Formation of Carbyne-like Ligands by the Protonation of Isonitriles Ligating Electron-rich Metal Centres; *X*-Ray Structure of *trans*-$[Mo(CNMe)_2(Ph_2PCH_2CH_2PPh_2)]$

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Summary The compounds *trans*-$[M(CNR)_2(dpe)_2]$ (M = Mo or W; R = Me, Bu^t or aryl; dpe = $Ph_2PCH_2CH_2PPh_2$) have been prepared, and they can be protonated at one or both nitrogen atoms giving carbyne-like ligands, but alkylated at only one; *X*-ray structure analysis shows that the CNMe angle in *trans*-$[Mo(CNMe)_2(dpe)_2]$ is 156(1)°.

The co-ordination of isonitriles to transition metals in their normal or higher oxidation states results in electron drift from the isonitrile, causing a rise of ν(NC) relative to the free isonitrile and in some cases susceptibility to nucleophilic attack at carbon.[1] Metals in low oxidation states reverse the electron drift and cause a lowering of ν(NC) but the electrophilic attack at the ligating isonitrile has not apparently been reported.

We have now examined the case of isonitriles attached to the electron-rich site, $M(dpe)_2$ [equation (1)] and find that the build up of charge on the isonitrile gives it some carbyne-like' character, promoting ready electrophilic attack at its nitrogen atom, and causes the greatest observed decrease in ν(NC) for terminal isonitrile ligands in uncharged complexes {*e.g.*, 281 cm^{-1} for *trans*-$[Mo(MeNC)_2(dpe)_2]$ (A) in tetrahydrofuran solution}.

$$trans\text{-}[M(N_2)_2(dpe)_2] + 2\ RNC \xrightarrow{THF} trans\text{-}[M(CNR)_2(dpe)_2] + 2N_2 \qquad (1)$$

($M{=}Mo$ or W; $dpe{=}Ph_2PCH_2CH_2PPh_2$; $R{=}Me,Bu^t$, or aryl)

An *X*-ray analysis of (A), based on 3579 diffractometer intensities (R = 0·06), gives the results displayed in the

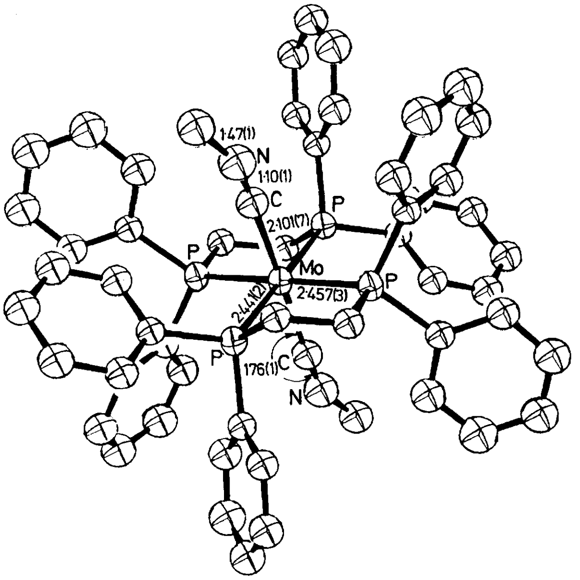

Figure. The structure of *trans*-$[Mo(MeNC)_2(dpe)_2]$ (A). Crystals of (A) are triclinic, with one molecule in a cell of dimensions a = 10·747, b = 10·555, c = 12·565 Å, α = 72·37, β = 87·78, γ = 61·80°, space group $P\bar{1}$.

Figure. Crystallographic C_i symmetry is imposed on each molecule of (A).

The Mo–C bond length [2·101(7) Å] is larger than in [$\mathrm{Mo(CO)_4(Ph_2PCH_2PPh_2)}$] (2·04 Å),[2] the difference being similar to that between corresponding distances in [Mo-(π-$\mathrm{C_5H_5}$)I$\mathrm{(CO)_2}$(CNPh)],[3] suggesting that although isonitrile is a strong back-acceptor in our compounds, carbon monoxide would be more effective.

The most notable feature of the structure is that the CNMe angle is only 156(1)°, much smaller than the *ca.* 180° usually found in terminal isonitrile compounds[4] except perhaps in *cis*-[$\mathrm{Fe(CN)_2(CNMe)_4}$],$\mathrm{4CHCl_3}$ [$\angle$ CNMe = 156(7)°], where accurate dimensions were unobtainable. This unusual bending may be steric in origin, but an electronic effect is strongly suggested by the following observations. (a) Throughout the series of bisisonitrile complexes the lowering of ν(NC) in the spectra of the solids is very large (Mo, 281—221 $\mathrm{cm^{-1}}$; W, 331—231 $\mathrm{cm^{-1}}$) and remains the same to within $\pm$ 8 $\mathrm{cm^{-1}}$ for each complex on its dissolution in tetrahydrofuran. (b) The compounds protonate readily at their nitrogen atoms.

The protonation [equation (2)] gives the grouping M$=\!\!=$C$=\!\!=$N(H)R containing a carbyne-like ligand.[6] This type of ligand, obtained by a more complicated series of reactions, has also been reported by Fischer and his co-workers.[7]

$$\textit{trans}\text{-}[\mathrm{M(MeNC)_2(dpe)_2}] + \mathrm{2HBF_4} \xrightarrow{\mathrm{CH_2Cl_2}} \underset{\text{(B)}}{[\mathrm{M\{CN(H)Me\}_2(dpe)_2}][\mathrm{BF_4}]_2} \qquad (2)$$

Compound (B, M = Mo) is pink, a 1:2 electrolyte in nitromethane, has ν(NH) at 3410 $\mathrm{cm^{-1}}$ [ν(ND) 2515 $\mathrm{cm^{-1}}$], and has a band at 1643 $\mathrm{cm^{-1}}$ [mainly ν(NC)]. The quartet N–H [δ 4·73, ^3J(HCNH) 4·6 Hz] and doublet N–Me [δ 2·2, ^3J(HNCH) 4·6 Hz] n.m.r. signals (relative to $\mathrm{Me_4Si}$ in $\mathrm{CD_2Cl_2}$ solution at −20 °C) simplify to singlets on decoupling. $\mathrm{D_2O}$ causes the N–H resonance to disappear and the N–Me resonance to collapse to a sharp singlet. A tungsten analogue has been prepared [ν(NH) at 3410 $\mathrm{cm^{-1}}$ and ν(NC) at 1633 $\mathrm{cm^{-1}}$].

Mono-protonation or -alkylation can also occur at nitrogen giving respectively, for example, [W{CN(H)Me}(MeNC)$\mathrm{(dpe)_2}$][$\mathrm{BF_4}$] (C) [green, ν(NH) 3310 $\mathrm{cm^{-1}}$, ν(N$\equiv$C) 2155 $\mathrm{cm^{-1}}$, ν(N$=\!\!=$C) 1520 $\mathrm{cm^{-1}}$, δ(NH) 4·18] or [W-($\mathrm{CNMe_2}$)(MeNC)$\mathrm{(dpe)_2}$][$\mathrm{SO_3F}$] (D) [green, ν(N$\equiv$C) 2168 $\mathrm{cm^{-1}}$, ν(N$=\!\!=$C) 1553 $\mathrm{cm^{-1}}$] (from $\mathrm{MeSO_3F}$). These compounds appear to be labile in solution; thus (C) gives the hydride [$\mathrm{WH(MeNC)_2(dpe)_2}$][$\mathrm{BF_4}$][yellow, ν(N$\equiv$C) 2010 $\mathrm{cm^{-1}}$, ν(W–H) 1938 $\mathrm{cm^{-1}}$, δ(W–H) 15·5] whilst (D) transforms into [W{C(Me)=NMe}(MeNC)$\mathrm{(dpe)_2}$][$\mathrm{SO_3F}$] [brown, ν(NC) 2030 $\mathrm{cm^{-1}}$, ν(N=C) 1545 $\mathrm{cm^{-1}}$]. The molybdenum analogues have also been prepared.

The compounds described above are the first isolable products of protonation or alkylation. Some of them undergo protonation or rearrangements giving a variety of other products which will be described elsewhere.

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