Phosphonitrilic Derivatives. Part XXI.[1] Complexes with Metal Carbonyls

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Octamethylcyclotetraphosphonitrile and decamethylcyclopentaphosphonitrile react with the hexacarbonyls of molybdenum and tungsten to give tricarbonyls $L,M(CO)_3$, co-ordination of the ligand occurring most probably through its nitrogen atoms. The octadimethylamido-derivative $N_4P_4(NMe_2)_8$ forms a tetracarbonyl $L,W(CO)_4$. The quaternary iodide $N_4P_4Me_9I$ reacts with $M(CO)_6$ (M = Cr or Mo) to give the salts $[N_4P_4Me_9]^+$ $[M(CO)_5I]^+$, in which ^1H n.m.r. and i.r. spectra indicate donor–acceptor interaction between the ions.

THERE have been several investigations [2] of the interaction of cyclophosphonitriles with metal ions, and, for those compounds of which the crystal structures are known,[2e,2f,3] co-ordination through the nitrogen atoms of the ring has been established. We now report the formation of complexes from $N_4P_4Me_8$, $N_5P_5Me_{10}$, and $N_4P_4(NMe_2)_8$ with $Mo(CO)_6$ and $W(CO)_6$, and of salts from the quaternary iodide $N_4P_4Me_9I$ with $Cr(CO)_6$ and $Mo(CO)_6$.

The reaction of $N_4P_4Me_8$ with $Mo(CO)_6$ in the solid state at 160° yields a yellow solid $N_4P_4Me_8,Mo(CO)_3$, earlier reported [4] erroneously as the tetracarbonyl. The pentameric methyl derivative $N_5P_5Me_{10}$ gives $N_5P_5Me_{10},Mo(CO)_3$, the corresponding compounds $N_4P_4Me_8,W(CO)_3$ and $N_5P_5Me_{10},W(CO)_3$ being obtained from hexacarbonyl tungsten. The tetrameric dimethylamide $N_4P_4(NMe_2)_8$, either in solution or in the solid state, gives yellow $N_4P_4(NMe_2)_8,W(CO)_4$, which can be recrystallized from diethyl ether. The quaternary iodide $N_4P_4Me_9I$ also reacts with $Cr(CO)_6$, $Mo(CO)_6$, but the phosphonitrile does not act as a ligand. The reaction is analogous to that of *N*-methylpyridinium iodide with $Mo(CO)_6$,[5] and of the tetra-alkylammonium halides with chromium, molybdenum, and tungsten carbonyls,[6] and the yellow crystalline ionic compounds $N_4P_4Me_9^+$ $M(CO)_5I^-$ (M = Cr or Mo) are obtained quantitatively when $N_4P_4Me_9I$ is heated with the carbonyls.

Compounds containing the *cis*-tricarbonyl group show two C–O stretching bands ($A + E$) if the ligand symmetry is high enough; if not, the degenerate band may be broadened, as it is in (dien)(Mo,W)$(CO)_3$,[7] or split, as it is in $L,M(CO)_3$ (L = cycloheptatriene,[8] cyclo-octatetraene,[9] M = Cr or Mo). The frequencies of the C–O stretching modes are given in the Table. All the compounds $(NPMe_2)_n,M(CO)_3$ ($n = 4, 5$; M = Mo, W) show a band at 1880—1910 cm^{-1}, and a pair centred at 1735—1770 cm^{-1}. Either the degeneracy is lifted by the low symmetry of the ligand, or the complex is of the *trans*-type. The numerical values are similar to those of the strong bands in the complex $(py)_3Mo(CO)_3$ (1888, 1746 cm^{-1}) [7] and in (dien)$Mo(CO)_3$ (1883, 1723 cm^{-1}),[7] and quite different from those of the olefin complexes [$C_7H_8Mo(CO)_3$,[8] 2000, 1925, 1895; $C_8H_8Mo(CO)_3$,[9] 2006, 1945, 1916 cm^{-1}] or the phosphine complexes $(F_3P)_3Mo(CO)_3$, (2090, 2055 cm^{-1}) [10] or $(Me_3P)_3Mo(CO)_3$ (1945, 1854 cm^{-1}),[11] in all of which the carbonyl bonds are strengthened, to different extents, by interaction of the metal *d*-orbitals with acceptor orbitals of the ligands. Co-ordination of the phosphonitrile to the metal apparently involves six electrons, as for the olefins, but on the evidence of the numerical values of the frequencies, is nevertheless believed to occur by σ-donation from the nitrogen atoms of the ring. A detailed structure determination would be of great interest, especially to find out if the compounds are truly mono-nuclear, because *cis*-co-ordination is not possible for the $N_4P_4Me_8$ molecule in the form of known crystal structure,[12] and, even if the ring had the crown conformation,[13] normal bond angles could be retained only if co-ordination took place through *p*π-orbitals at nitrogen, rather than the conventional

Carbonyl stretching frequencies [a]

Compound	Frequencies (cm^{-1})
$N_4P_4Me_8,Mo(CO)_3$	1906, 1778, 1755br [b]
$N_4P_4Me_8,W(CO)_3$	1899, 1770, 1742
$N_5P_5Me_{10},Mo(CO)_3$	1898, 1758, 1742
$N_5P_5Me_{10},W(CO)_3$	1883, 1740, 1730
$N_4P_4(NMe_2)_8,W(CO)_4$	1994, 1858, 1838, 1809
	2000, 1870, 1849, 1809 [c]
$N_4P_4Me_9Cr(CO_5)I$	2052, 1972, 1923, 1866 [c]
	2051, 1966, 1875 [d]
$N_4P_4Me_9Mo(CO)_5I$	2060, 1978, 1930, 1860 [c]
	2063, 1973, 1847 [d]

[a] Infrared, Nujol mulls, unless otherwise stated. [b] Additional sharp band at 1914 cm^{-1}, possibly due to splitting in solid state. [c] Chloroform solution. [d] Raman spectrum, solid.

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lone-pair directions. The complex $N_4P_4(NMe_2)_8,W(CO)_4$ is more stable. It shows four bands in the carbonyl stretching region, the frequencies suggesting a similarity with (en)$W(CO)_4$ (2006, 1867, 1852, 1809 cm^{-1})[14] rather than $[C_2H_4(PPh_2)_2]W(CO)_4$ (2016, 1912, 1901, 1876 cm^{-1})[15] or $C_8H_8,Mo(CO)_4$ (2049, 1969, 1959, 1902 cm^{-1}).[16]

To a first approximation the products of the interaction of the hexacarbonyls with nonamethyltetraphosphonitrilium iodide are similar to those with *N*-methylpyridinium iodide[5] and tetra-alkylammonium halides.[6] In $C_5H_5NMe^+Cr(CO)_5I^-$ (2049, 1859, 1923 cm^{-1}) and in $Et_4N^+Cr(CO)_5I^-$ (2055, 1871, 1914 cm^{-1}) the anion shows the three $(2A_1 + E)$ i.r. bands characteristic of C_{4v} symmetry, and the same is true of the analogous molybdenum compounds. These bands are present, at similar frequencies, in the spectra of the phosphonitrilic derivatives, but they are accompanied by a fourth band, at 1972 cm^{-1} (Cr) or 1978 cm^{-1} (Mo), which, by reason of its Raman activity, is assigned to the B_1 carbonyl stretching mode. Its i.r. activity is evidently due to a reduction in symmetry such as occurs in (py)$Mo(CO)_5$[14] for which the pattern of frequencies (allowance being made for the effect of the anionic charge) is very similar. In the present compounds, the i.r. activity of the B_1 band could arise from an off-axis displacement of the iodine atom.

There is further evidence of the donor–acceptor interactions beteeen the anion and cation which could cause such a distortion. In the ^1H n.m.r. spectrum of $[C_5H_5NMe]^+[Mo(CO)_5I]^-$, some bands are shifted relative to those of the simple iodide,[17] that of the methyl protons moving upfield by 0·05 p.p.m. from τ 5·33. In $N_4P_4Me_9I$ [and $N_4P_4Me_9Mo(CO)_5I$] the methyl resonances of the *N*-methyl group and the increasingly remote pairs of PMe_2 groups are (τ): 6·86 (7·01); 7·95 (8·05); 8·45 (8·47), both determined in $CDCl_3$, internal Me_4Si. For the analogous chromium compound the results are almost identical. The upfield shift is greatest at the quaternary centre, presumably because of its formal positive charge, and the results suggest that (1) donor–acceptor interaction occurs primarily at the quaternary centre, (2) $Mo(CO)_5I^-$ is a better donor than I^-, and (3) $N_4P_4Me_9^+$ is a better acceptor than $C_5H_5NCH_3^+$. A much bigger effect is found if the spectra of the carbonylates are determined in benzene, in which the shifts are (Mo, τ): 8·07, 8·96, 9·13 (external Me_4Si). Benzene may act as a donor through its π-system, or may promote ion association through its low dielectric constant; whether the π-system of the phosphonitrile is involved, other than in π-inductive interactions within the ring,[18,19] is not yet known.

EXPERIMENTAL

Octadimethylamidocyclotetraphosphonitrile was prepared by the reaction of dimethylamine with the octachloro-compound, and octamethylcyclotetraphosphonitrile and decamethylcyclopentaphosphonitrile from the fluorides and methyl-lithium;[18] further reaction of the octamethyl compound with methyl iodide gave the quaternary salt $N_4P_4Me_9I$.[20] Solvents were distilled from lithium aluminium hydride and degassed. N.m.r. spectra were obtained on a Varian HA100 instrument, Raman spectra on a Cary 81 spectrophotometer equipped with a Spectra-Physics helium-neon laser source, and i.r. spectra on a Perkin-Elmer 457 spectrophotometer.

Reaction of Octamethylcyclotetraphosphonitrile with Tungsten Hexacarbonyl.—Octamethylcyclotetraphosphonitrile (0·198 g, 0·66 mmol) and an excess of tungsten hexacarbonyl (0·38 g, 1·08 mmol) were heated together in a nitrogen atmosphere in a tube connected to a gas burette. Evolution of carbon monoxide began at 150°; the reaction mixture was subsequently kept at 160°. The tungsten carbonyl that sublimed out of the reaction mixture was returned periodically, and the reaction was continued until no further carbon monoxide was released (total 1·79 mmol, 90% of theory for tricarbonyl). The excess of tungsten hexacarbonyl was sublimed out at 100°/0·005 Torr, leaving $N_4P_4Me_8,W(CO)_3$ as a yellow powder (Found: C, 23·3; H, 4·1; N, 9·9. $C_{11}H_{24}N_4O_3P_4W$ requires C, 23·3; H, 4·2; N, 9·9%). Similar reactions yielded $N_4P_4Me_8,Mo(CO)_3$ (Found: C, 27·1; H, 5·1; N, 11·9. $C_{11}H_{24}MoN_4O_3P_4$ requires C, 27·5; H, 5·0; N, 11·7%), $N_5P_5Me_{10},Mo(CO)_3$ (Found: C, 27·9; H, 5·6; N, 13·1. $C_{13}H_{30}MoN_5O_3P_5$ requires C, 28·1; H, 5·4; N, 12·6%), $N_5P_5Me_{10}W(CO)_3$ (Found: C, 24·4; H, 4·9; N, 10·8. $C_{13}H_{30}N_5O_3P_5W$ requires C, 24·3; H, 4·7; N, 10·9%). None of the compounds was stable to potential solvents, decomposition being apparently least rapid in acetone.

Reaction of Octadimethylamidocyclotetraphosphonitrile with Tungsten Hexacarbonyl.—Octadimethylamidocyclotetraphosphonitrile (0·258 g, 0·48 mmol) and tungsten hexacarbonyl (0·183 g, 0·52 mmol) were heated under reflux in light petroleum (60—70°) for 60 h, with precipitation of a yellow solid. The solvent was decanted, and the product washed with 2 × 50 ml light petroleum. The excess of tungsten carbonyl was sublimed out at 70°/0·005 Torr, and the yellow product was recrystallized from diethyl ether (Found: C, 28·9; H, 5·8; N, 20·1. $C_{20}H_{48}N_{12}O_4P_4W$ requires C, 29·0; H, 5·8; N, 20·3%). A similar product was obtained from hexacarbonylmolybdenum, and the pattern of its four infrared bands in the carbonyl stretching region was almost identical to that of the tungsten compound. Its analysis was less good, and in general, the tungsten compounds appear to be the more stable.

Reaction of Nonamethylcyclotetraphosphonitrilium Iodide with Chromium Hexacarbonyl.—The quaternary iodide (0·804 g, 1·82 mmol) was added to chromium hexacarbonyl (0·657 g, 2·99 mmol) in a tube attached to a gas burette, degassed, and flooded with nitrogen. The reaction began at 140°, and took place mostly in the range 145—150°. The carbonyl which sublimed through the product was

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periodically returned, until the evolution of carbon monoxide had ceased. The excess was then removed at 50°/0·001 Torr, and the whole product (1·10 g, 96%) was recrystallized as yellow needles from diethyl ether (Found: C, 26·7; H, 4·2; I, 20·0; N, 8·6; P, 19·2. $C_{14}H_{27}CrIN_4O_5P_4$ requires C, 26·5; H, 4·3; I, 20·0; N, 8·8; P, 19·5%). The same compound was prepared by heating the components together in benzene under reflux, and the corresponding bright yellow molybdenum complex $N_4P_4Me_9Mo(CO)_5I$ was also obtained by both methods (Found: C, 25·0; H, 4·1; I, 18·7; N, 8·5; P, 18·3. $C_{14}H_{27}MoIN_4O_5P_4$ requires C, 24·8; H, 4·0; I, 18·7; N, 8·3; P, 18·3%).

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