New Phosphite Complexes of the Platinum Metals

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ALTHOUGH the chemistry of platinum-metal–phosphine complexes has been extensively studied, relatively little work has been reported on the corresponding phosphite derivatives. The paucity of data on such complexes may be partly due to difficulties of synthesis and isolation. Most previously reported syntheses involve displacement of carbon monoxide from metal carbonyl complexes to yield mixed carbonyl–phosphite derivatives.[1] As part of a study of phosphorus donor-ligands, we have now isolated simple phosphite complexes of ruthenium, osmium, rhodium, and iridium, in excellent yields, by ligand-exchange reactions. A related reaction has previously been reported[2] for the preparation of platinum(0)–phosphite complexes.

Treatment of the complexes $MX_2(PPh_3)_4$, (M = Ru, Os; X = Cl, Br) with excess phosphite $P(OR)_3$ (R = aryl), in warm n-hexane suspension leads to rapid formation of the white crystalline phosphite complexes $MX_2[P(OR)_3]_4$. These compounds, the first simple phosphite derivatives of ruthenium and osmium halides to be reported, are readily soluble in organic solvents and melt sharply without decomposition.

The compounds $M'H(CO)(PPh_3)_3$, (M' = Rh, Ir) rapidly lose triphenylphosphine, carbon monoxide, and hydrogen on reaction with triaryl phosphites in refluxing n-alkanes to yield a variety of phosphite complexes, depending on the conditions employed. From these we have isolated and characterised the complexes $\{M'[P(OR)_3]_4\}_2$ as low-melting, crystalline, white solids. These compounds are formulated as dimeric metal–metal bonded species on the evidence of their diamagnetism, and the absence of hydride ligands. An analogous structure has recently been postulated[3] for the diamagnetic cobalt(0)–phosphite complex $\{Co[P(OEt)_3]_4\}_2$. Trialkyl phosphites undergo similar reactions, however the extremely high solubility of the products formed renders their isolation difficult.

Molecular weight data (osmometric, benzene, 37°) indicate that the rhodium(0) and iridium(0) complexes are extensively dissociated in solution (calc. for $\{Rh[P(OPh)_3]_4\}_2$ $M = 2686$; found 675). N.m.r. studies reveal no appreciable concentration of paramagnetic, monomeric, species in solutions of these complexes. The low molecular weight results are therefore attributed to ligand-dissociation processes and not to metal–metal bond cleavage. Similar, extensive ligand dissociation has been reported,[3] for the related cobalt(0)–phosphite complex mentioned above and other examples of this phenomenon involving phosphorus donor-ligands are well documented.

The observed removal of co-ordinated hydride from several complexes on reaction with phosphites prompted attempts to synthesize new complexes containing phosphite and hydride ligands co-ordinated to the same metal atom. The complex $IrCl(CO)(PPh_3)_2$ reacts with phosphites in n-hexane to give excellent yields of $IrHCl_2(CO)(PPh_3)_2$, no exchange of phosphine being observed. However, the cyclo-octa-1,5-diene complex $[IrCl(C_8H_{12})]_2$ reacts under similar conditions to yield the complex $IrHCl_2[P(OPh)_3]_3$, (ν_{Ir-H} 2180 cm.$^{-1}$) in excellent yield as a stable, white, crystalline solid.

These ligand exchange reactions are being extended to other metal–phosphine complexes *e.g.* $ReH_7(PPh_3)_2$ and to other phosphorus donor ligands.

(*Received, March 14th*, 1968; *Com.* 318.)

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[1] For typical examples see, L. Vallarino, *J. Chem. Soc.*, 1957, 2473; F. Zingales, F. Canziani, and U. Sartorelli, *Rend. Ist. Lombardo Sci. Lettere* (*A*), 1962, **96**, 771; W. Hieber and V. Frey, *Chem. Ber.*, 1966, **99**, 2697; L. A. W. Hales and R. J. Irving, *J. Chem. Soc.* (*A*), 1967, 1932.

[2] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

[3] M. E. Vol'pin and I. S. Kolomnikov, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.* 1966. 2041.