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Preliminary Communication

Aminocarbyne coupling reactions leading to the bis(amino)acetylene complexes *trans*-$[MF(\eta^2\text{-}MeHNC{\equiv}CNHMe)(Ph_2PCH_2CH_2PPh_2)_2][BF_4]$ (M = Mo or W) and cleavage of the acetylenic-triple bond. A reformulation, and X-ray structure of the Mo compound

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Abstract

Reactions of $[Et_2OH][BF_4]$ with the aminocarbyne complexes *trans*-$[M(CNHMe)(CNMe)(dppe)_2][BF_4]$ (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) give the corresponding bis(amino)acetylene compounds *trans*-$[MF(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2][BF_4]$ (the molecular structure of the Mo complex being authenticated by an X-ray analysis). Previously this was formulated as *trans*-$[M(CNHMe)_2(dppe)_2][BF_4]_2$ and, unknowingly, it had provided the first example of reductive coupling of isocyanide ligands. Base-induced CC cleavage (by Li Bu^n) of the bis(amino)acetylene to two isocyanide ligands has been recognized to form quantitatively *trans*-$[M(CNMe)_2(dppe)_2]$ for the first time.

Reductive coupling of small unsaturated C_1 molecules (typically carbon monoxide [1–3] or isocyanides [1–6]) at a transition metal is a matter of current and growing interest [1].

Carbyne complexes with groups $M{\equiv}COSiR_3$ (siloxycarbynes) [1–3] and $M{\equiv}CNER$ (E = H or R) (aminocarbynes) [1–6] formed upon addition of an electrophile (E^+) which promotes a coupling reaction to a suitable substrate are key intermediates, leading to acetylene diethers ($R_3SiOC{\equiv}COSiR_3$) or bis(amino) acetylenes ($RENC{\equiv}CNER$). However, the detailed mechanistic pathways have been a matter of considerable debate [3–6].

Recent developments in this field have led us to re-examine some of our previous studies [7–10] on the reactions of the diisocyanide complexes *trans*-$[M(CNMe)_2(dppe)_2]$ (**1**, M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) with HBF_4 which provided the first examples of electrophilic attack at an isocyanide ligand and a novel route to carbyne-type species. We now report that such studies *also* achieved, although unknowingly, the first reductive coupling of isocyanide ligands, a reaction which later was unambiguously recognized by others [11,1] in the seven-coordinate complexes $[MX(CNR)_6]^+$ (M = Mo or W; X = halide or cyanide) who used a reducing agent (Zn) and a proton source.

Originally we reported a series of well-defined aminocarbyne complexes, such as *trans*-$[M(CNHMe)(CNMe)(dppe)_2][BF_4]$ (**2**) [7,8] and $[MH(CNHMe)(CNMe)(dppe)_2][BF_4]_2$ (**3**) [9] as well as [7,3] other compounds, formulated, on the basis of the then available data, as the diaminocarbynes *trans*-$[M(CNHMe)_2\text{-}(dppe)_2[BF_4]_2$. However, in the light of new evidence, confirmed by an X-ray structural analysis, we now reformulate the last complexes as the bis(amino)acetylene-fluorido compounds *trans*-$[MF(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2][BF_4]$ (**4**).

The presence of the fluoride in **4** is unambiguously proved by the quintet resonance [$^2J(PF) = 39.7$ or 50.4 Hz for M = Mo or W, respectively, with the expected ^{183}W satellites, $J(WF) = 49$ Hz, in the latter case] observed ($\delta = -209.03$ or -214.75 ppm, respectively) at −20°C in the ^{19}F NMR spectra (CD_2Cl_2). The intensity, relative to that of the singlet resonance for the BF_4^- counter-ion ($\delta = -151.46$ ppm), was 1:4. At ambient temperature, the resonance of the fluoride ligand is rather broad, without any apparent structure, and it was missed in our previous studies [7,8]. In agreement with the above data, the ^{31}P NMR spectra of **4** exhibit a doublet resonance at $\delta = -92.45$ or -105.31 ppm (M = Mo or W, respectively, at −20°C), with $^2J(PF)$ identical to those observed in the ^{19}F NMR spectra.

The ^1H NMR spectra of **4** do not need reassignment, but the low field resonance at $\delta = -204.7$ or

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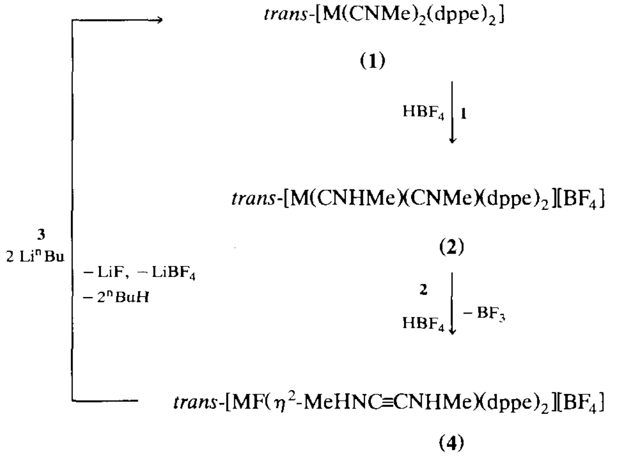
−194.5 ppm (for M = Mo or W, respectively) observed in the ^{13}C NMR spectra and previously assigned [8] to the metal ligating aminocarbene-carbons, can now be attributed to the metal-bonded carbons of the bis(amino)acetylene. Such low field resonances are indicative [12] of a 4-electron donor acetylene, giving the complexes an 18-electron configuration.

In addition, the strong IR bands assigned to ν(C=N) are observed [8] at considerably higher frequencies (1645 or 1630 cm^{-1}, for M = Mo or W, respectively) than those known [8,9] for the related and well-defined aminocarbyne complexes **2** and **3** (*ca.* 1520 and *ca.* 1560 cm^{-1}, respectively), and are also consistent [5,6] with the bis(amino)acetylene formulation for **4**.



Finally, their reformulation has been confirmed by an X-ray structural analysis of the molybdenum complex (**4**, M = Mo) *.

In the crystals of **4**, two independent (**A** and **B**), but very similar, complex cations have been recognized, and a view of one of them (**A**) is depicted in Fig. 1. The coordination around Mo is distorted octahedral with four P atoms in the equatorial positions and the apical sites occupied by the fluoride and by the midpoint of the unsaturated C–C bond of the alkyne. The NCCN skeleton of the alkyne, the Mo, and the F atom are roughly co-planar.

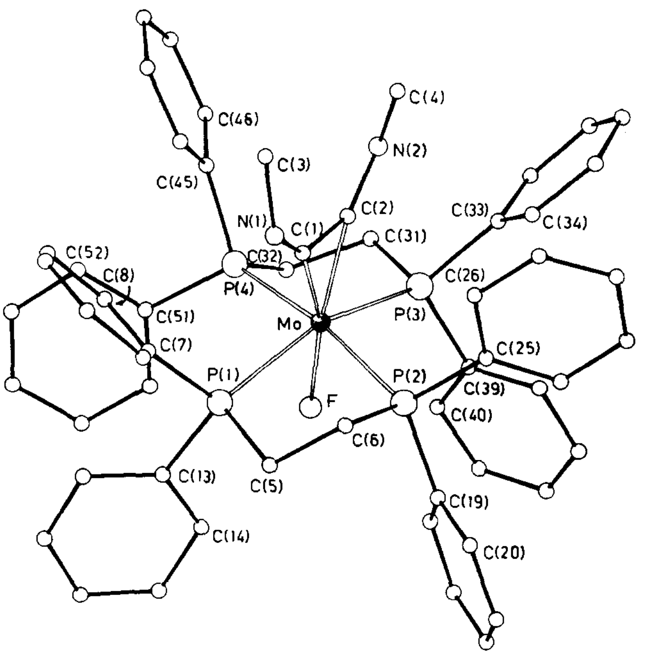
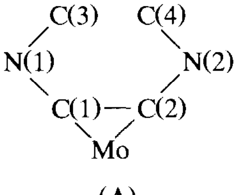
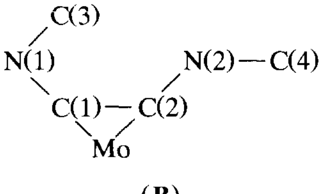


Fig. 1. View of the structure of one of the two independent cationic complexes of **4**. Selected bond distances (Å) and angles (°): Mo–P(1) 2.573(5) [2.544(6)], Mo–P(2) 2.536(6) [2.510(5)], Mo–P(3) 2.524(5) [2.540(6)], Mo–P(4) 2.495(6) [2.517(5)], Mo–F 2.019(8) [2.017(8)], Mo–C(1) 2.018(15) [2.002(13)], Mo–C(2) 2.014(13) [2.016(18)], C(1)–C(2) 1.37(2) [1.37(3)], C(1)–N(1) 1.36(2) [1.38(2)], C(3)–N(1), 1.50(2) [1.43(2)], C(2)–N(2) 1.35(2) [1.39(3)], C(4)–N(2) 1.46(2) [1.46(3)]; C(3)–N(1)–C(1) 125(2) [123(2)], N(1)–C(1)–C(2) 136(2) [136(2)], C(1)–C(2)–N(2) 140(2) [127(2)], C(2)–N(2)–C(4) 124(2) [124(2)]. The values in square brackets refer to the second independent complex.

Molecules **A** and **B** differ in 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*.



(A)



(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), *ca.* 1.30–1.39 Å [13], and is comparable with the average value, 1.304(27) Å [14], for a 4e-donor alkyne and considerably longer than that reported, (1.26(1) Å [15]) for the 4e-donor phenyl-

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* Crystal data for **4**: [$C_{56}H_{56}FN_2P_4Mo$][BF_4]·CH_2Cl_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, $\bar{\lambda}$ = 0.71073 Å, μ = 4.88 cm^{-1}.

The intensity data for the compounds were collected on a Siemens AED diffractometer, using the θ–2θ scan technique at room temperature. 19898 unique reflections were measured with θ in the range 3–25°; 6788, having $I > 3\sigma(I)$, were used in the refinement. 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, coordinated 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. The R and R_w values were 0.0825 and 0.1069. Atomic co-ordinates, thermal parameters and a complete list of bond distances and angles have been deposited at Cambridge Crystallographic Data Centre.

acetylene species *trans*-$[MoF(\eta^2\text{-}PhC{\equiv}CH)(dppe)_2]^+$. The Mo–C distance, 2.013(15) Å (av.), is close to the average (2.027(28) Å [14]) for the bond to a 4e-donor alkyne and significantly shorter than that expected (2.129(31) Å [14]) for a 2e-donor alkyne. The C(alkyne)–N distance, 1.37(2) Å, is somewhat shorter than that (1.416(18) Å [13]) for a $C(sp^2)\text{–}N(sp^3)$ bond and approaches the average value, 1.339(16) Å [13], for a $C(sp^2)\text{–}N(sp^2)$ bond length.

These data indicate extensive π-electron delocalization along the framework of the bis(amino)acetylene, consistent with the structures for $[MoX(\eta^2\text{-}{}^tBuHNC{\equiv}CNH{}^tBu)(CN{}^tBu)_4]^+$ (**5**, X = Br [16], I [16] or CN [17]) and $[WBr(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)(CN{}^tBu)_4]^+$ [6]. However, in our complex (**4**, M = Mo), at least one of the methyl groups points away from the metal, thus lowering the steric repulsion from phenyl groups of the bulky phosphines, whereas in compounds **5** the steric effects within the aminoacetylene itself appear to dominate and the only observed isomer has the opposite orientations of the bulky ${}^tBu$ groups.

Complexes **4** are derived from the reaction of $HBF_4 \cdot Et_2O$ with the intermediate **2** (eqns. (1) and (2)) and, although the detailed mechanism is still unknown, the hydride-carbyne complex **3** does not appear to be involved. The reaction seems to occur via protonation at **2**, forming intermediates of the type $[M(CNHMe)_2(dppe)_2][BF_4]_2$ or $[M(CHNHMe)(CNMe)(dppe)_2][BF_4]_2$, related to those suggested by others in different systems such as $[M(CNEt_2)_2(CNEt)_4]^{2+}$ [6] and $[Mo(CHNH{}^tBu)(CN{}^tBu)_5]^{2+}$ [5]. The coupling step would then be promoted by fluorination, upon nucleophilic attack by BF_4^-. This should not be surprising in view of the ready metal fluorinating ability of this anion which we have observed in the formation of *trans*-$[MoF({\equiv}CCH_2{}^tBu)(dppe)_2][BF_4]$ [18] and *trans*-$[WF({=}CH\text{-}CH_2Ph)(dppe)_2][BF_4]$ [19] in reactions of HBF_4 with parent alkynyl complexes. Moreover, $[MoF(\eta^2\text{-}PhC{\equiv}CH)(dppe)_2][BF_4]$ has been reported [15] as the product of the reaction of $[MoH_4(dppe)_2]$ with $PhC{\equiv}CH$ in the presence of HBF_4.

Base-induced cleavage of the acetylenic CC bond to C_1 fragments, is very rare, and occurs with deprotonation of the amino groups and defluorination of the metal on treatment of **4** with Li^nBu (in a twofold molar ratio). This regenerates quantitatively the parent diisocyanide complexes **1** (eqn. (3)), in a process which reverses the isocyanide coupling and which we also previously achieved [10] unknowingly for the first time using LiMe, Li, or NaOMe. Cleavage of the triple bond of bis(dialkylamino)alkynes upon reaction with some metal carbonyls is known [20] to give 2- or 3-metal-bridging aminocarbyne-type units, whereas a related alkyne cleavage to a carbyne and an isocyanide has been reported [21] for the conversion of $[WBr_2(\eta^2\text{-}PhC{\equiv}CNH{}^tBu)(CN{}^tBu)_3]$ to $[WBr(CPh)(CN{}^tBu)_4]$ upon reaction with LiPh.

We are currently investigating the mechanisms of these coupling and cleavage reactions.

Acknowledgements

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References

1 R.N. Vrtis and S.J. Lippard, *Isr. J. Chem., 30* (1990) 331 and refs. cited therein.

2 R.N. Vrtis, S. Liu, C.P. Rao, S.G. Bott and S.J. Lippard, *Organometallics, 10* (1991) 275.

3 E.M. Carnahan and S.J. Lippard, *J. Am. Chem. Soc., 112* (1990) 3230.

4 A.C. Filippou, *Polyhedron, 9* (1990) 727 and refs. cited therein.

5 E.M. Carnahan and S.J. Lippard, *J. Chem. Soc., Dalton Trans.*, (1991) 699; C.M. Giandomenico, C.T. Lam and S.J. Lippard, *J. Am. Chem. Soc., 104* (1982) 1263.

6 A.C. Filipou, C. Völkl, W. Grünleitner and P. Kiprof, *J. Organomet. Chem., 434* (1992) 201.

7 J. Chatt, A.J.L. Pombeiro, R.L. Richards, G.H.D. Royston, K.W. Muir and R. Walker, *J. Chem. Soc., Chem. Commun.*, (1975) 708.

8 J. Chatt, A.J.L. Pombeiro and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1980) 492.

9 J. Chatt, A.J.L. Pombeiro and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1979) 1585.

10 A.J.L. Pombeiro and R.L. Richards, *Transition Met. Chem.*, 5 (1980) 55.

11 C.T. Lam, P.W.R. Corfield and S.J. Lippard, *J. Am. Chem. Soc., 99* (1977) 617.

12 J.L. Templeton and B.C. Ward, *J. Am. Chem. Soc., 102* (1980) 3288.

13 F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. II*, (1987) S1.

14 A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) S1.

15 R. Ellis, R.A. Henderson, A. Hills and D.L. Hughes, *J. Organomet. Chem., 333* (1987) C6.

16 P.W.R. Corfield, L.M. Baltusis and S.J. Lippard, *Inorg. Chem., 20* (1981) 922.

17 J.C. Dewan, C.M. Giandomenico and S.J. Lippard, *Inorg. Chem., 20* (1981) 4069.

18 M.A.N.D.A. Lemos, A.J.L. Pombeiro, D.L. Hughes and R.L. Richards, *J. Organomet. Chem., 434* (1992) C6.

19 A. Hills, D.L. Hughes, N. Kashef, M.A.N.D.A. Lemos, A.J.L. Pombeiro and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1992) 1775.

20 R.B. King and C.A. Harmon, *Inorg. Chem., 15* (1976) 879.

21 A.C. Filipou, C. Völkl, W. Grünleitner and P. Kiprof, *Angew. Chem., Int. Ed. Engl., 29* (1990) 207.