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Organometallic chemistry of diphosphazane ligands

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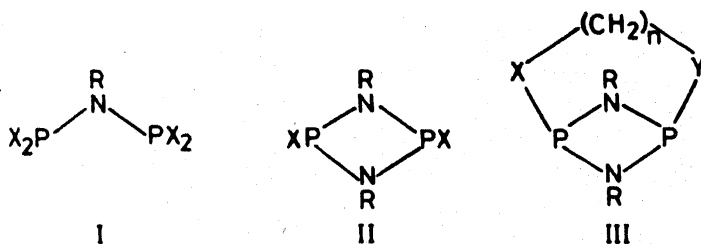
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Abstract. The reactions of a range of acyclic, cyclic and bicyclic diphosphazanes with several transition metal organometallic derivatives have been investigated. The structures of the products have been deduced from IR and NMR spectroscopic data and confirmed by single crystal X-ray analysis of a few representative compounds.

Keywords. Diphosphazane ligands; group 6, iron carbonyl and Pd, Pt and Rh complexes.

1. Introduction

The ubiquitous use of tertiary monophosphines and diphosphines as ligands in transition metal organometallic chemistry is well documented (Pignolet 1983; Puddephatt 1982; Wilkinson 1982). In recent years, interest in the organometallic chemistry of a class of ligands known as diphosphazanes or diphosphinoamines(I) has been growing rapidly (King 1980; Blagg *et al* 1985; Ellermann *et al* 1985; de Leeuw *et al* 1989; Hill *et al* 1989; Mague *et al* 1989; Uson *et al* 1989) since a range of such ligands with different substituents on nitrogen and phosphorus can be readily synthesised from suitable chloro precursors (Keat *et al* 1981; Hill *et al* 1989). Cyclophosphazanes(II) are also readily accessible from the same type of reactions viz. condensation of chlorophosphanes with primary amines or their silylated derivatives) that lead to the acyclic diphosphazanes(I) (Keat 1982, 1987). The coordination chemistry of cyclodiphosphazanes(II) has been investigated only to a limited extent as compared to that of the acyclic diphosphazanes(I) (Burckett St. Laurent *et al* 1983; Scherer *et al* 1984). Bicyclic diphosphazanes(III, R = Bu') were first reported by Keat and Thompson (1977). Recently our group has reported the synthesis of several new bicyclic diphosphazanes(III, R = Ph) and crystallographic studies on two such compounds have revealed a puckering of the P–N ring in a manner opposite to that observed for *cis*-(RNPX)₂ type compounds(II) (Kumaravel *et al* 1988). It would be interesting to investigate the effect of this novel structural feature on the ligating



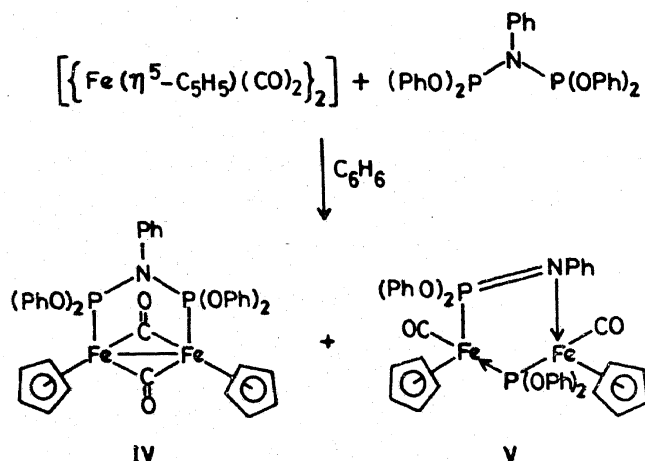
behaviour of III and compare the results with those available for other phosphorus cage compounds (Stricklen *et al* 1983). For the last 4–5 years, we have been interested in the organometallic chemistry of diphosphazanes(I–III) (Balakrishna 1989; Balakrishna *et al* 1989, 1990) and a brief review of recent results is presented in this paper.

2. Reactions of diphosphazanes with group 6 metal- and iron carbonyl derivatives

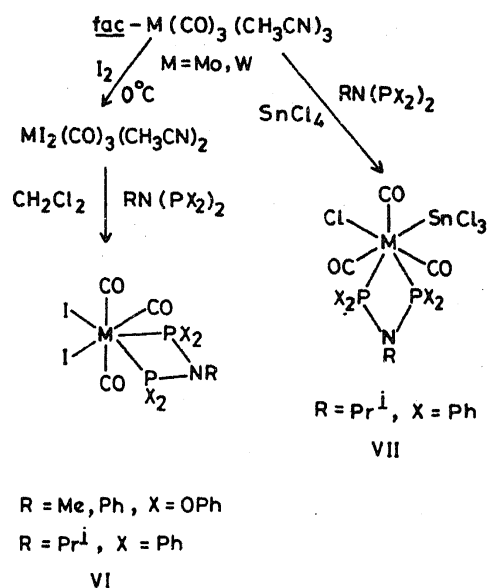
We have earlier reported that the reactions of several diphosphazane ligands (I, R = Me or Ph, X = OCH₂CF₃ or OPh; R = Prⁱ, X = Ph) with metal carbonyl derivatives generally yield monometallic chelate complexes, [M(CO)_n(L₂-PP')] (L₂ = diphosphazane, M = Cr, Mo or W, n = 4; M = Fe, n = 3) (Balakrishna 1989; Balakrishna *et al* 1990). The structures of two such compounds, [M(CO)₄{(Ph₂P)₂NPrⁱ}] and [M(CO)₄{(PhO)₂PN(Ph)P(OPh)₂}] have been confirmed by single crystal X-ray analysis (Balakrishna *et al* 1989a). The mean P–N distance (1.71 Å) in the former complex shows little variation from that of the free ligand (Keat *et al* 1981); however, the P–N–P angle [122.8(3)°] in the ligand (which exists in C_s conformation in the solid state) decreases to 102.9(5)° upon chelate formation.

The reaction of [$\{\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}_2$] with the diphosphazane I (R = Ph, X = OPh) in boiling benzene affords two isomeric complexes IV and V (scheme 1) whose structures have been established from elemental analyses, IR spectra and ³¹P NMR measurements. The formation of V is interesting in that it involves the cleavage of one of the P–N bonds of the ligand to give the fragments (PhO)₂P=NPh and P(OPh)₂, both of which act as bridging ligands between the two iron centres. Such a cleavage of the P–N bond in diphosphazanes has been observed by Brown *et al* (1976) in the reaction of MeN(PF₂)₂ with [$\{\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}_2$].

Seven-coordinated Mo(II) and W(II) complexes of diphosphazanes(I) have been synthesized as shown in scheme 2. The structure of the tungsten complex VI (R = Ph, X = OPh) (determined by single crystal X-ray analysis) reveals a pentagonal bipyramidal geometry around the metal. One CO group, the two iodine and the two phosphorus atoms lie in the basal plane while the other two CO groups occupy the



Scheme 1.



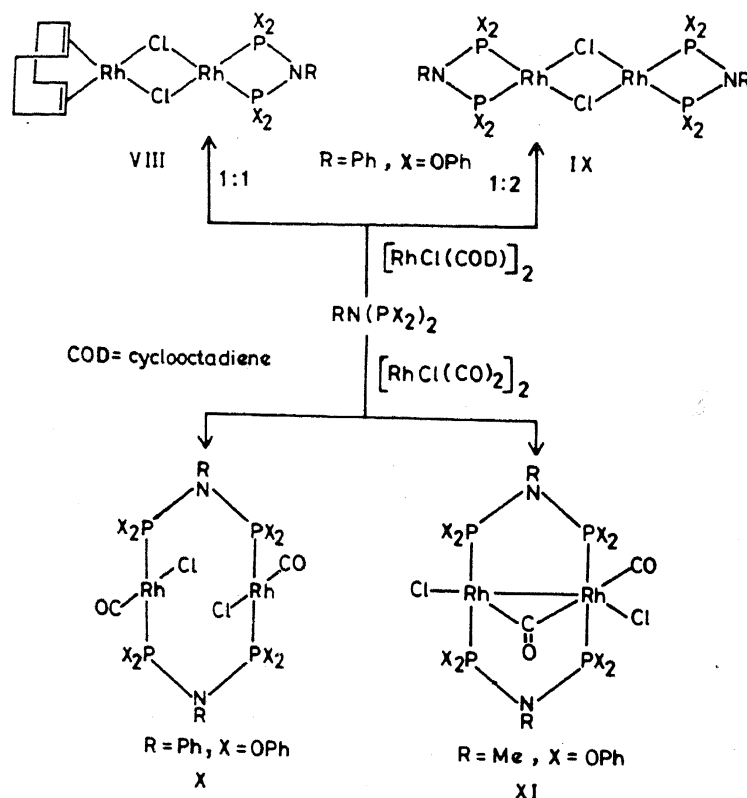
Scheme 2.

apical positions. Seven-coordinated Mo(II) or W(II) complexes of the type $[\text{MX}_2(\text{CO})_3(\text{L-L})](\text{L-L} = \text{diphosphine or two monophosphines})$ usually possess a capped octahedral geometry around the metal centre (Drew 1977; Kepert 1979). Pentagonal bipyramidal geometry is found in only one instance, viz. $[\text{Wl}_2(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ (Foy *et al* 1980), the exceptional behaviour of which as well as that of VI ($\text{M} = \text{W}, \text{R} = \text{Ph}, \text{X} = \text{OPh}$) is due to the small 'bite' of the bidentate phosphine or the phosphazane ligand. Recently there has been an upsurge of interest in 7-coordinated Mo(II) and W(II) complexes containing carbonyl groups and nitrogen or phosphorus donor ligands (Baker and Quinlan 1989).

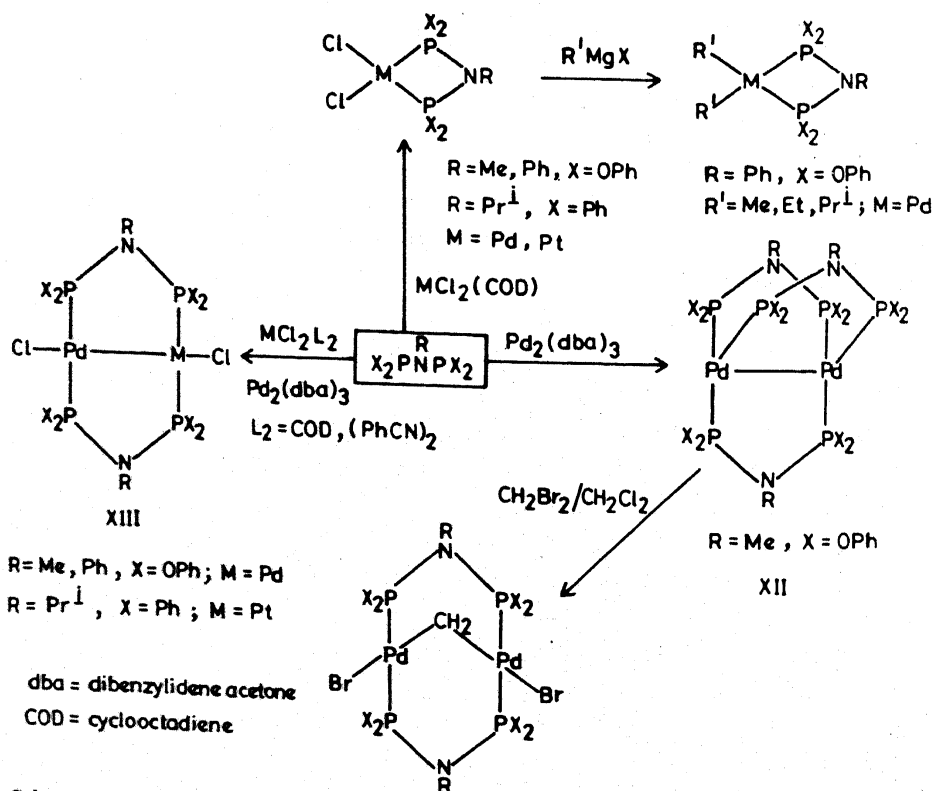
3. Reactions of I with Rh, Pd and Pt derivatives

The reactions of diphosphazanes I ($\text{R} = \text{Me}$ or $\text{Ph}, \text{X} = \text{OPh}$) with $[\text{RhCl}(\text{COD})]_2$ ($\text{COD} = 1,5\text{-cyclooctadiene}$) and $[\text{RhCl}(\text{CO})_2]_2$ lead to the isolation of dinuclear complexes which are shown in scheme 3. The ^{31}P NMR spectra of these complexes clearly show $^{103}\text{Rh}-^{31}\text{P}$ coupling; the $^1J_{\text{RhP}}$ value for the chelate complexes (VIII and IX) is 280 Hz whereas it is 214 Hz for complex X which contains bridging diphosphazane ligands. It has been noted by Haines *et al* (1979, 1981) that subtle changes in the nature of the substituents on the phosphorus atoms of diphosphazane ligands can lead to the formation of one or the other type of complexes X and XI.

Several palladium and platinum complexes of diphosphazanes(I) have been prepared as shown in scheme 4. The structure of complex XII reveals an unusually short Pd-Pd distance of 2.856(3) Å which may be compared with the values of 2.959(2) Å and 3.023(1) Å for the analogous *bis*(diphenylphosphino)methane complexes of palladium and platinum $[\text{M}_2(\text{dppm})_3]$ ($\text{M} = \text{Pd}$ or Pt) respectively (Muir *et al* 1986; Kirss and Eisenberg 1989). The structure of the Pd derivative XIII ($\text{M} = \text{M}' = \text{Pd}, \text{R} = \text{Ph}, \text{X} = \text{OPh}$) has also been determined; the molecule is centrosymmetric and the Cl-Pd-Pd-Cl linear chain lies on the two-fold axis. The Pd-Pd distance of 2.619(1) Å is slightly shorter than that [2.638(6) Å] in the recently



Scheme 3.



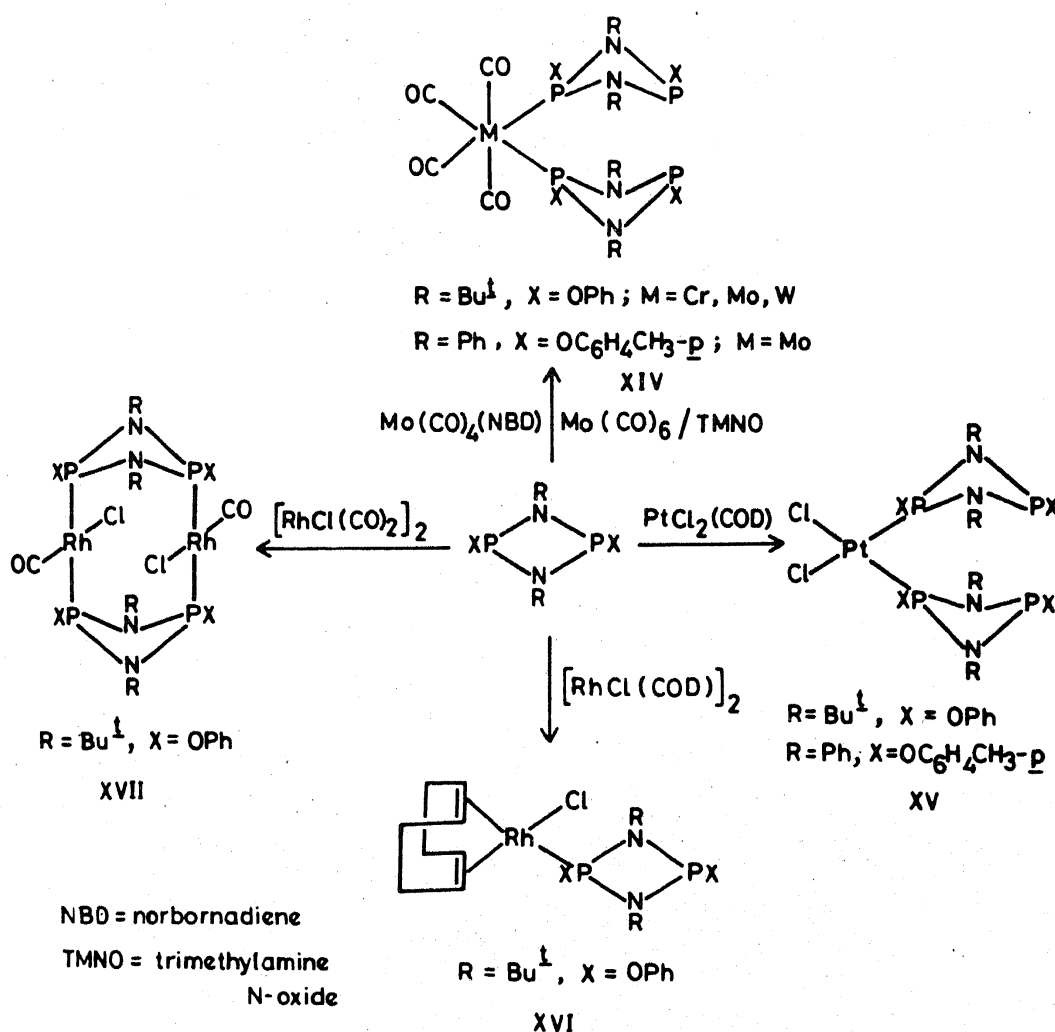
Scheme 4.

reported *bis*(diphenylphosphino)amine (dppa) complex, $[\text{Pd}_2\text{Cl}_2(\text{dppa})_2]$ (Uson *et al* 1989).

4. Organometallics of cyclic(II) and bicyclic(III)diphosphazanes

The reactions of cyclodiphosphazanes (*cis* II, $\text{R} = \text{Bu}^t$, $\text{X} = \text{OPh}$; $\text{R} = \text{Ph}$, $\text{X} = \text{OC}_6\text{H}_4\text{Me-}p$) with group 6 hexacarbonyls or their derivatives yield the tetracarbonyl complexes XIV in which the cyclodiphosphazane behaves as a monodentate ligand. Such monoligated mononuclear complexes (XV) are also obtained from the reactions of II with $[\text{M}(\text{COD})\text{Cl}_2]$ ($\text{M} = \text{Pt}$ or Pd) (scheme 5). However, the reaction of II ($\text{R} = \text{Ph}$, $\text{X} = \text{OCH}_2\text{CF}_3$) (which has a *trans* configuration) with $[\text{Mo}(\text{CO})_4(\text{NHC}_5\text{H}_{10})_2]$ gives the dinuclear complex, $[(\text{CO})_4\text{Mo}(\text{NHC}_5\text{H}_{10})\mu\text{-[PhNP(OCH}_2\text{CF}_3)_2\text{Mo}(\text{CO})_4(\text{NHC}_5\text{H}_{10})]$. (Balakrishna *et al* 1989a; Sreenivasa Reddy and Krishnamurthy 1989).

Treatment of II ($\text{R} = \text{Bu}^t$, $\text{X} = \text{OPh}$) with $[\text{RhCl}(\text{COD})]_2$ and $[\text{RhCl}(\text{CO})_2]_2$ yield the mononuclear and dinuclear complexes XVI and XVII, respectively (scheme 5). The structure proposed for XVII is tentative; a trimeric (Mague *et al* 1989) or a tetrameric (Stricklen *et al* 1983) structure with bridging cyclophosphazane ligands

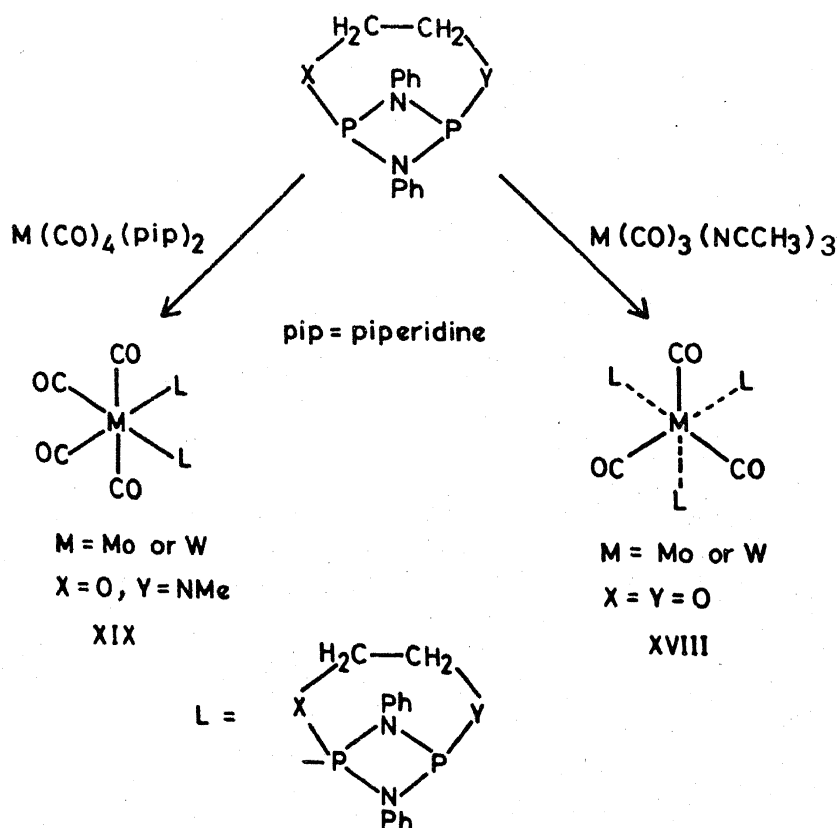


Scheme 5.

would also be consistent with available analytical and spectroscopic data (Balakrishna 1989).

The bicyclic diphosphazane IIIa ($R = \text{Ph}, X = Y = \text{O}, n = 2$) reacts with *fac*- $[\text{M}(\text{CO})_3(\text{MeCN})_3]$ ($M = \text{Mo}$ or W) to afford complexes of the type, *fac*- $[\text{M}(\text{CO})_3\text{L}_3]$ ($L =$ monoligated diphosphazane) (XVIII). On the other hand, reaction of IIIa ($X = Y = \text{O}, n = 2$) with $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ or $[\text{M}(\text{CO})_4(\text{NBD})_2]$ is not clean and the nature of the products could not be ascertained. However, the reaction of IIIb ($X = \text{NMe}, Y = \text{O}, n = 2$) with $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ gives a *cis*-tetracarbonyl complex XIX in which coordination of the diphosphazane through the P-O-phosphorus is more likely (scheme 6) (Prakasha and Krishnamurthy 1989).

The reactions of IIIa ($R = \text{Ph}, X = Y = \text{O}, n = 2$) with platinum and palladium derivatives have yielded interesting results. Whereas treatment of IIIa with $[\text{Pt}(\text{COD})\text{Cl}_2]$ gives an insoluble material, the analogous reaction with the palladium derivative gives a complex of composition $[\text{Cl}_2\text{Pd}(\mu\text{-L})]_n$ ($L =$ diphosphazane). The presence of a bridging diphosphazane is indicated by the ^{31}P chemical shift (69.7δ) for this complex. The reaction of IIIa with $[(\text{Et}_3\text{P})\text{PdCl}_2]_2$ gives a dinuclear complex $[(\text{Cl}_2\text{PdPEt}_3)_2(\mu\text{-L})]$ ($L =$ diphosphazane) in which the two Et_3P groups have *cis-trans* orientation with respect to the bridging diphosphazane ligand; in contrast, the analogous platinum derivative has a *cis-cis* disposition of the PEt_3 groups with respect to the bridging diphosphazane ligand (Nixon 1989, private commun.). A notable feature of the NMR spectra of the Pt complexes (XV) of cyclodiphosphazanes (II) and the Pt complex of the bicyclic diphosphazane (IIIa) referred to above is the



Scheme 6.

surprisingly large $^1J_{\text{P-P}}$ value (4800–5800 Hz) which is 2000 Hz higher than that observed for the PEt_3 groups bonded to platinum.

5. Summary and outlook

The results clearly bring out the versatility and considerable scope of acyclic diphosphazanes(I) as ligands. Pronounced differences in the reactivity pattern and the structures of the resulting products are observed even with minor changes in the nature of the substituents attached to phosphorus and/or nitrogen. Our future studies will be directed towards an understanding of the factors responsible for these differences. Studies with cyclic and bicyclic diphosphazanes also show that they can act as monodentate as well as bridging-bidentate ligands. Some of the complexes isolated may prove valuable synthons for the preparation of bimetallic and high-nuclearity clusters and this aspect merits a detailed investigation. The potential utility of some of the complexes as homogeneous catalysts in organic synthesis is another area which will also engage our attention in the future.

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