡CH)(dppe)$_2$][BF$_4$] in the reaction of [MoH$_4$(dppe)$_2$] with PhC≡CH and HBF_4,[18] and of *trans*-[MoF(≡CCH$_2$Bu^t)(dppe)$_2$][BF$_4$][19] or *trans*-[WF(=CHCH$_2$Ph-)(dppe)$_2$][BF$_4$][20] from the reactions of HBF_4 with alkynyl complexes.

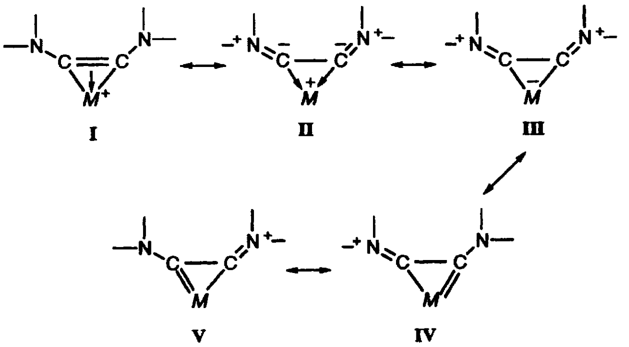
The formation of the diaminoacetylene complexes *trans*-[MX(η^2-MeHNC≡CNHMe)(dppe)$_2$]A **2** (X = Cl, A = HCl_2; X = A = ClO_4) from the reactions with an excess of HCl (in CH_2Cl_2) or $HClO_4$ (in methanol) is substantially slower than the formation of **2** from the reactions with HBF_4 or HPF_6. With $HClO_4$ the reaction can take *ca.* 3 h to go to completion. The slowness of these reactions has allowed the isolation of intermediates in the pathway leading to the diaminoacetylene complexes, namely the di(aminocarbyne)-type species *trans*-[M(CNHMe)$_2$(dppe)$_2$]A$_2$ **3** (A = HCl_2 or ClO_4) (Scheme 1).

It is important to emphasize that complexes **3** are obtained *via* the formation of the corresponding aminocarbyne species *trans*-[M(CNHMe)(CNMe)(dppe)$_2$]$^+$ **4**,[12,14,15] derived from the initial protonation at one of the isocyanide ligands in **1** and which precipitate from the solution when the reaction is carried out in benzene on addition of 1 mol equivalent of acid. Complexes **4** are green and their involvement in the preparation of compounds **2** and **3**, in CH_2Cl_2, is consistent with the immediate darkening of the reaction solution, on addition of acid, from red (the colour of the diisocyanide complexes) to brown before changing towards the colour of the final product.

Therefore, the formation of the diaminoacetylene complexes **2** proceeds according to Scheme 1 in which each member of the reaction pathway has been isolated and fully characterized. The detailed mechanistic investigation of the reactions is described in the following paper.[17]

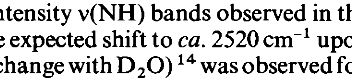
Complexes **2** and **3** have been isolated in high yields and characterized by elemental analysis, IR, ^1H, ^{31}P, ^{13}C or ^{19}F NMR spectroscopy (Tables 1 and 2), as well as by the structure determination of **2** (M = Mo, X = F, A = BF_4).

Diaminoacetylene Complexes **2**.—Spectroscopic and structural data, discussed below, indicate that in compounds **2** the diaminoacetylene ligand behaves as a formal four-electron donor, thus conferring the closed shell 18-electron configuration to its complexes. An extensive π-electron delocalization along the framework of this ligand occurs, which can be represented by forms **I**–**V** [*M* = M(dppe)$_2$ (M = Mo or W)], or related ones, showing a relevant contribution from the C=N bond in the description of the system.



In fact, the IR spectra of complexes **2** (Table 1) exhibit a strong band at *ca.* 1645–1630 cm^{-1} which is assigned to ν(C=N) of the ligating diaminoacetylene. This frequency is comparable with those exhibited by other reported diaminoacetylene compounds, such as [MX(η^2-RHNC≡CNHR)(CNR)$_4$]$^+$ (M = Mo or W, X = halide or CN, R = Bu^t or C_6H_{11}) (*ca.* 1660–1590 cm^{-1})[21] or [M(η^2-Et$_2$NC≡CNEt$_2$)(CNR)$_4$]$^+$ (M = Mo or W, R = Et or Bu^t) (1671–1655 cm^{-1}).[6] All these complexes exhibit no obvious band assignable to ν(C≡C) stretching of the diaminoacetylene ligand, as is known[22] to occur for acetylene ligands acting as four-electron donors.

The ν(C=N) value is substantially higher than those observed (*ca.* 1595–1515 cm^{-1}) for ν(C=N) of the aminocarbyne in *trans*-[M(CNHMe)(CNMe)(dppe)$_2$]$^+$,[13] and in *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$ (R = H[23] or Me[24]) in which this ligand is best represented by forms **VI** and **VII** [*M* = M(CNMe)(dppe)$_2$ (M = Mo or W) or ReCl(dppe)$_2$], as indicated by crystallographic data[23,24] for the rhenium complexes. A pronounced character of the 'iminomethylenium' (or carbene) form **VII** has also been indicated in *trans*-[WCl(CNH$_2$)(dppe)$_2$][BF$_4$]$_n$ (*n* = 0 or 1) by crystallographic analyses.[25]



VI **VII**

Other significant IR data for complexes **2** include the usually medium intensity ν(NH) bands observed in the 3415–3370 cm^{-1} range. The expected shift to *ca.* 2520 cm^{-1} upon deuteriation (by proton exchange with D_2O)[14] was observed for complex **2** (M = Mo or W, X = F, A = BF_4). Moreover, for the perchlorate complexes, the bands at *ca.* 1170 (sh) and 960w cm^{-1} are assigned to co-ordinated ClO_4^-, that at 990w cm^{-1} is due to the free ion, and the very strong band at *ca.* 1085 cm^{-1} could result from the overlap of the strong bands of both free and bound ClO_4^-.[26a] In addition, for **2** (M = Mo, X = Cl, A = HCl_2), the medium intensity and broad band at 320 cm^{-1} is assigned to ν(MoCl).

In the ^{13}C NMR spectra of complexes **2**, the low-field unresolved multiplet resonance which is observed at δ *ca.* 205 (M = Mo) or *ca.* 195 (M = W) [the exact value depends on the counter ion (Table 2)] is assigned to the metal-bonded carbons

Table 1 Some physical properties of *trans*-[$MX(\eta^2$-MeHNC≡CNHMe)(dppe)$_2$]A **2** and *trans*-[M(CNHMe)$_2$(dppe)$_2$]A$_2$ **3**

						Analysis (%)[b]			Infrared (cm^{-1})[c]	
Compound	M	X	A	Colour and yield (%)	Λ_M[a]	C	H	N	ν(NH)	ν(C=N)
2[d]	Mo	F	BF_4	Pink (90)	77	58.6 (58.6)	5.0 (5.0)	2.5 (2.4)	3400	1645
2	W	F	BF_4	Red (90)	85	54.9 (54.6)	4.8 (4.8)	2.5 (2.2)	3410	1630
2	Mo	F	PF_6	Red (90)		58.0 (58.9)	4.8 (5.0)	2.4 (2.5)	3406	1638
2[e]	W	F	PF_6	Orange (90)		53.7 (53.4)	4.8 (4.5)	2.1 (2.2)	3415	1634
2[e]	Mo	ClO_4[f]	ClO_4	Pale brown (85)	100	55.1 (55.7)	4.7 (4.7)	2.0 (2.3)	3370	1635
2	W	ClO_4[f]	ClO_4	Pink (85)	125	54.4 (53.2)	4.1 (4.3)	2.2 (2.2)	3375	1635
2[g]	Mo	Cl	HCl_2	Pale brown (75)		59.4 (59.4)	5.5 (5.2)	1.6 (2.5)	3400w (br)	1635
3[h]	Mo	—	ClO_4	Pink (70)	173	53.0 (53.2)	4.3 (4.5)	2.2 (2.2)	3370	1648
3[i]	W	—	ClO_4	Pink (70)	195	48.4 (48.6)	4.2 (4.2)	2.0 (2.0)	3375	1635
3[j]	Mo	—	HCl_2	Pink (85)		59.3 (59.4)	5.5 (5.2)	1.4 (2.5)	3400w (br)	1670

[a] Values in Ω^{-1} cm^2 mol^{-1} measured in nitromethane solution. [b] Calculated values in parentheses. [c] In KBr pellets; ν(NH) bands medium and ν(C=N) strong unless indicated otherwise; w = weak, m = medium, s = strong, vs = very strong, br = broad. The bands assigned to the counter ion (A^-) are as follows: 1050vs (br) (BF_4^-); 838vs (br) (PF_6^-); *ca.* 1090vs (br), 990w cm^{-1} (ClO_4^-). [d] With CH_2Cl_2 of crystallization. [e] With 0.5 CH_2Cl_2 of crystallization. [f] IR bands assigned to co-ordinated ClO_4^- are observed at 1170 (sh), 1085vs (br) (overlapping with that of free ClO_4^-) and 960w cm^{-1}. [g] With 0.7 CH_2Cl_2 of crystallization; ν(Mo–Cl) 320m (br) cm^{-1}. [h] With 1.5 CH_2Cl_2 of crystallization. [i] With 2 CH_2Cl_2 of crystallization. [j] With 0.2 CH_2Cl_2 of crystallization.

Table 2 Proton, $^{31}P-\{^1H\}$, ^{19}F and ^{13}C NMR data[a] for *trans*-[$MX(\eta^2$-MeHNC≡CNHMe)(dppe)$_2$]A **2** and *trans*-[M(CNHMe)$_2$(dppe)$_2$]A$_2$ **3**

Compd.	M	X	A	^1H[b]	$^{31}P-\{^1H\}$[c]	^{19}F[d]	$^{13}C-\{^1H\}$[b]
2	Mo	F	BF_4 PF_6	7.46–6.93 (m, 40, C_6H_5) 4.62 (q, 2, N*H*CH_3)[e] 2.72 (m), 2.52 (m) (8, PCH_2) 2.22 (d, 6, NHC*H*$_3$)[e]	−92.45 (d)[f]	−210.37 (qnt)[f]	204.7 (m, br, MoC) 136.7–125.2 (m, C_6H_5) 38.7 (s, NCH_3)[g] 27.2 (s, br, PCH_2)[h]
2	W	F	BF_4 PF_6	7.49–6.92 (m, 40, C_6H_5) 4.12 (q, 2, N*H*CH_3)[i] 2.69 (m), 2.50 (m) (8, PCH_2) 2.24 (d, 6, NHC*H*$_3$)[i]	−105.31 (d)[j,k]	−216.00 (qnt)[j,l]	195.4 (m, br, WC) 137.3–128.3 (m, C_6H_5) 39.2 (s, NCH_3)[g] 29.6 (s, PCH_2)[m]
2	Mo	ClO_4	ClO_4	7.66–6.87 (m, 40, C_6H_5) 4.76 (q, 2, N*H*CH_3)[i] 2.97 (m), 2.73 (m) (8, PCH_2) 2.17 (d, 6, NHC*H*$_3$)[i]	−97.24 (s)		204.9 (m, br, MoC) 137.2–128.7 (m, C_6H_5) 39.6 (s, NCH_3)[g] 25.0 (s, PCH_2)[m]
2	W	ClO_4	ClO_4	7.79–6.76 (m, 40, C_6H_5) 4.22 (q, 2, N*H*CH_3)[i] 2.93 (m), 2.73 (m) (8, PCH_2) 2.12 (d, 6, NHC*H*$_3$)[i]	−114.19 (s)[m]		193.7 (m, br, WC) 137.1–128.9 (m, C_6H_5) 39.9 (s, NCH_3)[g] 27.6 (s, PCH_2)[n]
2	Mo	Cl	HCl_2	7.51–6.87 (m, 40 H, C_6H_5) 4.13 (s, br, 2, N*H*CH_3) 2.73 (m), 2.54 (m) (8, PCH_2) 2.38 (s, br 6, NHC*H*$_3$)	−98.62 (s)		205.7 (m, br, MoC) 131.1–127.9 (m, C_6H_5) 33.8 (s, NCH_3) 22.4 (s, PCH_2)
3	Mo	—	ClO_4	7.51–6.87 (m, 40, C_6H_5) 4.13 (s, br, 2, N*H*CH_3) 3.00 (m, br, 8, PCH_2) 2.38 (s, br, 6, NHC*H*$_3$)	−91.64 (s)		263.8 (m, br, MoC) 133.6–128.8 (m, C_6H_5) 39.8 (s, NCH_3) 27.5 (s, PCH_2)
3	Mo	—	HCl_2	7.71–6.80 (m, 40, C_6H_5) 5.33 (s, br, 2, N*H*CH_3) 2.72 (m), 2.51 (m) (8, PCH_2) 2.11 (s, br, 6, NHC*H*$_3$)	−92.94 (s)		262.3 (m, br, MoC) 138.1–126.1 (m, C_6H_5) 33.8 (s, NCH_3) 28.8 (s, PCH_2)
3	W	—	ClO_4	7.88–6.80 (m, 40, C_6H_5) 4.12 (s, br, 2, N*H*CH_3) 2.92 (m, 8, PCH_2) 2.21 (s, br, 6, NHC*H*$_3$)	−107.92 (s)[o]		254.8 (m, br, WC) 133.9–129.8 (m, C_6H_5) 39.7 (s, NCH_3) 29.8 (s, PCH_2)

[a] In CD_2Cl_2; s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, sp = septet, m = multiplet, br = broad; resonance pattern, relative integration and assignment in parentheses. [b] δ values in ppm relative to $SiMe_4$, at −20 °C. [c] δ values in ppm relative to $P(OMe)_3$, at −25 °C; only the resonances of the dppe ligands are quoted; PF_6^- resonance (when A = PF_6) at δ −285.65 [sp, *J*(PF) = 714 Hz]. [d] δ values in ppm relative to $CFCl_3$; only the resonances of the fluoride ligand are quoted [they present ^2J(PF) values very close to those found in $^{31}P-\{^1H\}$ NMR]; BF_4^- (when A = BF_4) and PF_6^- (when A = PF_6) resonances observed at δ −151.5 (s) and −323.0 [d, *J*(PF) = 713 Hz], respectively. [e] ^3J(HH) = 4.6 Hz. [f] ^2J(PF) = 39.1 Hz. [g] Quartet in proton-coupled spectrum, *J*(CH) = 137.7 Hz. [h] Triplet in proton-coupled spectrum, *J*(CH) = 132.8 Hz. [i] ^3J(HH) = 4.2 Hz. [j] ^2J(PF) = 49.5 Hz. [k] With ^{183}W satellites, *J*(WP) = 231.9 Hz. [l] With ^{183}W satellites, *J*(WF) = 50.5 Hz. [m] With ^{183}W satellites, *J*(WP) = 219.2 Hz. [n] Triplet in proton-coupled spectrum, *J*(CH) = 134.3 Hz. [o] With ^{183}W satellites, *J*(WP) *ca.* 228 Hz.

of the diaminoacetylene ligand. Such a low-field resonance is indicative of a four-electron donor acetylene,[26b] and is comparable with those[4,6] for other diaminoacetylene complexes. Moreover, it occurs at a substantially higher field than that of the metal-ligating carbon of the aminocarbyne CNHMe ligand in *trans*-[M(CNHMe)(CNMe)(dppe)$_2$]$^+$ [δ *ca.* 249 (M = Mo) or *ca.* 242 (M = W)],[14] *trans*-[M(CNHMe)$_2$(dppe)$_2$]$^{2+}$ **3** [δ *ca.* 263 (M = Mo) or *ca.* 255 (M = W)] (see below) and *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$ (R = H or Me) (δ *ca.* 223).[23,24]

The methyl carbon resonance in the $^{13}C-^1H$ undecoupled spectra appears as the expected quartet, *e.g.*, with *J*(HC) *ca.* 138 Hz at δ *ca.* 39 for the fluoride complexes, whereas the dppe methylene carbons are observed as a triplet [*J*(HC) *ca.* 134 Hz] at δ *ca.* 30 (Table 2).

In the ^{1}H NMR spectra, the resonances of the methyl and NH protons of the diaminoacetylene ligand are observed, at room temperature, as a singlet and a broad resonance at δ *ca.* 2.2 and 4.7–4.1, respectively, which, on lowering the temperature (to −25 °C) split into the expected doublet and broad quartet [^3J(HH) *ca.* 4 Hz]. In addition, coupling between the methyl and NH protons was confirmed by selective decoupling experiments. Upon the addition of D_2O, the doublet attributable to the methyl protons collapses to a sharp singlet and the broad NH resonance disappears. These observations suggest the occurrence of rapid proton exchange associated with both amino groups of the diaminoacetylene ligand.

The *trans* geometry of complexes **2** (X = Cl or ClO_4) is indicated by the singlet in their ^{31}P-{^{1}H} NMR spectra. In addition, the ^{31}P-{^{1}H} NMR spectra of the fluoro complexes show a doublet, and the corresponding quintet resonance is observed in the ^{19}F NMR spectra (Table 2) of these compounds. In particular, for *trans*-[MF(η^2-MeHNC≡CNHMe)(dppe)$_2$]$^+$, the presence of the fluoride ligand is demonstrated by the quintet resonance [^2J(PF) = 39.1 or 49.5 Hz for M = Mo or W, respectively, with the expected ^{183}W satellites, J(WF) = 50.5 Hz, in the latter case] at δ −210.37 or −216.00, respectively, in their ^{19}F NMR spectra (CD_2Cl_2) at low temperature (−25 °C). Its intensity, relative to that of the BF_4^- or PF_6^- counter ion [singlet at δ −151.5 or doublet, J(PF) ≈ 713 Hz, at δ −323.0, respectively] is, as expected, 1:4 or 1:6, respectively. At ambient temperature, the resonance of the fluoride ligand is rather broad and unresolved. This signal was not located in our previous studies.[12,14]

In accord with the ^{19}F NMR data, the ^{31}P-{^{1}H} NMR spectra of the fluoro complexes exhibit a doublet resonance at δ −92.45 (M = Mo) or −105.31 (M = W) with values of ^2J(PF) which are identical to those observed in the ^{19}F NMR spectra.

The molar conductivity of nitromethane solutions of the fluoro complexes **2** (Λ_M = 77–85 Ω^{-1} cm^2 mol^{-1}) is in the range expected for a 1:1 electrolyte,[27] whereas that of the perchlorate species (Λ_M = 100–125 Ω^{-1} cm^2 mol^{-1}) is somewhat higher possibly as a result of a partial dissociation of the labile perchlorate ligand from the metal.

The diaminoacetylene ligand in complexes **2** (X = F) undergoes base-induced cleavage of the C≡C triple bond (by LiBu^n or LiMe) to form quantitatively the parent diisocyanide compounds [equation (2), R = Bu^n or Me], a process which

$$\textit{trans}\text{-}[\mathrm{MF}(\eta^2\text{-MeHNC}{\equiv}\text{CNHMe})(\mathrm{dppe})_2][\mathrm{BF_4}] + 2\mathrm{LiR} \longrightarrow \textit{trans}\text{-}[\mathrm{M(CNMe)_2(dppe)_2}] + \mathrm{LiF} + \mathrm{LiBF_4} + 2\mathrm{RH} \qquad (2)$$

involves deprotonation of the amino groups and defluorination of the metal.

Base-induced cleavage of the acetylenic C≡C bond to C_1 fragments is a rare reaction, but it has been recognized to occur in the partial conversion of [MoI(Bu^{t}HNC≡CNHBu^t)(CNBu^t)$_4$]$^+$ to [MoI(CNBu^t)$_6$]$^+$ by treatment with *n*-butyllithium followed by addition of 1,2-dibromoethane,[2] as well as in the conversion of [WBr$_2$(η^2-PhC≡CNHBu^t)(CNBu^t)$_3$] into [WBr(CPh)(CNBu^t)$_4$] by reaction with LiPh,[28] involving cleavage of an aminoalkyne ligand into a carbyne and an isocyanide. Moreover, cleavage of bis(dialkylamino)alkynes by reaction with some metal carbonyls has been reported[29] to form two- or three-metal bridging aminocarbyne-type groups.

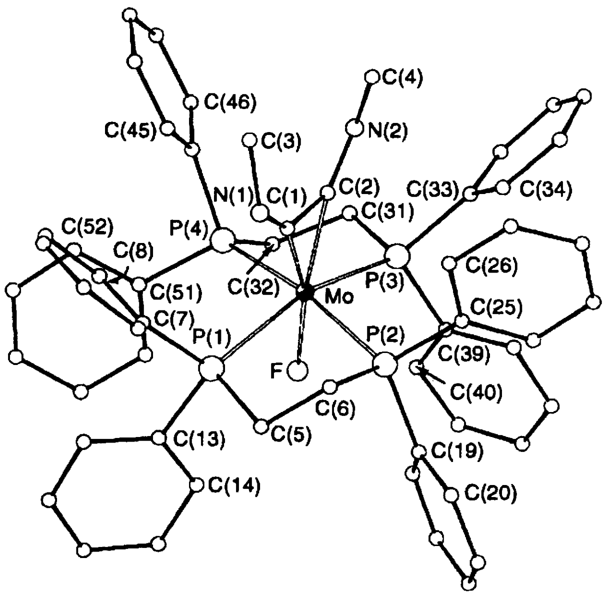


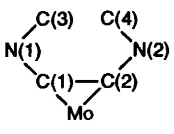
Fig. 1 View of the structure of one (**A**) of the two independent cationic complexes *trans*-[MoF(η^2-MeNHC≡CNHMe)(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for *trans*-[MoF(η^2-MeHNC≡CNHMe)(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$

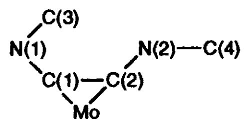
	A	**B**
Mo–P(1)	2.573(5)	2.544(6)
Mo–P(2)	2.536(6)	2.510(5)
Mo–P(3)	2.524(5)	2.540(6)
Mo–P(4)	2.495(6)	2.517(5)
Mo–F	2.019(8)	2.017(8)
Mo–C(1)	2.018(15)	2.002(13)
Mo–C(2)	2.014(13)	2.016(18)
N(1)–C(1)	1.357(21)	1.378(22)
N(1)–C(3)	1.497(22)	1.427(23)
N(2)–C(2)	1.353(19)	1.391(28)
N(2)–C(4)	1.461(24)	1.458(34)
C(1)–C(2)	1.374(23)	1.370(29)
P(1)–Mo–P(2)	78.7(2)	78.6(2)
P(1)–Mo–P(4)	97.6(2)	100.2(2)
P(2)–Mo–P(3)	98.9(2)	97.4(2)
P(3)–Mo–P(4)	81.1(2)	80.3(2)
P(1)–Mo–F	82.0(3)	82.1(3)
P(2)–Mo–F	91.9(3)	92.5(3)
P(3)–Mo–F	77.3(3)	76.3(3)
P(4)–Mo–F	78.0(3)	78.7(3)
F–Mo–C(1)	162.8(6)	160.6(5)
F–Mo–C(2)	155.9(5)	158.7(6)
P(1)–Mo–C(1)	81.0(5)	78.6(5)
P(1)–Mo–C(2)	120.2(5)	117.7(5)
P(2)–Mo–C(1)	87.3(4)	84.1(5)
P(2)–Mo–C(2)	101.2(4)	99.0(5)
P(3)–Mo–C(1)	119.8(5)	123.1(5)
P(3)–Mo–C(2)	80.7(4)	84.5(5)
P(4)–Mo–C(1)	101.8(4)	104.4(5)
P(4)–Mo–C(2)	89.0(4)	89.3(5)
C(1)–N(1)–C(3)	125.2(15)	123.2(16)
C(2)–N(2)–C(4)	123.9(15)	124.5(16)
Mo–C(1)–N(1)	154.3(13)	153.5(13)
N(1)–C(1)–C(2)	135.8(16)	135.9(15)
Mo–C(1)–C(2)	69.9(10)	70.6(10)
N(2)–C(2)–C(1)	139.7(15)	127.4(16)
Mo–C(2)–C(1)	70.2(10)	69.5(10)
Mo–C(2)–N(2)	149.6(13)	162.0(15)

Crystal Structure of trans-[MoF(η^2-MeHNC≡CNHMe)(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$.—The structure of one of the complexes **2** has been confirmed by an X-ray diffraction study. In the crystals, which contain dichloromethane molecules of solvation, two independent (**A** and **B**), but very similar, cationic complexes have been found; a view of one of them (**A**) is shown in Fig. 1 together with the atomic labelling scheme. Selected bond distances and angles in both complexes **A** and **B** are given in Table 3.

The co-ordination around Mo can be viewed as distorted octahedral with four P atoms in the equatorial positions and the



A



B

apical sites occupied by the fluorine atom and by the midpoint of the C–C bond of the alkyne. The NCCN skeleton of the alkyne ligand, the Mo and the F atom are roughly co-planar.

Molecules **A** and **B** differ by the conformation of the C(1)–C(2)–N(2)–C(4) group, in the former C(4) is *cis* with respect to C(1), whereas in the latter these atoms are *trans*.

The torsion angles are as follows: C(2)–C(1)–N(1)–C(3) 19(3)° and C(1)–C(2)–N(2)–C(4) 27(3)° for molecule **A**; C(2)–C(1)–N(1)–C(3) 1(3)° and C(1)–C(2)–N(2)–C(4) 162(2)° for molecule **B**.

The acetylenic C–C distance, 1.37(2) Å (averaged for the molecules **A** and **B**), lies within the range known for $C(sp^2)$=$C(sp^2)$ bonds, *ca.* 1.30–1.39 Å,[30] and is comparable with the average value, 1.304(27) Å,[31] for a four-electron-donor alkyne ligand, being even considerably longer than that reported, 1.26(1) Å,[18] for the four-electron-donor phenylacetylene species *trans*-$[\mathrm{MoF}(\eta^2\text{-PhC}{\equiv}\mathrm{CH})(\mathrm{dppe})_2]^+$. The value of the Mo–C distance, 2.013(15) Å (av.), is close to the average one, 2.027(28) Å,[31] for the bond to this metal from a four-electron-donor alkyne, being significantly shorter than that expected, 2.129(31) Å,[31] from a two-electron-donor alkyne. The C(alkyne)–N distance, 1.37(2) Å, is somewhat shorter than that, 1.416(18) Å,[30] for a $C(sp^2)$–$N(sp^3)$ bond and approaches the average value, 1.339(16) Å,[30] for a $C(sp^2)$–$N(sp^2)$ bond length.

These structural features, together with the spectroscopic properties discussed above, indicate an extensive π-electron delocalization along the framework of the diaminoacetylene ligand. This is in agreement with the reported structures for $[\mathrm{MoX}(\eta^2\text{-Bu}^t\mathrm{HNC}{\equiv}\mathrm{CNHBu}^t)(\mathrm{CNBu}^t)_4]^+$ (X = Br,[32] I[32] or CN[33]) and $[\mathrm{WBr}(\eta^2\text{-Et}_2\mathrm{NC}{\equiv}\mathrm{CNEt}_2)(\mathrm{CNBu}^t)_4]^+$.[6] However, in our complex, at least one of the methyl groups points away from the metal, thus lowering the steric repulsion from the phenyl groups of the bulky phosphines, whereas in the compounds with the bulky Bu^t groups steric effects within the aminoacetylene ligand appear to dominate and the only observed isomer corresponds to the opposite orientations of such groups.

Di(aminocarbyne) Complexes **3**.—The 'aminocarbyne' ligands in *trans*-$[\mathrm{M}(\mathrm{CNHMe})_2(\mathrm{dppe})_2]^{2+}$ **3** are better considered as the ligating 'iminomethylenium' group $=\mathrm{C}{=}\overset{+}{\mathrm{N}}\mathrm{HMe}$ (as shown in form **VIII**), not only on account of the maximum number of available d electrons for the Group 6 metal (see below) but also as suggested by spectroscopic data.

$$\mathrm{MeH}\overset{+}{\mathrm{N}}{=}\mathrm{C}{=}\mathrm{M}{=}\mathrm{C}{=}\overset{+}{\mathrm{N}}\mathrm{HMe}$$

VIII

In fact, in their IR spectra, complexes **3** show strong bands, assigned to ν(C=N), in the range 1655–1635 cm^{-1}, which is comparable with that observed, *ca.* 1690–1640 cm^{-1},[34] for the CN stretch of the salts $\mathrm{R_2CHCR}{=}\overset{+}{\mathrm{N}}\mathrm{R}_2$. Moreover, those bands are at frequencies *ca.* 100 cm^{-1} higher than those reported for the monocarbyne species *trans*-$[\mathrm{M}(\mathrm{CNHMe})(\mathrm{CNMe})(\mathrm{dppe})_2]^+$,[14] or *trans*-$[\mathrm{ReCl}(\mathrm{CNHMe})(\mathrm{dppe})_2]^+$,[24] indicating a larger contribution of form **VII** (compared to **VI**) for complexes **3** relative to the monocarbyne compounds.

For species **3**, ν(C=N) values are very close to those (at *ca.* 1645–1630 cm^{-1}) for the diaminoacetylene compounds **2** (Table 1). Similar behaviour has been observed[7] for the di(aminocarbyne) species $[\mathrm{W}(\eta^5\text{-C}_5\mathrm{Me}_5)(\mathrm{CNEt}_2)_2(\mathrm{CNEt})][\mathrm{BF}_4]$ [ν(C=N) at 1610 and 1539 cm^{-1}] and the related diaminoacetylene complex $[\mathrm{W}(\eta^5\text{-C}_5\mathrm{Me}_5)(\eta^2\text{-Et}_2\mathrm{NC}{\equiv}\mathrm{CNEt}_2)(\mathrm{CNEt})_2][\mathrm{BF}_4]$. Other notable IR spectroscopic characteristics for **3** are: ν(NH) is observed at 3400–3370 cm^{-1}, and the complexes with ClO_4^- as the counter ion exhibit bands characteristic of this ion at *ca.* 1085vs and 995w cm^{-1}.

The *trans* geometry of complexes **3** is consistent with the detection of a single ν(C=N) band in their IR spectra, and of a singlet resonance in the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectra which occurs at *ca.* 6 ppm downfield from that of the corresponding diaminoacetylene compound (Table 2).

The $^{13}\mathrm{C}$ NMR spectra of complexes **3** (Table 2) show the resonances for the *C*NHMe carbon [δ *ca.* 263 (M = Mo) or 255 (M = W)] at lower field not only to those for the acetylene MeHN*C*≡*C*NHMe carbons in **2**, but also to those observed[14] for *C*NHMe in the corresponding mono(aminocarbyne) compounds *trans*-$[\mathrm{M}(\mathrm{CNHMe})(\mathrm{CNMe})(\mathrm{dppe})_2][\mathrm{BF}_4]$. The same trend is observed[7] for $C\mathrm{NEt}_2$ in the di(aminocarbyne) complex $[\mathrm{W}(\eta^5\text{-C}_5\mathrm{H}_5)(\mathrm{CNEt}_2)_2(\mathrm{CNEt})]^+$ (δ 276), the corresponding diaminoacetylene compound $[\mathrm{W}(\eta^5\text{-C}_5\mathrm{H}_5)(\eta^2\text{-Et}_2\mathrm{NC}{\equiv}\mathrm{CNEt}_2)(\mathrm{CNEt})_2]^+$ (δ 207, 210) and the mono(aminocarbyne) species $[\mathrm{WBr}(\eta^5\text{-C}_5\mathrm{H}_5)(\mathrm{CNEt}_2)(\mathrm{CNEt})_2]$ (δ 258).

The $^{13}\mathrm{C}$ NMR spectra of complexes **3** also show the resonances attributable to the methyl carbon of the aminocarbyne ligand and of the dppe methylene carbons at δ *ca.* 39–34 and *ca.* 29, respectively. In the $^1\mathrm{H}$ NMR spectra, the $\mathrm{CNHC}H_3$ and the $\mathrm{CN}H\mathrm{CH}_3$ resonances occur as a singlet (δ *ca.* 2.2) and a broad resonance (δ *ca.* 4–5), whose structures are not resolved even upon lowering the temperature to −80 °C. The NH resonance disappears on addition of $\mathrm{D_2O}$.

The molar conductivity of nitromethane solutions of complexes **3** (Λ_M = 173–195 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$) is significantly higher than that exhibited by the solutions of compounds **2** (77–125 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$), consistent with the 1:2 electrolyte character of the former species.

Dicarbyne complexes with six metal–ligand π electrons are electron-deficient systems and expected[11,35] to have low stability. However, our complexes **3** are better considered as the di(iminomethylenium) species **VIII**, in which the nitrogen electron lone pairs are involved in the π system (amino groups behaving as electron donors), and therefore they can have 10 π electrons delocalized along the NCMCN framework with a resulting enhancement of their stability. The bonding can thus be represented by a simplified qualitative π molecular orbital scheme[36] such as that shown in Fig. 2 in which the multiple bond character of both the M–C and the adjacent C–N bonds is evident. The significant π-electron release from the electron-rich $\{\mathrm{M}(\mathrm{dppe})_2\}$ metal centre to π*–CN orbitals of the CNHMe ligands is reflected in the composition of the proposed highest occupied molecular orbital (HOMO).

The di(aminocarbyne) complexes **3** in dichloromethane solution, at room temperature, convert into the corresponding η^2-diaminoacetylene compounds **2**, and this conversion can be monitored by $^{31}\mathrm{P}$ and $^{13}\mathrm{C}$ NMR spectroscopy. Thus, with *trans*-$[\mathrm{Mo}(\mathrm{CNHMe})_2(\mathrm{dppe})_2][\mathrm{ClO}_4]_2$ the formation of *trans*-$[\mathrm{Mo}(\mathrm{OClO}_3)(\eta^2\text{-MeHNC}{\equiv}\mathrm{CNHMe})(\mathrm{dppe})_2][\mathrm{ClO}_4]$ is complete within *ca.* 3 h, but for *trans*-$[\mathrm{Mo}(\mathrm{CNHMe})_2(\mathrm{dppe})_2][\mathrm{HCl}_2]_2$ the formation of *trans*-$[\mathrm{MoCl}(\eta^2\text{-MeHNC}{\equiv}\mathrm{CNHMe})(\mathrm{dppe})_2][\mathrm{HCl}_2]$ is much faster. No intermediates were detected in the conversion, possibly due to their high reactivity and resulting low concentration.

It is worth noting that in our system the coupling process results from a sequence of two electrophilic additions to the ligands activated by an electron-rich metal centre (protonation of both isocyanides with resulting oxidation of the metal which thus is activated towards a nucleophilic attack) followed by a nucleophile addition to the activated metal (Scheme 2). Therefore, there is a combination of alternative effects leading to the promotion of the final coupling step.

Finally, it is also noteworthy to recognize the occurrence of the first example of coupling of two *trans*-'carbyne' ligands.

Table 4 Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of *trans*-$[MoF(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2][BF_4]\cdot CH_2Cl_2$

	A				**B**		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*		*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	1034(1)	672(1)	1657(1)		3957(1)	3986(1)	3566(1)
P(1)	1629(3)	2045(2)	928(2)		4221(3)	4038(2)	4572(2)
P(2)	981(3)	1084(2)	2567(2)		4013(3)	5458(2)	3134(2)
P(3)	−98(3)	−342(2)	2353(2)		4361(3)	3941(3)	2417(2)
P(4)	850(3)	463(2)	719(2)		4167(3)	2492(2)	3939(2)
F	−183(5)	1347(5)	1517(4)		5344(5)	3740(5)	3327(4)
N(1)	3280(8)	426(8)	1434(7)		2015(9)	4448(8)	4562(7)
N(2)	2110(9)	−1147(7)	2065(6)		1878(10)	3921(9)	3469(7)
C(1)	2392(10)	309(9)	1591(7)		2663(9)	4235(9)	4068(7)
C(2)	1930(9)	−343(8)	1868(7)		2645(11)	4035(8)	3575(7)
C(3)	4107(12)	−170(12)	1342(11)		1045(11)	4521(13)	4661(10)
C(4)	2930(13)	−1636(10)	2289(11)		1917(12)	3496(12)	3072(9)
C(5)	1671(14)	2448(10)	1527(8)		4097(14)	5116(10)	4413(9)
C(6)	1888(12)	1743(10)	2190(8)		3568(12)	5682(8)	3892(8)
C(7)	2771(11)	2073(9)	334(8)		3454(11)	3568(10)	5403(8)
C(8)	2918(12)	1791(10)	−150(8)		3297(12)	2790(11)	5605(9)
C(9)	3799(14)	1762(11)	−621(10)		2692(15)	2374(12)	6261(11)
C(10)	4502(14)	1977(12)	−520(10)		2305(15)	2792(14)	6682(11)
C(11)	4415(14)	2252(12)	−58(10)		2430(16)	3528(15)	6506(12)
C(12)	3519(13)	2291(11)	412(9)		3029(13)	3952(11)	5847(10)
C(13)	968(11)	2919(9)	402(8)		5358(10)	3700(9)	4738(7)
C(14)	59(14)	3097(12)	713(10)		6097(13)	4026(11)	4223(9)
C(15)	−492(14)	3824(12)	333(11)		6986(14)	3795(12)	4349(10)
C(16)	−89(15)	4308(12)	−345(11)		7087(13)	3258(11)	4991(10)
C(17)	831(15)	4084(13)	−636(11)		6413(14)	2922(11)	5475(10)
C(18)	1396(13)	3389(11)	−289(10)		5435(13)	3128(11)	5403(9)
C(19)	−40(11)	1691(9)	2885(8)		5075(11)	5898(10)	2737(8)
C(20)	53(14)	2031(12)	3294(10)		5106(14)	6665(12)	2652(10)
C(21)	−742(15)	2502(12)	3544(10)		5999(15)	6947(13)	2368(11)
C(22)	−1573(16)	2632(14)	3355(11)		6761(14)	6497(12)	2156(10)
C(23)	−1625(14)	2274(12)	2950(10)		6775(13)	5742(12)	2231(10)
C(24)	−852(11)	1809(10)	2730(8)		5894(12)	5427(10)	2530(9)
C(25)	1302(11)	307(9)	3327(8)		3271(11)	6182(9)	2597(8)
C(26)	2223(11)	−93(10)	3253(8)		2302(13)	6219(11)	2850(9)
C(27)	2432(12)	−746(10)	3844(9)		1718(14)	6713(12)	2413(10)
C(28)	1761(12)	−1010(11)	4489(9)		2131(14)	7141(12)	1724(10)
C(29)	859(12)	−590(10)	4552(9)		3086(13)	7092(11)	1459(9)
C(30)	638(11)	70(10)	3975(8)		3674(11)	6602(10)	1890(8)
C(31)	−337(10)	−630(10)	1768(8)		4590(12)	2871(10)	2546(9)
C(32)	−285(10)	70(9)	1047(7)		4929(10)	2315(9)	3182(8)
C(33)	139(10)	−1314(9)	3027(7)		3601(11)	4372(10)	1858(8)
C(34)	692(11)	−1438(9)	3432(8)		2925(12)	5013(11)	1881(9)
C(35)	861(12)	−2200(11)	3958(9)		2313(17)	5359(14)	1447(12)
C(36)	494(12)	−2850(11)	4075(9)		2411(18)	5020(15)	896(12)
C(37)	−104(14)	−2725(12)	3692(10)		3072(18)	4403(15)	961(12)
C(38)	−280(11)	−1992(10)	3201(8)		3724(14)	4040(12)	1388(11)
C(39)	−1248(10)	23(9)	2781(8)		5404(11)	4336(9)	1850(8)
C(40)	−1923(13)	449(11)	2438(9)		6261(11)	3892(10)	1936(8)
C(41)	−2771(14)	723(12)	2813(10)		7103(13)	4200(12)	1499(10)
C(42)	−2944(13)	601(11)	3462(10)		7051(14)	4973(13)	970(10)
C(43)	−2273(14)	177(11)	3806(10)		6231(14)	5414(11)	882(10)
C(44)	−1410(11)	−126(10)	3468(8)		5379(13)	5105(12)	1301(10)
C(45)	1711(10)	−230(9)	404(7)		3136(10)	2025(9)	4186(7)
C(46)	1451(11)	−783(9)	270(8)		3124(11)	1487(10)	3930(8)
C(47)	2180(13)	−1226(11)	−67(9)		2283(14)	1147(11)	4147(10)
C(48)	3094(13)	−1160(11)	−220(9)		1543(13)	1344(11)	4588(10)
C(49)	3337(12)	−632(10)	−61(9)		1551(13)	1853(11)	4867(9)
C(50)	2652(11)	−177(9)	269(8)		2387(10)	2199(9)	4656(7)
C(51)	675(10)	1299(9)	−87(7)		4805(11)	1774(9)	4556(8)
C(52)	1227(11)	1326(10)	−711(8)		4459(13)	1101(11)	5088(10)
C(53)	1042(13)	2005(12)	−1291(10)		5023(16)	553(13)	5555(11)
C(54)	352(14)	2599(12)	−1265(10)		5907(14)	701(12)	5429(10)
C(55)	−213(12)	2575(11)	−643(9)		6210(14)	1390(12)	4923(10)
C(56)	−57(11)	1903(10)	−31(8)		5658(11)	1945(10)	4471(8)
Anions and solvation molecules							
B(1)	728(37)	5422(32)	6048(27)	F(5′)	4470(36)	838(31)	1858(27)
F(1)	1215(13)	5312(11)	6494(10)	F(6′)	3870(21)	1913(19)	2036(17)
F(2)	1347(14)	5432(11)	5472(11)	F(7′)	5230(46)	2031(38)	1325(33)
F(3)	172(14)	6127(13)	5934(10)	F(8′)	5052(20)	1171(17)	2450(15)

Table 4 (*contd.*)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
F(4)	279(16)	4771(15)	6345(11)	Cl(1)	4887(7)	1334(6)	7018(5)
B(2)	4637(24)	1470(21)	1902(17)	Cl(2)	3268(7)	772(5)	8047(5)
F(5)	4900(15)	1093(13)	1454(11)	Cl(57)	4171(20)	581(17)	7383(15)
F(6)	4190(19)	2204(16)	1607(14)	Cl(3)	2483(12)	7272(10)	−798(8)
F(7)	5506(18)	1498(15)	1906(14)	Cl(4)	3832(11)	6660(10)	−36(9)
F(8)	4138(23)	968(20)	2563(17)	C(58)	3587(28)	6835(23)	−741(20)

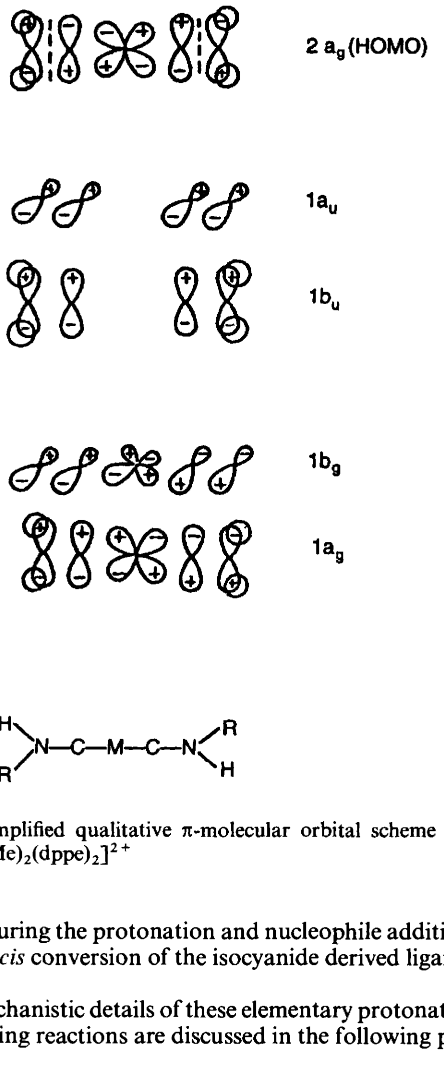


Fig. 2 Simplified qualitative π-molecular orbital scheme for *trans*-$[M(CNHMe)_2(dppe)_2]^{2+}$

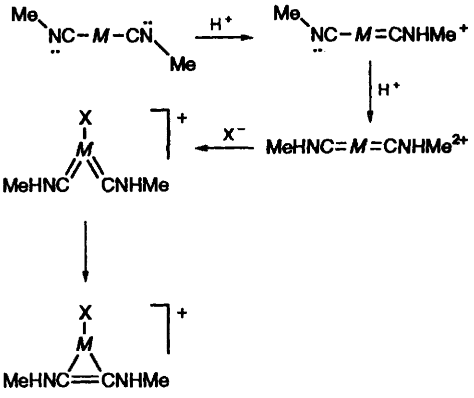
Clearly, during the protonation and nucleophile addition steps, a *trans* to *cis* conversion of the isocyanide derived ligands must occur.

The mechanistic details of these elementary protonation steps and coupling reactions are discussed in the following paper.[17]

Experimental

All reactions were carried out using standard dinitrogen-flow or high-vacuum techniques. The complexes *trans*-$[M(CNMe)_2(dppe)_2]$ were prepared by published methods.[13] The acids were used as purchased from Aldrich and only freshly prepared solutions were used. The solvents were dried by standard methods and freshly distilled under dinitrogen. The NMR spectra were recorded with a Varian Unity 300 spectrometer and IR spectra with a Perkin-Elmer 683 or 457 spectrophotometer.

Preparation of trans-$[MF(\eta^2\text{-MeHNC}{\equiv}\text{CNHMe})(dppe)_2][BF_4]$ (M = Mo *or* W).—HBF_4 {0.20 mmol, 0.14 cm^3 of a diethyl ether solution prepared by 1:4 dilution of $[Et_2OH][BF_4]$ (85%, ρ = 1.1 g cm^{-3})} was rapidly (*ca.* 2 s) added to a solution of *trans*-$[M(CNMe)_2(dppe)_2]$ [0.10 mmol, 97 mg (M = Mo) or 106 mg (M = W)] in CH_2Cl_2 (20 cm^3). During the addition, the red solution darkened initially to brown, then lightened to orange. The solution was concentrated under reduced pressure to *ca.* 5 cm^3 followed by addition of diethyl ether at low temperature (*ca.* −30 °C) to give a precipitate which was filtered off, washed with Et_2O and dried *in vacuo*. The product was purified by recrystallization from CH_2Cl_2–Et_2O to give red (for W) or orange (for Mo) crystals (*ca.* 90% yield).



Scheme 2 *M* = $M(dppe)_2$ (M = Mo or W); X^- = F^-, Cl^- or ClO_4^-

Preparation of trans-$[MF(\eta^2\text{-MeHNC}{\equiv}\text{CNHMe})(dppe)_2][PF_6]$ (M = Mo *or* W).—HPF_6 [0.39 mmol, 0.082 cm^3 of a methanol solution prepared by 1:2 dilution of commercial HPF_6 (75 w% in water, ρ = 1.85 g cm^{-3}, which was degassed before use)] was rapidly (*ca.* 2 s) added to a solution of *trans*-$[M(CNMe)_2(dppe)_2]$ [0.18 mmol, 175 mg (M = Mo) or 191 mg (M = W)] in CH_2Cl_2 (20 cm^3). During the addition, the red solution darkened to brown, then lightened to orange. The solution was concentrated under reduced pressure to *ca.* 5 cm^3 followed by addition of MeOH–Et_2O at low temperature (*ca.* −30 °C) to give a precipitate which was filtered off, washed with Et_2O–MeOH and Et_2O and dried *in vacuo*. The product was purified by recrystallization from CH_2Cl_2–Et_2O to form red (for W) or orange (for Mo) crystals (*ca.* 90% yield).

Preparation of trans-$[M(ClO_4)(\eta^2\text{-MeHNC}{\equiv}\text{CNHMe})(dppe)_2][ClO_4]$ (M = Mo *or* W).—These compounds can be obtained either in a one-pot synthesis from *trans*-$[M(CNMe)_2(dppe)_2]$ [route (*i*)] or upon conversion [route (*ii*)] of the corresponding isolated 'dicarbyne'-type intermediates *trans*-$[M(CNHMe)_2(dppe)_2][ClO_4]_2$.

(*i*) The acid $HClO_4$ [0.39 mmol, 0.17 cm^3 of a methanol solution prepared by 1:4 dilution of commercial $HClO_4$ (60% in water and ρ = 1.53 g cm^{-3})] was rapidly added to a solution of *trans*-$[M(CNMe)_2(dppe)_2]$ [0.13 mmol, 123 mg (M = Mo) and 138 mg (M = W)] in CH_2Cl_2 (30 cm^3). The solution was stirred for *ca.* 3 h, then concentrated under reduced pressure to *ca.* 5 cm^3 and MeOH–Et_2O added to give a pink precipitate which was filtered off, washed with MeOH–Et_2O and Et_2O and dried *in vacuo*. The final product was purified by recrystallization from CH_2Cl_2–Et_2O giving a pale brown (Mo) or pink (W) solid (*ca.* 85% yield).

(*ii*) The compound *trans*-[M(CNHMe)$_2$(dppe)$_2$][ClO$_4$]$_2$ [0.10 mmol, 118 mg (M = Mo) or 126 mg (M = W)] (see below) was dissolved in CH$_2$Cl$_2$ (20 cm^3) and the solution stirred for *ca.* 48 h. The solution was concentrated under reduced pressure to *ca.* 5 cm^3. Addition of Et$_2$O gave a precipitate which was filtered off, washed with Et$_2$O and dried *in vacuo*. The product was purified by recrystallization from CH$_2$Cl$_2$–Et$_2$O to give pale brown (Mo) or pink (W) crystals (*ca.* 85% yield).

Preparation of trans-[M(CNHMe)$_2$(dppe)$_2$][ClO$_4$]$_2$ (M = Mo *or* W).—The acid HClO$_4$ [0.34 mmol, 0.15 cm^3 of a methanol solution prepared by 1:4 dilution of commercial HClO$_4$ (60% in water and ρ = 1.53 g cm^{-3})] was rapidly added to a solution of *trans*-[M(CNMe)$_2$(dppe)$_2$] [0.13 mmol, 123 mg (M = Mo) or 138 mg (M = W)] in CH$_2$Cl$_2$ (30 cm^3). The solution was concentrated under reduced pressure to *ca.* 5 cm^3 and addition of MeOH–Et$_2$O gave a pink precipitate which was filtered off, washed with MeOH–Et$_2$O and Et$_2$O and dried *in vacuo* to give *trans*-[M(CNHMe)$_2$(dppe)$_2$][ClO$_4$]$_2$ as a pink crystalline solid (*ca.* 70% yield).

Preparation of trans-[Mo(CNHMe)$_2$(dppe)$_2$][HCl$_2$]$_2$ *and trans*-[MoCl(η^2-MeHNC$\equiv$CNHMe)(dppe)$_2$][HCl$_2$].—The acid HCl [0.74 mmol, 1.0 cm^3 of a dichloromethane solution obtained by mixing SiMe$_3$Cl (0.22 cm^3, 1.70 mmol) and MeOH (0.070 cm^3, *ca.* 1.70 mmol) with CH$_2$Cl$_2$ (2 cm^3)] was rapidly added to a solution of *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (0.072 mmol, 70 mg), in CH$_2$Cl$_2$ (10 cm^3). During the addition the red solution lightened immediately to yellow followed by pink. The solution was rapidly taken to dryness under reduced pressure to give *trans*-[Mo(CNHMe)$_2$(dppe)$_2$][HCl$_2$]$_2$ (*ca.* 85% yield).

This product (0.038 mmol, 40 mg) was dissolved in CH$_2$Cl$_2$ (10 cm^3) and the solution stirred for *ca.* 2 h; then it was taken to dryness under reduced pressure to give *trans*-[MoCl(η^2-MeHNC$\equiv$CNHMe)(dppe)$_2$][HCl$_2$] as a pale brown powder (*ca.* 75% yield). This compound decomposed on attempting its recrystallization from CH$_2$Cl$_2$–Et$_2$O.

Reaction of trans-[MoF(η^2-MeHNC$\equiv$CNHMe)(dppe)$_2$][BF$_4$] *with* LiBu^n. *Formation of trans*-[Mo(CNMe)$_2$(dppe)$_2$].—LiBu^n (0.21 mmol, 0.21 cm^3 of a 1 mol dm^{-3} solution in hexane) was slowly added dropwise to a tetrahydrofuran solution (10 cm^3) of *trans*-[MoF(η^2-MeHNC$\equiv$CNHMe)(dppe)$_2$][BF$_4$] (0.10 mmol, 108 mg). During the addition, the initial orange solution changed to pale red and then turned to deep red. After *ca.* 10 min the solution was filtered and concentrated under reduced pressure to *ca.* 3 cm^3. Addition of diethyl ether led to the precipitation of *trans*-[Mo(CNMe)$_2$(dppe)$_2$] as a red solid which was filtered off, washed with diethyl ether and dried *in vacuo* (*ca.* 95 mg, 89% yield).

Crystal Structure Determination of trans-[MoF(η^2-MeHNC$\equiv$CNHMe)(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$—C$_{56}$H$_{56}$BF$_5$MoN$_2$P$_4$·CH$_2$Cl$_2$, M = 1167.64, triclinic, space group $P\bar{1}$, a = 15.601(16), b = 19.052(11), c = 23.071(14) Å, α = 61.92(5), β = 69.59(6), γ = 74.31(6)°, U = 5623(8) Å^3, Z = 4, D_c = 1.379 g cm^{-3}, $F(000)$ = 2400, Nb-filtered Mo-Kα radiation, $\bar{\lambda}$ = 0.710 73 Å, μ = 4.88 cm^{-1}.

Intensity data were collected on a Siemens AED diffractometer, using the θ–2θ scan technique at room temperature. 19 898 Unique reflections were measured with θ in the range 3–25°; 6788, having $I \geqslant 3\sigma(I)$, were used in the refinement. The individual profiles were analysed according to Lehmann and Larsen.[37] The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. No correction for the absorption effects was applied.

The structure was solved by Patterson and Fourier methods and refined by blocked full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement only for the Mo, P, N, co-ordinated F and some carbon [C(1)–C(6) and C(31), C(32)] atoms. One of the two BF$_4^-$ anions was found disordered and distributed in two positions of equal occupancy factor. No attempts were made to calculate the positions of the hydrogen atoms. A weighting scheme $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement; at convergence the g value was 0.0038. Final R and R' values were 0.0825 and 0.1069. The SHELX 76 and SHELXS 86 systems of computer programs were used.[38] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 39. Final atomic coordinates for the non-hydrogen atoms are given in Table 4. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional data available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

This work has been partially supported by JNICT (Junta Nacional de Investigação Cientifica e Tecnológica, Portugal) and by the JNICT/British Council protocol. We also acknowledge the Oriente Foundation for a scholarship (to Y. W.).

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Received 15*th August* 1994; *Paper* 4/04974H