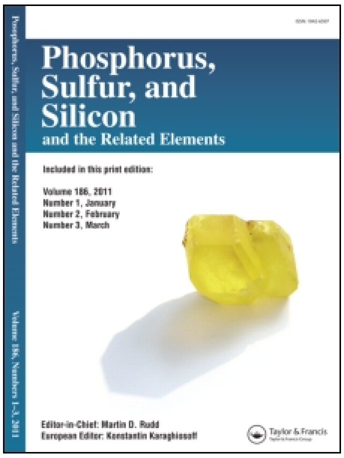

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Diphosphazanes as Ligands: Links Betwen Phospeorus Ceiwistry and Organohetallic Cejmistry

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DIPHOSPHAZANES AS LIGANDS : LINKS BETWEEN PHOSPHORUS CHEMISTRY AND ORGANOMETALLIC CHEMISTRY

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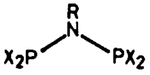
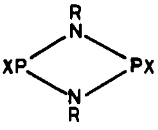
Abstract The reactivity of several new acyclic, cyclic and bicyclic diphosphazanes towards Group-6 metal and iron carbonyls, and Pd, Pt and Rh derivatives has been studied. The structures of the products have been elucidated by IR and NMR spectroscopy and confirmed in a few instances by single crystal X-ray analyses.

INTRODUCTION

Organometallic chemistry of diphosphazane ligands of the type, $X_2PN(R)PX_2$(I) was initiated by Payne et al and Nixon and coworkers[1] and later elaborated by King and coworkers[2]. There is a renewed interest in these systems[3] as it is realised that the substituents on both nitrogen and phosphorus can be varied with attendent changes in the P-N-P bond angle and the conformations around the phosphorus centres[4]. The chemistry of cyclodiphosphazanes(II) related to the acyclic derivatives(I) would be interesting too but it has received sparse attention[5]. During the past few years, we have explored the organometallic chemistry of several new acyclic(I), cyclic(II) and bicyclic(III) diphosphazane ligands.[6] A brief account of our results is presented here.



I



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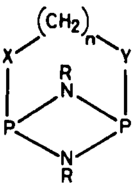
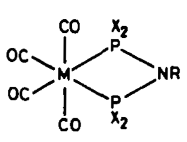


III

REACTIONS OF I WITH METAL CARBONYLS AND THEIR DERIVATIVES

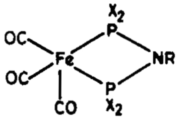
Acyclic diphosphazanes(I) react with Group 6 metal carbonyl derivatives to give chelating *cis*-tetracarbonyl complexes (IV). The structures of two such complexes (M = Mo, R = Ph, X = OPh; M = W, R = $Pr^{\underline{i}}$, X = Ph) have been confirmed by single crystal X-ray analyses. Further replacement of CO has proved difficult except with $(Ph_2P)_2NPr^{\underline{i}}$ which also affords dinuclear compounds in its reactions with *fac*-$M(CO)_3(MeCN)_3$ (M = Mo or W) or $[Mo(CO)_3Cp]_2$ (Cp = η^5-C_5H_5).

Reactions of I with iron pentacarbonyl yield either chelating tricarbonyl complexes V or the dinuclear complex VI depending on the reaction conditions. The reaction of I (R = Ph, X=OPh) with $[Fe(Cp)(CO)_2]_2$ affords the complexes VII and VIII (^{31}P NMR data-VII, δ_P = 175.8; VIII, AB pattern δ_A = 169.4, δ_B = 126.8, $^2J_{AB}$ = 124 Hz.).

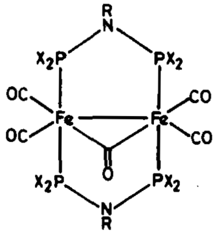


IV

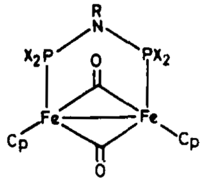
M = Cr, Mo, W



V

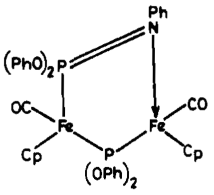


VI

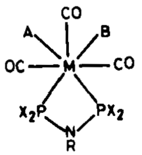


Cp = η^5-C_5H_5

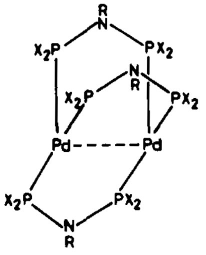
VII



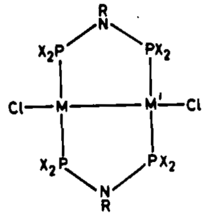
VIII



IX



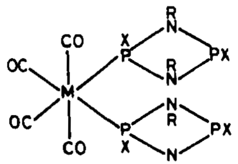
X



M = M'= Pd

M = Pd, M' = Pt

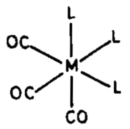
XI



R = $Bu^{\underline{t}}$, X = OPh

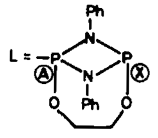
M = Cr, Mo or W

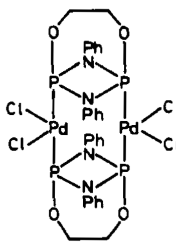
XII



M = Mo, W

XIII





XIV

Seven coordinated diiodo complexes of the type [$M(CO)_3(A)(B)$-($X_2PN(R)PX_2$)](IX,A=B=I) have been isolated from the reaction of [$M(CO)_3I_2(MeCN)_2$] with the diphosphazanes (I). An analogous tricarbonyl(stannyl)(chloro) derivative, (IX,A=$SnCl_3$,B=Cl) has also been prepared. The X-ray crystal structure of the tungsten complex IX (M=W,R=Ph,X=OPh,A=B=I) reveals a near pentagonal bipyramidal geometry around tungsten with a mean P-N distance of 168.0(2) pm and the P-N-P angle 98.1(5)^o.

REACTIONS WITH Pd, Pt AND Rh SPECIES

Reactions of I with [$M(COD)Cl_2$] (COD = 1,5-cyclooctadiene) (M = Pd, Pt) afford the chelate complexes, [$MCl_2((X_2PNRPX_2)$-PP')] which react with Grignard reagents to afford the alkyl derivatives, [$R_2M(NR(PX_2)_2$-PP')]. Treatment of the Pd(0) derivative $Pd_2(dba)_3$ (dba = dibenzylidene acetone) with an excess of I (R=Me,X=OPh) yields the dinuclear Pd(0) complex X; X-ray analysis of X reveals an unusually short metal-metal distance of 285.6(3) pm. When a mixture of Pd(0) and either Pd(II) or Pt(II) derivatives is treated with I, homo or hetero bimetallic complexes (XI) are obtained. The X-ray structural analysis of XI (M = M'= Pd, R = Ph,X = OPh) reveals a Pd-Pd distance of 261.9(4) pm ; other relevant data are: mean P-N distance 168.1(3) pm ; P-N-P angle 113.3(6)^o).

Reactions of I with [$Rh(COD)Cl]_2$ and [$RhCl(CO)_2]_2$ have also been investigated and several dirhodium complexes of the type [$Rh(\mu$-$Cl)(X_2PNRPX_2)]_2$ and [$RhCl(CO)(\mu$-$X_2PNRPX_2)]_2$ have been isolated.

ORGANOMETALLICS OF CYCLIC(II) AND BICYCLIC(III) DIPHOSPHAZANES

Reactions of the cyclodiphosphazanes II (R = Bu^t, X = OPh) with $M(CO)_6$ in the presence of trimethylamine N-oxide give monoligated mononuclear complexes XII. Such monoligated complexes are also isolated from the reaction of II (R=Bu^t, X=OPh) with $MCl_2(COD)$ (M = Pd or Pt) as revealed by ^{31}P NMR data.

The bicyclo diphosphazanes, III (R = Ph, X = Y = O,n=2) can act as a monodentate or a bridging-bidentate ligand as typified by the complexes XIII and XIV respectively. The ^{31}P NMR spectra of XIII are of the $[AX]_n$ type (XIII, M=W, δ_A=167.4,δ_X= 140.8); the spectrum of XIV shows a singlet at δ 69.7 (δ_P for ligand = 172.2).

CONCLUSION

Our results and those of others[1-5] demonstrate the versatility and considerable scope of diphosphazanes as ligands. Fairly small changes in the diphosphazane ligand leads to pronounced changes in the structural features of the resulting complexes. Further studies aimed at unravelling the factors responsible for this versatile behaviour should prove rewarding.

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