

## "Mixed" Nitrogen-Phosphorus Polydentate Ligands and their Hexacarbonylmolybdenum Derivatives

By GERARD R. DOBSON, R. CRAIG TAYLOR, and THOMAS D. WALSH

(Department of Chemistry, University of Georgia, Athens, Georgia)

ALTHOUGH polydentate ligands containing Group VA and Group VIA donor atoms have received considerable attention in the past few years, relatively little interest has been shown, until recently, in "mixed" polydentate ligands—those containing two different donor atoms—and their transition-metal complexes. Recently Fritz, Venanzi, and their co-workers<sup>1</sup> have reported Pt and Pd halide derivatives in which the nitrogen and phosphorus donor atoms occupy *ortho*-positions on a phenylene ring. A few other mixed nitrogen-phosphorus polydentate ligands have also been reported, although their transition-metal complexes have been little studied.<sup>2-5</sup> We have employed a preparative method of Mann and Millar<sup>2</sup> to synthesise three ethylene-bridged "mixed" ligands, Ph<sub>2</sub>PC<sub>2</sub>H<sub>4</sub>NEt<sub>2</sub> (NP), previously prepared through another route,<sup>5</sup> PhP(C<sub>2</sub>H<sub>4</sub>NEt<sub>2</sub>)<sub>2</sub> (NPN), and (Ph<sub>2</sub>PC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NEt (PNP), and have investigated their hexacarbonylmolybdenum derivatives.

The ligands were prepared through reaction of phenylphosphorus Grignard reagents with the appropriate 2-bromoethylethylamines. NP and NPN are colourless liquids, b.p. 140–143°/0.05 mm. and 135–137°/0.03 mm., respectively, while PNP is a white solid, m.p. 43–45°.

The ligands react under nitrogen in refluxing heptane with a stoichiometric amount of Mo(CO)<sub>6</sub> with the stepwise displacement of carbonyls to yield yellow complexes Mo(CO)<sub>4</sub>(NP) ( $\nu_{CO}$  in

CHCl<sub>3</sub>: 2019m, 1905s, 1893s and 1949s cm.<sup>-1</sup>); Mo(CO)<sub>4</sub>(NPN) ( $\nu_{CO}$  in ethyl ether: 2017m, 1905s, 1890s, and 1862s); and Mo(CO)<sub>3</sub>(PNP) ( $\nu_{CO}$  in CHCl<sub>3</sub>: 1932s, 1834s, and 1804s). For each ligand, the carbonyls were displaced successively by each phosphorus, and then by a single nitrogen, as determined by comparison of CO stretching spectra for the reaction mixtures to those of the "model" derivatives, Ph<sub>3</sub>PMo(CO)<sub>5</sub>,<sup>6</sup> (diphos)Mo(CO)<sub>4</sub>,<sup>7,8</sup> Et<sub>3</sub>NMo(CO)<sub>5</sub>,<sup>9</sup> and (teen)Mo(CO)<sub>4</sub>.<sup>7,10</sup> Evidence thus supports a superior bonding ability of phosphorus in these complexes, in keeping with its ability to function as an acceptor of metallic *d<sub>π</sub>*-electrons. The failure of the second amine in NPN to co-ordinate may be attributed to the steric influence of the amine ethyls; although (en)Mo(CO)<sub>4</sub>,<sup>7,11</sup> and (tmen)Mo(CO)<sub>4</sub>,<sup>7,9</sup> are air-stable, (teen)Mo(CO)<sub>4</sub> undergoes decomposition even *in vacuo*, despite the order of increasing basicity for the parent amines, NH<sub>3</sub> < NMe<sub>3</sub> < NEt<sub>3</sub>. The failure of more than one amine to co-ordinate was also noted by Fritz, Venanzi, and their co-workers<sup>1</sup> for the Pt and Pd halide complexes of the phenylene-bridged mixed ligands, and was attributed to deactivation by the phenylene ring. Investigations of the bonding properties of NP, NPN, and PNP with transition-metal halides are in progress.

Satisfactory chemical analyses have been obtained for all of the reported compounds.

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<sup>1</sup> H. P. Fritz, I. R. Gordon, K. E. Schwarzshans, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 5210.

<sup>2</sup> F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 1952, 3039.

<sup>3</sup> F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 1957, 3950.

<sup>4</sup> B. A. Arbuzov, G. M. Vinokurova, and I. A. Perfil'eva, *Doklady Akad. Nauk S.S.S.R.*, 1959, **127**, 1217.

<sup>5</sup> K. Issleib and R. Rieschel, *Chem. Ber.*, 1965, **98**, 2086.

<sup>6</sup> R. Poilblanc and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 1301.

<sup>7</sup> diphos = bis(diphenylphosphino)ethane; teen = NNN'-tetraethylethylenediamine; en = ethylenediamine;

<sup>8</sup> J. Chatt and H. B. Watson, *J. Chem. Soc.*, 1961, 4980.

<sup>9</sup> R. Poilblanc, *Compt. rend.*, 1963, **256**, 4910.

<sup>10</sup> G. R. Dobson, unpublished results.

<sup>11</sup> C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 533.