

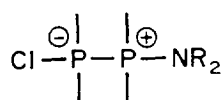
New phosphorus–nitrogen compounds and their transition metal coordination chemistry

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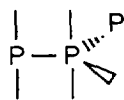
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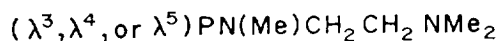
During the past few years a range of new and/or novel types of phosphorus–nitrogen compounds has been synthesized. They have involved, in particular, the following structural elements:



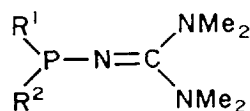
1 [1–3]



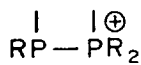
2 [4]



3 [5]

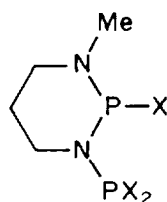


4 [6]



5 [7]

R¹, R²=hydrocarbon groups or
R¹=hydrocarbon group and
R²=tetramethylguanidyl group



6 [8]

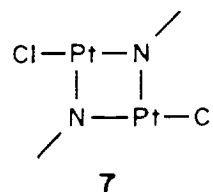
(X=Cl, OMe)

In compounds involving structural elements **1** or **2** the two phosphorus atoms are held together via a *N,N'*-dimethylurea group.

Because of the presence of P^{III} the new compounds offer a rich potential as ligands, and have been found to coordinate to transition metals in low oxidation

states, especially to those of Groups 6, 8 and 9–12 of the Periodic Table [1–3]. The following reactions are typical.

A compound involving structural element **1** (R=Et) was formed, for example with (C₂H₄)Pt(PPh₃)₂, with complete displacement of both ethylene and triphenylphosphine, and the formation of a dimeric Pt^ICl complex containing structural element **7**



7

as a central feature. Compounds containing element **2** are of interest because they contain both λ³P (usually considered as donating) and λ⁵P (normally displaying acceptor properties). Surprisingly, in a series of systems involving element **2** the donor properties of λ³P towards a range of transition metals were found to be almost unimpeded [4].

The *N,N,N'*-trimethylethylenediamine substituent at phosphorus in systems involving element **3**, with λ³P, λ⁴P or λ⁵P, was sometimes observed to undergo spontaneous intramolecular coordination to the phosphorus atom via the nitrogen atom of the terminal NMe₂ group. When that substituent was bonded to λ³P, various modes of coordination towards a range of transition metals, preferably as Group 6 metal carbonyl derivatives, were observed: (i) solely through λ³P; (ii) chelating through λ³P and the nitrogen atom of the NMe₂ group; or (iii) chelating via the two nitrogen atoms only, with λ³P not participating in the coordination [5].

A similar situation pertains to the P (III) tetramethylguanidyl derivatives containing element **4** [6]: as described above, compounds with element **4** may func-

tion as donors solely via $\lambda^3\text{P}$ (e.g. to Fe^0 , Ni^0) or they may act as chelating ligands (e.g. to Mo^0) via $\lambda^3\text{P}$ and the nitrogen atom of an NMe_2 group.

A variety of phosphinophosphonium (λ^3 , $\lambda^4\text{P}^{(+)}$) salts containing element **5** have been synthesized. The donating ability of the $\lambda^3\text{P}$ atom, e.g. towards W^0 , has been demonstrated by the synthesis of $\text{W}(\text{CO})_5$ derivatives [7].

The di(λ^3)phosphorus species with structural element **6** have been found to coordinate to transition metals in a different fashion, depending on the nature of X and of the transition metal. Thus, an $\text{Mo}(\text{CO})_4$ derivative involving two molecules of **6** (X = Cl) was synthesized in which one molecule of **6** was coordinated via the PCl_2 - and the other via the PCl_2 -phosphorus atom. The methoxy derivative (**6**; X = OMe) was found to function as a chelating ligand, coordinated via both phosphorus atoms to either $\text{Mo}(\text{CO})_4$ or to Pt^{2+} (in a 1:1 and a 1:2 molar ratio, respectively) [8].

The identity and structure of the various types of coordination compounds described here have been established from their NMR spectra [^1H , ^{13}C , ^{19}F (where appropriate) and ^{31}P]. In numerous cases, single-crystal X-ray diffraction studies were conducted, which confirmed the structures proposed on the basis of spectroscopic studies.

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