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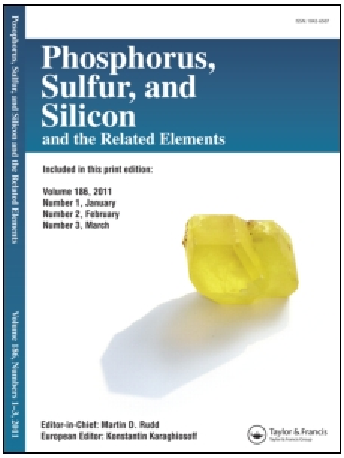

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Phosphorus-Nitrogen Heterocycles as Ligands in Organometallic Chemistry

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PHOSPHORUS-NITROGEN HETEROCYCLES AS LIGANDS IN ORGANOMETALLIC CHEMISTRY

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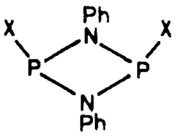
Abstract λ^3-Cyclodiphospha*zanes* of the type $(RNPX)_2$ (R=Ph, X=OC_6H_4-Me-*p* or OCH_2CF_3) react with Group 6 metal carbonyls to yield a variety of complexes depending on the geometrical disposition of the substituents on the phosphorus with respect to the P_2N_2 ring. Coordination occurs through the phosphorus centre(s) in the η^1- or bridged bidentate(μ-) modes. On the other hand (amino)λ^5-cyclotriphospha*zenes* afford Group 6 metal carbonyl complexes in which a phosphazene ring nitrogen atom is involved in coordination besides exocyclic nitrogen atoms. Complexes of Group 10 metal chlorides with cyclotriphosphazene ligands have also been synthesized. NMR spectroscopic and X-ray crystallographic studies have been carried out to elucidate the structures of the complexes.

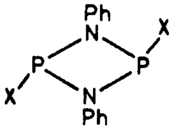
INTRODUCTION

Building upon our earlier work on the chemistry of λ^5- cyclotriphospha*zenes*[1] and λ^3-cyclodiphospha*zanes* [2], we have explored the use of these P-N ring systems as ligands in transition metal and organometallic chemistry. λ^5-Cyclophosphazenes coordinate to transition metals via their skeletal nitrogen atoms and/or exocyclic donor sites; λ^3-cyclodiphosphazanes bind to transition metals through their phosphorus atoms. Studies on the former systems are relevant from the point of view of anchoring transition metal moieties to phosphazene polymers[3] whilst the later system can generate metal complexes of potential catalytic interest[4].



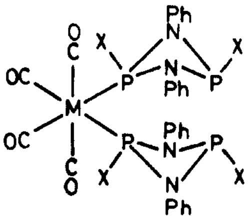
1

X = OC_6H_4Me-*p*



2

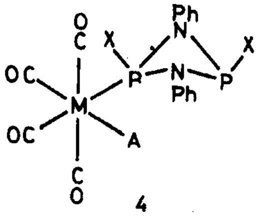
X = OCH_2CF_3



3

M = Cr, Mo, W

X = OC_6H_4Me

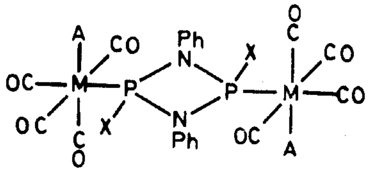


4

X = OC_6H_4Me

a M = Mo, A = $P(OMe)_3$

b M = W ; A = NHC_5H_{10}



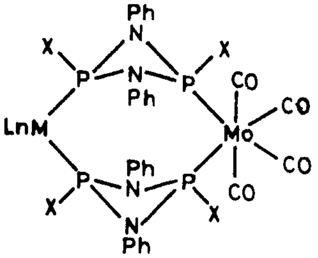
5

X = OCH_2CF_3

a M = Mo, W ; A = NHC_5H_{10}

b M = Mo ; A = $P(OMe)_3$

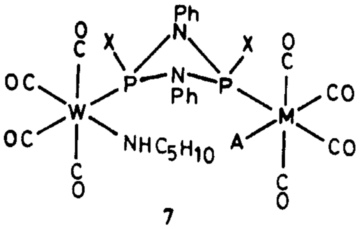
c M = Mo ; A = $[PhNP(OCH_2CF_3)]_2$



6

X = OC_6H_4Me

MLn = $Mo(CO)_4$, $PtCl_2$

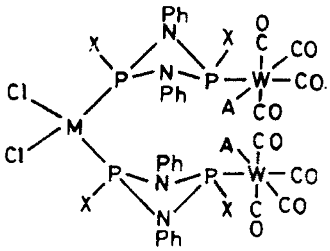


7

X = OC_6H_4Me

a M = Mo ; A = $P(OMe)_3$

b M = W ; A = NHC_5H_{10}



8

X = OC_6H_4Me

a M = Pt

b M = Pd

λ^3-CYCLODIPHOSPHAZANES AS LIGANDS

The coordination chemistry of λ^3-cyclodiphosphazanes of the type $(RNPX)_2$ has been investigated previously, but the question of the geometrical isomerism influencing the coordination behaviour of the four membered ring has not been addressed to specifically[5]. The present work is mainly concerned with this question. The reactions of the *cis*-cyclodiphosphazane, $[PhNP(OC_6H_4Me\text{-}p)]_2$ (**1**) with $[M(CO)_4(NBD)]$ (M = Cr,Mo or W)(NBD = norbornadiene) give the mononuclear complexes **3**, whereas analogous reactions with $[M(CO)_4(NHC_5H_{10})(A)]$ (M=Mo,A=$P(OMe)_3$; M=W,A=NHC_5H_{10}) yield the complexes of the type **4**. In contrast, the *trans*-cyclodiphosphazane $[PhNP(OCH_2CF_3)]_2$ (**2**) reacts with $[M(CO)_4(NHC_5H_{10})(A)]$ (M=Mo,A=$P(OMe)_3$; M=Mo or W,A= NHC_5H_{10}) to give dinuclear complexes of the type **5**. In the complexes **3** and **4**, the *cis*-ligand is coordinated in η^1 fashion whereas in **5** the *trans*-ligand is coordinated in bridged bidentate fashion. The ^{31}P NMR spectra for the mononuclear complexes **3** show two resonances owing to the presence of two different phosphorus nuclei; [δ_P 119-125 for the uncoordinated phosphorus and δ_P 186.4, 154.4 and 127.6 for the coordinated phosphorus of Cr, Mo and W complexes respectively]. The ^{31}P NMR of **5c** is of $[AMX]_2$ type (δ_A 195.8, δ_M 174.1 and δ_X 178.8 assigned to the coordinated and the free phosphorus of the η^1- ligand and phosphorus of the bridging ligand respectively).

The structures of **4** (M=W, A=NHC_5H_{10}) and **5** (M=Mo, A=NHC_5H_{10}) have been determined by single crystal X-ray studies. The structure of **4** reveals a distorted octahedral geometry around the metal centre; the cyclodiphosphazane ligand and piperidine groups are *cis* to each other. The aryloxy substituents on the P_2N_2 ring adopt a *cis* orientation and the P_2N_2 ring is slightly puckered. The average P-N distance (1.696(8) Å) at the coordinated phosphorus is shorter than that at the uncoordinated phosphorus atom (1.716(9) Å). In contrast, the structure of **5** reveals that the trifluoroethoxy substituents adopt *trans* orientation and the four membered P_2N_2 ring is virtually planar. The bond distances and bond angles within the P_2N_2 ring in the complex show little variation from those observed for the free ligand[2].

Complexes **3** and **4** bear uncoordinated phosphorus sites; hence they can be used as starting materials for homo- and hetero-bimetallic and polymetallic complexes. Thus, **3** (M=Mo) reacts with $[Mo(CO)_4(NHC_5H_{10})_2]$ or $[PtCl_2(COD)]$ to give dinuclear complexes **6**. The structure of the dimolybdenum complex

[**6**, ML_n=$Mo(CO)_4$] has been confirmed by single crystal X-ray diffraction. The tungsten complex **4** (M=W, A=NHC_5H_{10}) reacts with [$M(CO)_4(NHC_5H_{10})(A)$] (M=Mo, A=$P(OMe)_3$; M=W, A=NHC_5H_{10}) to give the dinuclear complexes **7**; on the other hand **4** reacts with $MCl_2(COD)$ (M=Pd or Pt) to yield the trinuclear complexes of the type **8**: [^{31}P NMR of **8a**: AA'XX' part of an AA'XX'MRR' spin system, δ_A 132.4 ($^2J_{PP}$= 23, $^1J_{WP}$=404 Hz) and δ_X 62.9 ($^2J_{PP}$=23, $^1J_{PtP}$=5344 Hz)]. The structure of the bimetallic complex **7a** has been determined by X-ray crystallography (Figure 1).

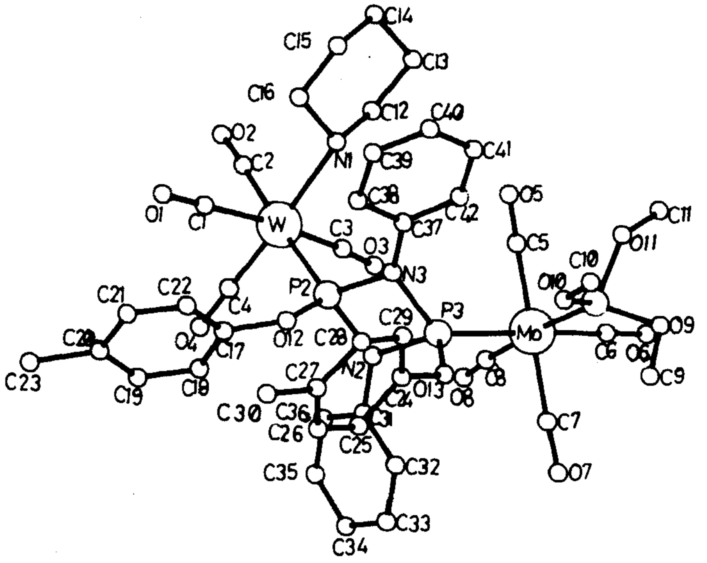


Figure 1. The PLUTO diagram of **7a**

λ^5-CYCLOTRIPHOSPHAZENES AS LIGANDS

We have studied the reactions of two types of cyclotriphosphazenes *viz.*, amino-spirocyclic and 3,5-dimethyl pyrazolyl (dmp) cyclotriphosphazenes with Group

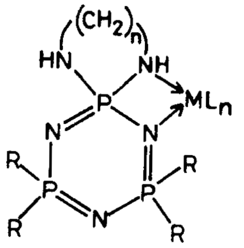
6 metal carbonyls, Pd and Pt chlorides. The cyclophosphazene ligands used are $N_3P_3(NMe_2)_4[NH(CH_2)_2NH]$(**9**), $N_3P_3(NMe_2)_4[NH(CH_2)_3NH]$ (**10**) and $N_3P_3Ph_2(dmp)_4$ (**11**), $N_3P_3Ph_4(dmp)_2$ (**12**), $N_3P_3(MeNCH_2CH_2O)_2(dmp)_2$ (**13**) and *cis*-$N_3P_3(OPh)_4(dmp)_2$ (**14**).

Complexes of aminospirocyclic phosphazenes

Aminospirocyclic phosphazenes **9** and **10** react with $M(CO)_6$ (M=Mo or W) to give complexes of the type $[M(CO)_4.L]$ (**15**), in which a phosphazene ring nitrogen atom and a nitrogen atom of the diaminoalkane moiety are involved in coordination. A similar type of complex is formed in the reaction of $PdCl_2$ with **10**. The ^{31}P NMR spectra of these complexes are of the AMX type and the data for a few typical complexes are:

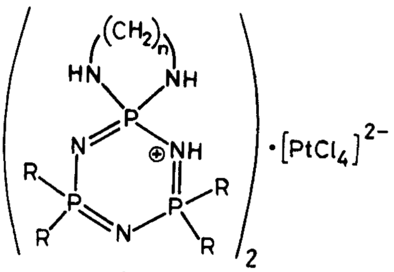
$[PdCl_2.(\mathbf{10})]$: (AMX) : 43.1, 18.3, 15.4 ppm; $J_{AM} = J_{MX} = 38$, $J_{AX} = 32$ Hz.
$[W(CO)_4.(\mathbf{9})]$: (AMX) : 42.1, 25.7, 22.4 ppm; $J_{AM} = J_{AX} = 38$, $J_{MX} = 48$ Hz.

Treatment of **10** with K_2PtCl_4 yields **16** in which the cyclotriphosphazene is merely protonated without being involved in coordination to the metal.



15

R = NMe$_2$; n = 2 or 3
ML$_n$ = Mo(CO)$_4$, W(CO)$_4$ or PdCl$_2$

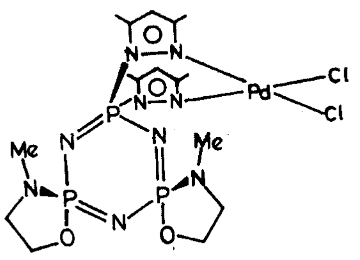


16

R = NMe$_2$ n = 3

Complexes of dimethylpyrazolyl phosphazenes

Previous work of Paddock and coworkers has shown that the *gem*-dimethylpyrazolyl derivatives **11** and **12** function as bidentate ligands toward palladium and platinum chlorides[6]. Ligand **13** also binds to palladium chloride in a bidentate fashion to give complex (**17**). The ^{31}P NMR spectrum of **17** at 265 K is of the ABX type[δ_P = 33.4(A), 30.2(B), 2.0(X) ppm; $J_{AX} = 67$, $J_{BX} = 7.3$, $J_{AB} = 47$ Hz]; but at 300 K the resonances are broadened presumably due to a fluxional process involving the flipping of the six membered metallocycle. The pyrazolyl derivatives **12** and **13** act as novel tridentate ligands toward Group 6 metal carbonyls (Mo or W) via the two pyrazolyl pyridinic nitrogen atoms and one of the P_3N_3 ring nitrogen atoms. The structures of $[Mo(CO)_3.(\mathbf{12})]$, **13** and $[W(CO)_3.(\mathbf{13})].CH_3CN$ (**18**) have been confirmed by single crystal X-ray diffraction. The pyrazolyl nitrogen-metal bonds(2.299,2.311 and 2.251,2.274 Å) are slightly shorter than the ring nitrogen-metal bonds(2.391 and 2.309 Å) in the Mo and W complexes respectively. The P_3N_3 ring of the ligand **13** becomes non-planar in the complex **18**; the nitrogen atom bonded to the metal deviates from the mean plane formed by the other five atoms by 0.18 Å. The ORTEP diagrams of **13** and **18** are shown in Figure 2.



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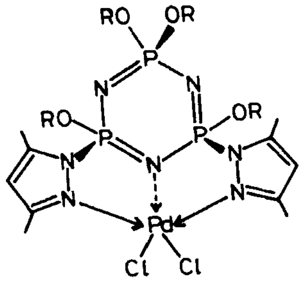

19

R = C_6H_5

The *nongemial*-bis(dimethylpyrazolyl)cyclotriphosphazene **14**, (prepared by the reaction of 2,2,4,6:4,6- $N_3P_3(OPh)_4Cl_2$ with 3,5-dimethylpyrazole in boiling toluene) reacts with palladium chloride to give a complex of the composition $[PdCl_2.\mathbf{14}]$ (**19**) whose structure has been determined by single crystal X-ray diffraction. Both the pyridinic pyrazolyl nitrogen atoms are involved in coordination and the geometry around the metal is planar. There is also an interaction between the metal and the ring nitrogen atom which connects the two phosphorus atoms bearing the pyrazolyl groups.The distance between them is 2.858 Åwhich is shorter than the sum of their van der Waal's radii (3.7 Å). The P_3N_3 ring maintains the planarity as in the ligand (**14**) whose structure has also been confirmed by X-ray crystallography. The P-N bond lengths in the ligand and the complex are nearly equal (mean 1.583 and 1.585 Å).

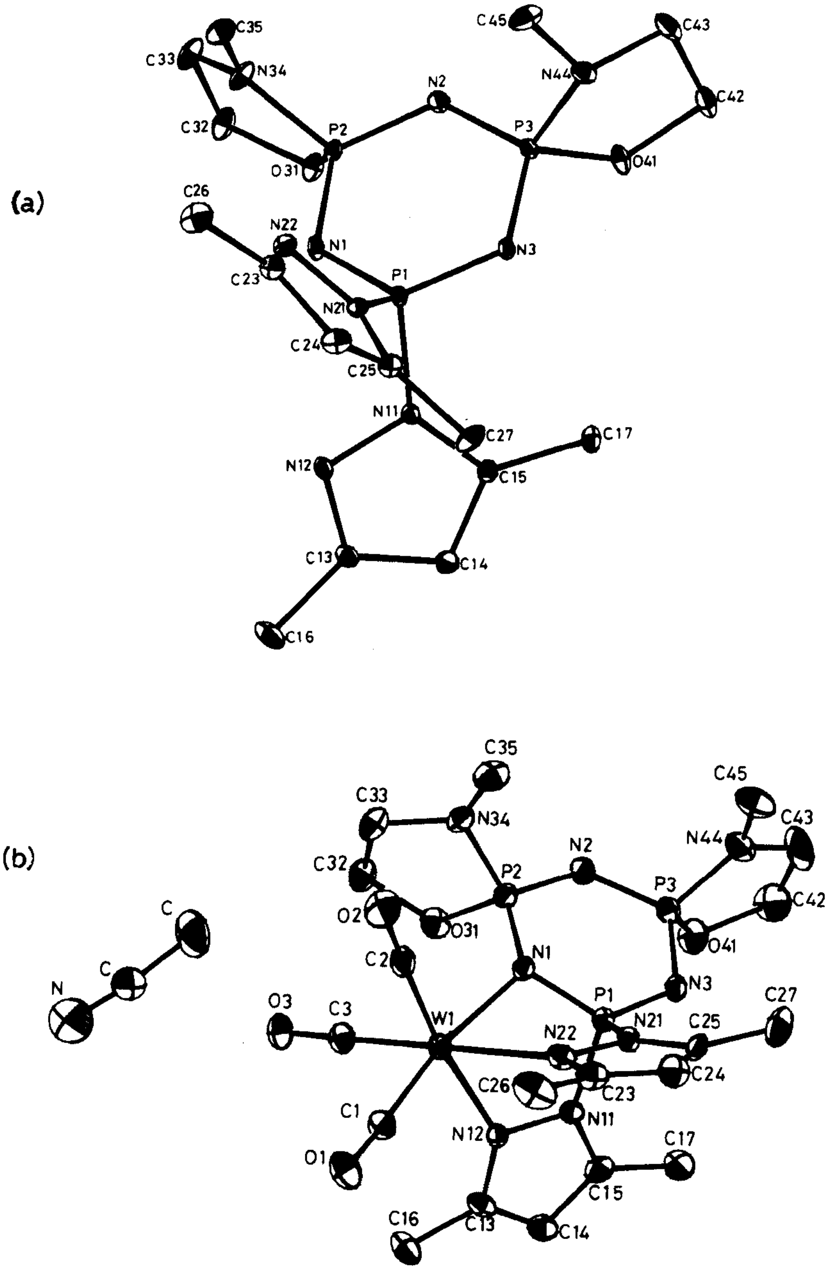

Figure 2. The ORTEP diagrams of (a) $N_3P_3(MeNCH_2CH_2O)_2(dmp)_2$ (**13**) and (b) $[W(CO)_3.(\mathbf{13})]CH_3CN$ (**18**).

CONCLUSIONS

The stereochemistry of λ^3-cyclodiphosphazanes appears to exert a significant effect on their coordination behaviour. Mononuclear complexes that contain η^1-coordinated cyclodiphosphazanes can be used as synthons to build homo- and hetero- dinuclear and polynuclear complexes.

The structural complexity of the λ^5-cyclophosphazene ring system can be judiciously exploited to design novel ligands and studies of their complexes could open up new approaches for the synthesis of transition metal catalyst systems anchored to poly(phosphazene) backbone.

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REFERENCES

1. S.S. Krishnamurthy, A.C. Sau and M. Woods, *Adv. Inorg. Chem. Radiochem.*, **21**, 41 (1978); S.S. Krishnamurthy, *Proc. Indian Natl. Sci. Acad.*, **52A**, 1020 (1986); C.W. Allen, *Chem. Rev.*, **91**, 119 (1991).
2. S.S. Kumaravel, S.S. Krishnamurthy, B.R. Vincent and T.S. Cameron, *Z. Naturforsch*, **B41**, 1067 (1986); S.S. Kumaravel, S.S. Krishnamurthy, T.S. Cameron and A. Linden, *Inorg. Chem.*, **27**, 4546 (1988).
3. H.R. Allcock, J.L. Desorcie and G.H. Riding, *Polyhedron*, **6**, 119 (1987).
4. S.S. Krishnamurthy, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **102**, 283 (1990).
5. J.C.T.R. Burkett St. Laurent, J. Sinclair and J.F. Nixon, *J. Organomet. Chem.*, **262**, 379 (1984); O.J. Scherer, R. Anselman and W.B. Sheldrick, *J. Organomet. Chem.*, **263**, C26 (1984); M.S. Balakrishna and S.S. Krishnamurthy, *unpublished results.*
6. K.D. Gallicano and N.L. Paddock, *Can. J. Chem.*, **60**, 521 (1982).
7. A. Chandrasekaran, S.S. Krishnamurthy and M.Nethaji,*Current Science*, (in Press).