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THE SYNTHESIS AND CHARACTERIZATION OF SOME NOVEL POLYDENTATE PHOSPHORUS-NITROGEN LIGANDS

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Polydentate chelating ligands of the Group V elements, particularly nitrogen, phosphorus, and arsenic in various combinations have been extensively studied over the years because of the multitude of ways in which they can bond to metals and because of the varied stereochemistries which they can impose on metal complexes.[1,2,3] Some very recent reports of new ligands show a continued high interest in this area.[4,5]

We report here an adaptation of the Mannich reaction using ethylene diamine or N-methyl substituted ethylene diamines with diphenylphosphine which leads to a new class of N-phosphinomethylethylene diamine compounds simply and in high yield. Previous workers have shown that the Mannich reaction can be applied to phosphorus compounds with an active P-H bond, such as $(RO)_2P(O)H$[6], R_2PH[7], $R_2P(S)H$[8], or H_3PO_3[9]. In the present work for example N,N,N'-trimethylethylene diamine (8.85g, 0.0866 mole) and diphenylphosphine (16.1g, 0.0866 mole) were dissolved in about 50 ml of benzene in a nitrogen atmosphere. Aqueous formalin (35%, 9.60 ml, about 20% excess of the stoichiometric amount) was added with stirring at room temperature. The mixture was then heated to 60°C. The progress of the reaction was monitored by obtaining ^{31}P nmr spectra of aliquots of the reaction mixture at various times. The starting material, $(C_6H_5)_2PH$, produces a sharp doublet (J_{PH}=215 Hz, δ=41 ppm), whereas the product gives a singlet (δ=26.6). The doublet decreases in intensity as the singlet grows during the progress of the reaction. The reaction is essentially complete in 1½ hours at 60°C, and the yield of product, N-diphenylphosphinomethyl-N,N',N'-trimethylethylene diamine, is very good (96%). Similarly prepared were $[(C_6H_5)_2PCH_2]_2NCH_2CH_2N(CH_3)_2$, $(C_6H_5)_2PCH_2N(CH_3)CH_2CH_2N(CH_3)CH_2P(C_6H_5)_2$,

$[(C_6H_5)_2PCH_2]_2NCH_2CH_2N(CH_3)CH_2P(C_6H_5)_2$, and $[(C_6H_5)_2PCH_2]_2NCH_2CH_2N[CH_2P(C_6H_5)_2]_2$. The yields and phosphorus chemical shift data are given in the Table. The compounds were further characterized by elemental analyses, proton nmr, and by the preparation of the corresponding phosphine oxides by reaction of the ligands with aqueous hydrogen peroxide and by the preparation of the sulfides by reaction with sulfur.

The series of compounds includes potential tridentate, tetradentate, pentadentate, and hexadentate ligands. However, since the $N-CH_2-P$ grouping would lead to a strained four membered ring when complexed to a metal it is doubtful that the ligands could use all possible donor sights. This is another reason for the preparation of the phosphine sulfides, which would form less strained five membered rings on complex formation and should be excellent ligands. The coordination chemistry of these compounds is currently being investigated.

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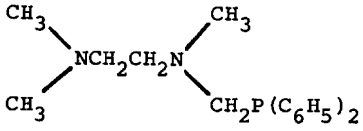
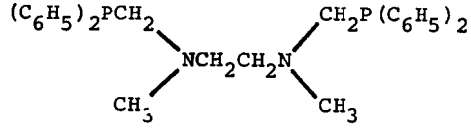
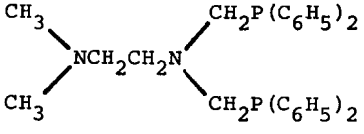
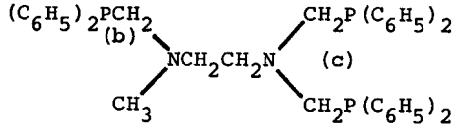
TABLE

Physical Properties of Polydentate Phosphorus-Nitrogen Ligands

Compound	Yield (%)	mp (°C)	δ (ppm)[a]	δ oxide (ppm)[a]	δ sulfide (ppm)[a]
	96	oil	26.6	-28.5	-36.5
	86	79-80	26.9	-27.4	-36.4
	70	oil	27.2	-29.9	-35.2
	75	74-75	26.9 (b) 28.4 (c)	-29.3 (broad)	-35.6 (broad)
$[(C_6H_5)_2PCH_2]_2NCH_2CH_2N[CH_2P(C_6H_5)_2]_2$	95	77-78	28.1	-28.8	-36.7

[a]Phosphorus chemical shift vs. 85% H_3PO_4.