

A NEW QUADRIDENTATE LIGAND*

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The "umbrella" type of ligand, in which two or three chains containing donor atoms bonded are to an apical donor atom, has been the subject of much recent study. In particular, Venanzi and co-workers¹ have concentrated on ligands possessing relatively rigid chains incorporating the edge of a benzene nucleus, while other workers² have looked at less rigid, usually saturated hydrocarbon, chain systems. The more rigid ligand system has, in particular, been found to readily give five-coordinate trigonal bipyramidal complexes with a large number of transition metal ions.

TABLE I
COMPLEXES OF tpp

Compound	Colour	Analysis (%)				
			C	H	N	M
[MnCl tpp]Cl	golden	Found	49.5	3.5	9.7	12.5
	yellow	Calc.	49.3	4.1	9.6	12.7
[CoCl tpp]ClO ₄	dark	Found	42.8	3.2	8.1	11.9
	blue	Calc.	43.0	3.6	8.4	11.8
[NiCl tpp]Cl	dark	Found	49.8	3.4	9.8	13.4
	green	Calc.	49.8	4.2	9.7	13.4

Although metal complexes of tri(2-pyridyl)amine have been described recently,³ there are no reported compounds derived from "umbrella" ligands, which possess an apical donor atom indirectly bonded to donor nitrogen heterocyclics. The stereochemistry of the above amine precludes the possibility of coordination of all four nitrogen atoms to the one metal ion, and thus the formation of trigonal bipyramidal complexes would not be favoured.

The interaction of dry ethereal solutions of three molecular proportions of *α*-picolyl⁴lithium and one molecular proportion of phosphorus trichloride at -40° leads to the formation of the new quadridentate ligand tris(*α*-picolyl)phosphine (tpp);

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¹ Venanzi, L. M., *Angew. Chem. int. Edn.*, 1964, **3**, 453, and references therein.

² Melson, G. A., and Wilkins, R. G., *J. chem. Soc.*, 1963, 2662, and references therein.

³ McWhinnie, W. R., Kulasingham, G. C., and Draper, J. C., *J. chem. Soc. A*, 1966, 1199.

⁴ Woodward, R. B., and Kornfeld, E. C., *Org. Synth.*, 1955, Coll. Vol. III, 413.

m.p. 115–120° (Found: C, 69.8; H, 6.7; N, 13.9. $C_{18}H_{18}N_3P$ requires C, 70.2; H, 5.9; N, 13.7%). The yields of this reaction have so far been very poor (0–5%), and the melting point range of the white crystals, which were triply recrystallized from ethanol, suggests that the compound was not completely pure. Attempts at purification via the hydrochloride were unsuccessful. Nevertheless, the analytical figures for both the free ligand and the complexes noted in Table 1 are satisfactory.

As $10^{-3}M$ nitromethane solutions of all three compounds have equivalent conductivity values in the range 80.1–85.4 mho, they are all postulated as five-coordinate species. The cobalt and nickel compounds are presumably structurally similar to the corresponding compounds of tris(*o*-diphenylarsinophenyl)arsine,¹ while the manganese compound probably also has a trigonal bipyramidal structure as does the manganese complex of tris(2-dimethylaminoethyl)amine.⁵

⁵ Ciampolini, M., and Nardi, N., *Inorg. Chem.*, 1966, 5, 1150.