Reactions of Phosphonitrilic Derivatives with Metal Carbonyls

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MOLYBDENUM HEXACARBONYL reacts almost quantitatively with both octamethyl tetraphosphonitrile[1] and with its methiodide[2] $(N_4P_4Me_9)^+I^-$. The product from the first reaction is a yellow solid $N_4P_4Me_8,Mo(CO)_4$, which is stable in air, but in solution is sensitive to atmospheric oxygen. Its infrared spectrum (in Nujol) exhibits four bands in the carbonyl stretching region, as expected for C_{2v} symmetry, the phosphonitrile occupying two *cis*-positions of the molybdebum octahedron. On the basis of their positions and relative intensities,[3] the carbonyl bands are assigned as: (1) Vibrations corresponding chiefly to movement of the *trans*-CO groups, at 1995 cm.$^{-1}$, (weak), A_1; 1904 cm.$^{-1}$, (strong), B_1; (2) vibrations of the *cis*-CO groups, at 1780 cm.$^{-1}$, (strong), A_1; 1760 cm.$^{-1}$, (strong), B_2. The principal change in the phosphonitrilic part of the spectrum is the separation of the broad band centred at 1220 cm.$^{-1}$ in the parent molecule[1] into three bands, of lower average frequency, at 1146, 1165, and 1225 cm.$^{-1}$, consistent with the D_{2d} symmetry which the molecule approaches in the crystal.[4] It seems most likely that the phosphonitrile is co-ordinated, without major structural change, through two nitrogen atoms at opposite ends of the molecule. The stretching frequencies of the *cis*-carbonyl groups are especially low as compared with (*e.g.*) those[3] (1864, 1818 cm.$^{-1}$) for

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the corresponding compound Mo(en)$(CO)_4$ of the stronger base ethylenediamine [$C_2H_4(NH_2)_2$, pK_a = 10·09; $N_4P_4Me_8$, pK_a = 5·75]. Inspection of molecular models suggests that co-ordination is more likely to occur through $p\pi$-orbitals at nitrogen than through the conventional lone-pair directions, and it is possible that the low frequencies are a result of greater charge transfer from the less electronegative orbitals. Further structural studies are in progress. The phosphonitrilium salt, by contrast, displaces one molecule of carbon monoxide from $Mo(CO)_6$ or $Cr(CO)_6$, the products being formulated as $(N_4P_4Me_9)^+[(Mo,Cr)\,(CO)_5I]^-$, on the basis of their infrared spectra.

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