

DIPHOSPHAZANES AS LIGANDS—SYMBIOSIS OF PHOSPHORUS CHEMISTRY AND ORGANOMETALLIC CHEMISTRY

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Diphosphazane ligands offer considerable scope and versatility for designing homo and heterobimetallic complexes and the structural features of the complexes can be altered significantly by altering the substituents on both nitrogen and phosphorus atoms. The reactivity of a range of new acyclic, cyclic and bicyclic diphosphazanes with Group 6 metal and iron carbonyl derivatives and organometallic derivatives of palladium, platinum and rhodium has been explored. Several novel and structurally interesting complexes including the seven coordinated species of the type, $M(\text{CO})_3\text{I}_3\text{L}$ ($M = \text{Mo}, \text{W}$; $L = \text{diphosphazane}$) have been isolated and their structures elucidated by infrared and ^1H , ^{13}C and ^{31}P NMR spectroscopy and in a few instances by single crystal X-ray analysis.

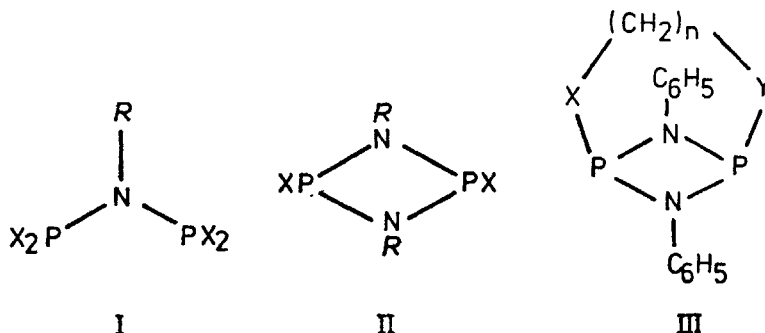
Key Words : Diphosphazane Ligands—Acyclic, Cyclic and Bicyclic; Group 6 and Iron Carbonyl and Pd, Pt and Rh Complexes

INTRODUCTION

THE importance of tertiary phosphines as ligands in numerous organometallic systems and the role of phosphine complexes as homogeneous catalysts for a variety of synthetic transformations are well documented.^{1,2} It is anticipated that the use of diphosphine or polyphosphine ligands would become increasingly popular in future studies because they would allow for more versatility in the design of new catalysts. Complexes with two or more metal centres can have several advantages over a catalyst containing only a single metal.¹ The organometallic chemistry of diphosphinoalkanes, in particular that of diphosphinomethane ligands, have been investigated extensively for more than two decades.^{2,3} Interest on the analogous diphosphinoamine ligands(I) has burgeoned rapidly in recent years.^{4,5} These diphosphinoamines (diphosphazanes) based on the P-N-P framework offer considerable scope and versatility as ligands since the substituents on both nitrogen and phosphorus atoms can be altered readily with attendant changes in the P-N-P angle and the conformations around the phosphorus centres.⁶ The organometallic chemistry of cyclodiphosphazanes(II) has also been studied to a limited extent.^{5,7} In the last three years, we have initiated a research

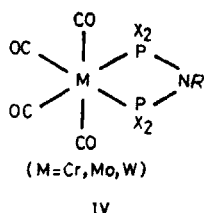
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programme aimed at the synthesis of several acyclic(I), cyclic(II) and bicyclic(III) diphosphine ligands containing the P-N-P skeleton and a study of their reactions with transition metal organometallic species. A brief amount of the results is presented in this paper.



REACTIONS OF I WITH METAL CARBONYLS

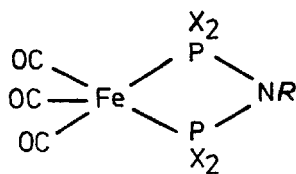
Substitution of CO from metal carbonyls by diphosphine ligands of type I has been realized by several standard techniques [thermal or photochemical activation, use of a precursor complex such as $M(\text{CO})_4(\text{norbornadiene})$ or $M(\text{CO})_4(\text{piperidine})_2$]. With Group 6 metal carbonyls, the products are the chelating *cis*-tetracarbonyl complexes(IV *a-f*). Reactions with iron pentacarbonyl yield mononuclear (V *c, e*) as well as the dinuclear (VI *c*) derivatives depending on the diphosphine ligand.



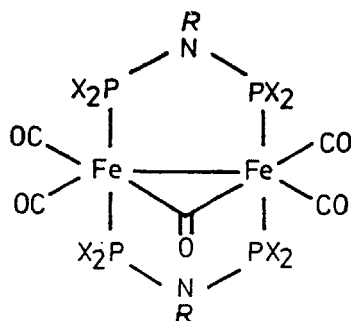
- a $R = \text{Pr}^i, X = \text{Ph}$
- b $R = \text{Me}, X = \text{OCH}_2\text{CF}_3$
- c $R = \text{Me}, X = \text{OPh}$
- d $R = \text{Ph}, X = \text{OCH}_2\text{CF}_3$
- e $R = \text{Ph}, X = \text{OPh}$
- f $R = \text{Ph}, X = \text{OC}_6\text{H}_4\text{Br-}p$

Structural assignments for the above compounds are based on infrared and ^1H , ^{13}C and ^{31}P NMR spectroscopic evidence. The ^{31}P chemical shifts of the ligands (48 — 140 δ) move downfield upon chelate formation, the extent of deshielding varying in the order $\text{Cr} > \text{Mo} > \text{W}$.

Further reaction of *cis* $[\text{Mo}(\text{CO})_4(X_2\text{PN}(R)\text{PX}_2)]$ ($R = \text{Pr}^i, X = \text{Ph}$) with an excess of the diphosphinoamine ligand in boiling xylene affords VII in which both chelating and monodentate coordination of the diphosphine is observed. Treatment of *fac*- $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ with $X_2\text{PN}(R)\text{PX}_2$ ($R = \text{Pr}^i, X = \text{Ph}$) in the molar ratio 1:3 gives VIII as the main product; reversing the stoichiometry of the reactants leads to the isolation of the dinuclear complex IX. In both the reactions, a small amount of *cis*- $[\text{Mo}(\text{CO})_4\{X_2\text{PN}(R)\text{PX}_2\}]$ is also obtained as a

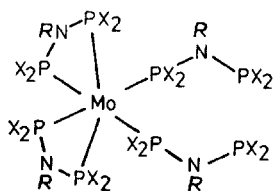


V

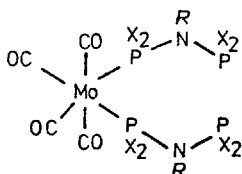


VI

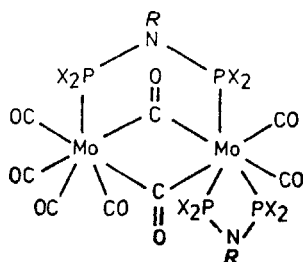
result of a reappropriation reaction. The ^{31}P NMR spectrum of VIII shows the expected AB pattern for the diposphine ligand ($\delta_{\text{A}} 32.4$ $\delta_{\text{B}} 40.9$, $^2J_{\text{PP}} 64\text{Hz}$). The infrared spectrum of IX shows the presence of both bridging ($1820\text{--}1850\text{cm}^{-1}$) and terminal carbonyls ($1900\text{--}2100\text{cm}^{-1}$); its ^{31}P NMR spectrum ($\delta 87.2, 30.8$) supports the structure assigned.



VII



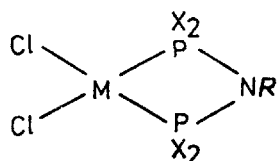
VIII



IX

REACTIONS OF I WITH Pd, Pt AND Rh ORGANOMETALLIC SPECIES

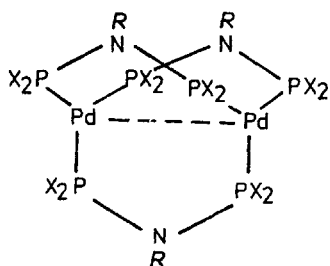
Reactions of palladium and platinum cyclooctadiene derivatives, $M(\text{COD})\text{Cl}_2$ with I give chelate complexes of the type X. The ^{31}P $\{^1\text{H}\}$ NMR spectra of the platinum complexes exhibit ^{195}Pt satellites with characteristic $^1J(\text{Pt-P})$ couplings ($3200\text{--}3600\text{Hz}$).



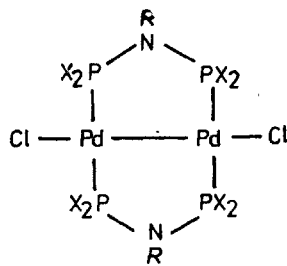
X

- a $R = \text{Pr}^i$, $X = \text{Ph}$
- b $R = \text{Me}$, $X = \text{OPh}$
- e $R = \text{Ph}$, $X = \text{OPh}$

Treatment of the Pd(0) derivative, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3^2$ with an excess of the diphosphine, $(\text{PhO})_2 \text{PN}(\text{Me})\text{P}(\text{OPh})_2$ gives the dinuclear complex XI containing three bridging diphosphine ligands. The structure of XI has been determined by single crystal X-ray analysis. The Pd-Pd distance is 2.85Å indicating a metal-metal bond. An analogous complex could not be obtained, with the N-phenyl ligand I ($R = \text{Ph}$, $X = \text{OPh}$). When a mixture of Pd(0) and Pd(II) derivatives are treated with I, the metal-metal bonded Pd(I) complexes(XII) are obtained.

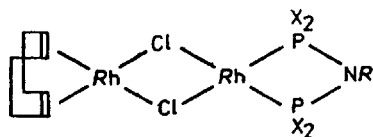


XI

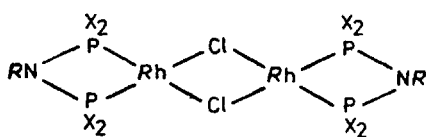


XII

The reaction of Ie ($R = \text{Ph}$, $X = \text{OPh}$) with $[\text{Rh}(\text{COD})\text{Cl}]_2$ results in the replacement of one or both the olefinic groups (depending on the stoichiometry of the reactants) to yield XIIIe and XIVe.

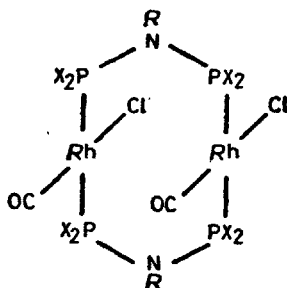


XIII



XIV

Treatment of Ie with the rhodium(1) chloro (carbonyl) dimer, $[\text{RhCl}(\text{CO})_2]_2$ affords the dinuclear complex XV in which the diphosphine exhibits a bridged bidentate mode of coordination.

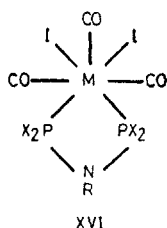


XV

The ^{31}P NMR spectra of the rhodium(I) complexes (XIII-XV) exhibit a doublet with a 1J (Rh-P) coupling of 280 — 285Hz.

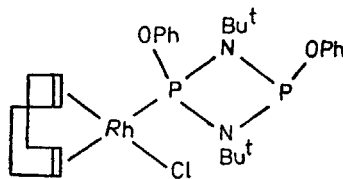
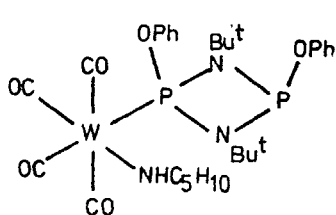
SEVEN COORDINATED MO(II) AND W(II) COMPLEXES

There has been a recent upsurge of interest in seven coordinated carbonyl derivatives of group 6 metals.⁸ New seven coordinated Mo(II) and W(II) complexes (XVI) of diphosphinoamines have been prepared by starting from $M(\text{CO})_3\text{I}_2(\text{MeCN})_2$ ($M = \text{MO}, \text{W}$).^{8a} The ^{31}P NMR spectra of XVI show a broad singlet presumably because of a fluxional process.^{8(d)} The determination of the structure of $\text{W}(\text{CO})_3\text{I}_2 [\text{PhN} \{ \text{P}(\text{OPh})_2 \}_2]$ by X-ray crystallography is in progress.



ORGANOMETALLIC DERIVATIVES OF CYCLODIPHOSPHAZANES (II) AND BICYCLIC DIPHOSPHAZANES (III)

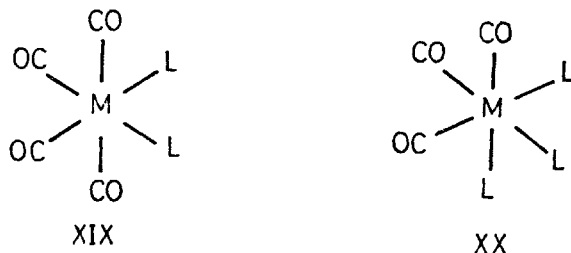
The reaction of the cyclodiphosphazane, *cis*- $[\text{Bu}^t\text{NP}(\text{OPh})_2]_2$ with *cis*- $[\text{W}(\text{CO})_4(\text{HNC}_5\text{H}_{10})_2]$ yields XVII in which the cyclodiphosphazane behaves as a monodentate ligand. A similar monodentate coordination is observed in the Rh complex XVIII prepared by the treatment of the cyclic ligand with $[\text{RhCl}(\text{COD})]_2$.



Recently, the authors have synthesized several bicyclic cyclodiphosphazanes(III) from the reactions of $[\text{PhNPCI}]_2$ with difunctional reagents. The compounds isolated are $(\text{PhN})_2\text{P}(\text{OCH}_2\text{CH}_2\text{O})\text{P}$ (IIIa, $R = \text{Ph}$, $X = Y = \text{O}$, $n = 2$), $(\text{PhN})_2\text{P}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{O})\text{P}$ (III b $R = \text{Ph}$, $X = Y = \text{O}$, $n = 3$) $(\text{PhN})_2\text{P}[\text{OCH}_2\text{CH}_2\text{N}(\text{Me})]\text{P}$ (III c, $R = \text{Ph}$, $X = \text{O}$, $Y = \text{NMe}$, $n = 2$) and $(\text{PhN})_2\text{P}[\text{NMe}]\text{CH}_2\text{CH}_2(\text{NMe})\text{P}$ (III d,

$R = \text{Ph}$, $X = Y = \text{NMe}$, $n = 2$). The X-ray crystal structures of IIIb and IIIc have been determined. The four-membered P-N ring is puckered, the deviation from planarity being greater in IIIc compared to IIIb.

A few complexes of the bicyclic diphosphazanes IIIa and IIIc have been synthesised starting from *cis*-[Mo(CO)₄(NHC₅H₁₀)₂] and *fac*-[Mo(CO)₃(MeCN)₃] respectively. The complexes isolated (XIX and XX) are shown below :



The ³¹P NMR spectrum of XX recorded at 100MHz is of the [AX]_n type and is consistent with the structure assigned.

The cyclodiphosphazane complexes (XVII-XX) are of considerable interest as they can be valuable synthons for the preparation of bimetallic complexes.

Further aspects of chemical reactivity, NMR spectra and determination of the structures of some of the complexes by X-ray crystallography are under investigation.

CONCLUDING REMARKS

The authors have thus tried to build bridges between "organometallic chemistry and phosphorus chemistry" and the preliminary results have been quite encouraging even though several questions remain unanswered concerning the effect of ligand structure on the synthesis and reactivity of transition metal organometallic compounds. The organometallic chemistry of diphosphazane ligands is at an early stage of development but has already demonstrated its vast potential for further fundamental studies and applications particularly in catalysis. The reactions of coordinated phosphorus ligands constitutes a fascinating area and can be used to generate many labile phosphorus compounds which are stable only in the coordinated state.^{5,10} A major goal of future studies will be to unfold comparisons and contrasts between the behaviour of diphosphazanes and that of the other well-known tertiary phosphines as ligands in organometallic systems.

ACKNOWLEDGEMENT

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