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Coordination chemistry of diphosphinoamine and cyclodiphosphazane ligands

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ABSTRACT

The transition metal coordination and organometallic chemistry of acyclic diphosphazane ligands has grown rapidly in the last two decades and a stage has been reached that permits a delineation of similarities and contrasts with the chemistry of diphosphinomethane type ligands. Diphosphazane complexes of Group 10 metals (particularly those of Pd and Pt) have received much less attention than the analogous complexes of transition metals of other groups in the Periodic Table. The coordination chemistry of cyclodiphosphazanes has been investigated to a limited extent compared with that of their acyclic analogues. An attractive feature of the diphosphinoamine chemistry is the ease with which a range of ligands with different electronic and steric attributes can be synthesized by varying the substituents on both nitrogen and phosphorous.

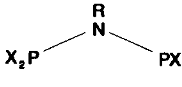
LIST OF ABBREVIATIONS

Acac	acetylacetonato group
Bu	butyl group
CHT	cycloheptatriene
C.N.	coordination number
COD	1,5-cyclooctadiene, C_8H_{12}
Cp	cyclopentadienyl group, (η^5-C_5H_5)
dba	dibenzylideneacetone
DMP	3,5-dimethyl pyrazole
dmpe	1,2-bis(dimethylphosphino)ethane
diphos	diphosphine ligand
dppa	bis(diphenylphosphino)amine
dppe	1,2-bis(diphenylphosphino)ethane
dppb	1,4-bis(diphenylphosphino)butane
dppf	2,5-bis(diphenylphosphino)furan
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
Et	ethyl group
fac	facial
M	the central metal in a complex
Me	methyl group
mer	meridional
NBD	norbornadiene, C_7H_8
NMR	nuclear magnetic resonance
[O]	oxidation
Ph	phenyl group
Pip	piperidine
Pr	propyl group
R	an alkyl or aryl group
TCE	1,1,2,2-tetrachloroethane

THF	tetrahydrofuran
THT-O_2	tetrahydrothiophen dioxide
TMNO	trimethylamine *N*-oxide
VPP	vinylbis(diphenylphosphine) (1,2-Bis(diphenylphosphino)ethylene)

1. INTRODUCTION

The coordination chemistry of transition metals in zero or low oxidation states has been extensively studied in the last 2–3 decades and considerable progress has been made in the use of transition metal complexes in homogeneous catalysis [1,2]. The preparation of stable complexes of transition metals in low oxidation states depends to a large extent upon the use of strong π-acceptor ligands such as carbon monoxide or tertiary phosphines. Organometallic compounds containing diphosphine ligands with a P—C—P framework have been the subject of numerous investigations during the past three decades [3–9] while, interest in analogous diphosphinoamine (diphosphazane) ligands, $RN(PX_2)_2$ (**I**) has been growing rapidly. Diphosphinoamine ligands have proved very versatile [10] because substituents on both phosphorus and nitrogen atoms can be varied with attendant changes in the P—N—P bond angle and the conformation around the phosphorous centres [11,12]. Furthermore, fairly small differences in these ligands can cause significant changes in their coordination behaviour and the structural features of the resulting complexes [13]. Recently, there has also been some interest in the use of cyclodiphosphazanes (diazadiphosphetidines), $[RNPX]_2$ (**II**) as ligands in transition metal complexes since the four-membered P_2N_2 ring contains four possible donor sites in close proximity [14–16].



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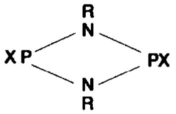


II

Although both six-membered and eight membered λ^3-cyclophosphazanes, $[RNPX]_n$ ($n=3, 4$) are known, their chemistry is not well-developed [14,15,17]. They can be useful intermediates in organometallic chemistry and their coordination chemistry would also be interesting because of the presence of trivalent phosphorus centres. The coordination chemistry of only the eight-membered cyclophosphazane ring has been investigated to a limited extent [16,18,19].

This review is concerned with the coordination chemistry of both acyclic and cyclic diphosphazanes. The synthetic methods for the ligands and their complexes are outlined followed by a discussion of the results obtained from spectroscopic and single crystal X-ray crystallographic studies.

2. SYNTHESES OF LIGANDS

2.1 Diphosphinoamines (diphosphazanes)

The synthesis of alkyl-aryliminobis(dichlorophosphines) involves the reaction of alkyl or aryl substituted primary amines or their hydrochlorides with PCl_3 [20–22].

$$2PCl_3 + RNH_3Cl \rightarrow RN(PCl_2)_2 + 3HCl$$

$$PCl_3 + RNH_2 \rightarrow RN(PCl_2)_2 + 2HCl$$

Instead of primary amines as a source of nitrogen, silylated amines such as heptamethyl or phenylhexamethyl disilazane can be used in condensation reactions with chlorophosphines to obtain bis(dichlorophosphino)amines [23–25].

$$2PCl_3 + MeN(SiMe_3)_2 \rightarrow MeN(PCl_2)_2 + 2Me_3SiCl$$

$$2PPh_2Cl + NH(SiMe_3)_2 \rightarrow HN(PPh_2)_2 + 2Me_3SiCl$$

Synthesis of $RN(PCl_2)_2$ with a sterically bulky group R, such as *tert*-butyl can be achieved through the condensation reaction of PCl_3 with aminodichlorophosphines [26]:

$$PCl_3 + PCl_2(NHBu^t) + Et_3N \rightarrow Bu^tN(PCl_2)_2 + Et_3N{\cdot}HCl$$

The range and generality of the above and other methods are illustrated in Tables 1 and 2. Diphosphinoamines with chiral organic substituents on the nitrogen have also been synthesized [45].

The chlorine atoms of bis(dichlorophosphino)amines can be easily replaced by alkoxy, aryloxy or amino substituents; fluorination can be effected by SbF_3 in pentane or hexane under mild conditions.

$$RN(PCl_2)_2 + 4X^- \rightarrow RN(PX_2)_2 + 4Cl^-$$

$(X = F, OR)$

$$RN(PCl_2)_2 + 4HNR'R'' \xrightarrow[-\mathrm{Base\cdot HCl}]{+\mathrm{Base}} RN(P(NR'R'')_2)_2$$

These reactions are listed in Table 3.

In contrast to the numerous studies on symmetrically substituted diphosphazanes, diphosphazanes with differently substituted phosphorus centres have received much less attention (Tables 1–3) [25]. Recently, several unsymmetrically substituted diphosphazanes have been synthesized by the following routes [44,46].

TABLE 1

Experimental details for the synthesis of diphosphinoamines

Reactants (amount, mol)	Reaction conditions °C/solvent/time, h	Product (yield, %)	Ref.
$NaPPh_2$(0.4)+1,2,4,5-$Br_4C_6H_2$(0.4)	liq. NH_3	$HN(PPh_2)_2$ (55)	27
$N(PF_2)_3$(0.2)+HBr(0.2)	—	$HN(PF_2)_2$ (50)	30
$PF_2(NH_2)+BrPF_2+Me_3N$	—	$HN(PF_2)_2$	31
PCl_3(0.10)+RNH_2(0.30)	−78/Et_2O/6	$RN(PCl_2)_2$ (25)^a	20,22
PCl_3(2.55)+$PhNH_2$(0.64)	110/—/48	$PhN(PCl_2)_2$ (72)	21,12
PCl_3(0.72)+p-$MeOC_6H_4NH_3Cl$(0.12)	110/—/48	p-$MeOC_6H_4N(PCl_2)_2$ (92)	21
PCl_3(0.36)+p-$NO_2C_6H_4NH_2$(0.22)	—/dioxan/12	p-$NO_2C_6H_4N(PCl_2)_2$ (31)	21
PCl_3(1.46)+m-$NO_2C_6H_4NH_3Cl$(0.20)	110/—/144	m-$NO_2C_6H_4N(PCl_2)_2$ (62)	21
PCl_3(0.55)+m-$ClC_6H_4NH_3Cl$(0.15)	110/—/40	m-$ClC_6H_4N(PCl_2)_2$ (56)	22
PCl_3(2.55)+m-$MeC_6H_4NH_2$(0.64)	110/—/48	m-$MeC_6H_4N(PCl_2)_2$ (72)	12
PMePhBr(0.10)+$MeNH_2$(0.78)	−10/Et_2O/3	MeN(P(MePh))$_2$ (20)	32
$P(Et_2N)_3$(0.06)+$PhNH_2$(0.18)	55/—/6	$PhN(P(NHPh)_2)_2$ (55)	33
PCl_3(9)+$Bu^tN(H)(PCl_2)$ (27)	−78/Et_2O/1	$Bu^tN(PCl_2)_2$ (88)	26
PCl_3(0.005)+$Bu^tCH_2NH_2$(0.025)+Et_3N(0.050)	−78/Et_2O/—	$(Bu^tCH_2)N(PCl_2)_2$ (48)^b	11
PPh_2Cl(0.016)+$Me_2NNHPPh_2$(0.016)+Et_3N(0.036)	110/toluene/1	$Me_2N\cdot N(PPh_2)_2$ (94)	34
PPh_2Cl(0.10)+RNH_2(0.78)	−50/Et_2O/2	$RN(PPh_2)_2$^{c}	29,32,35
PPh_2Cl(0.136)+$R'NH_2$(0.068)+Et_3N(0.158)		$R'N(PPh_2)_2$^{d}	36–38
$PPhCl_2$(1.0)+$Ph_2P(NHPr^i)$(1.0)+Et_3N(2.0)	25/C_6H_6/2	$Ph_2PN(Pr^i)P(Ph)Cl$	32
$P(O_2C_6H_4)Cl$(1.0)+$Ph_2P(NHPr^i)$ (1.0)+Et_3N(2.0)	0/toluene/1	$(C_6H_4O_2)PN(Pr^i)PPh_2$	44
$P(O_2C_6H_4)Cl$(2.0)+Pr^iNH_2(1.0)+Et_3N(2.0)	25/C_6H_6/1	$Pr^iN[P(O_2C_6H_4)]_2$	44
~~$P(OCH_2)_2Cl$(0.39)~~+$EtNH_2$(0.59)	−20/$CHCl_3$/1	$EtN[P(OCH_2)_2]_2$ (83)	28
PPh_2Cl(2.0)+$ClNH_3CHRCO_2Me$(1.0)+Et_3N(2.0)	25/$CHCl_3$/12	$MeCO_2RHCN(PPh_2)_2$^{e}	45

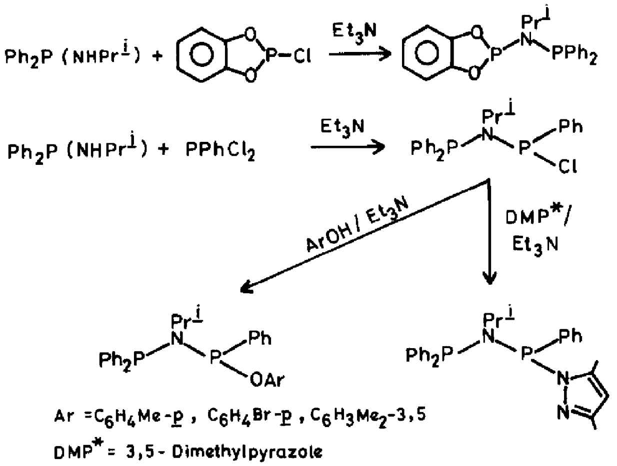
[a] R = Me, Et, Pr^n or Pr^i.

[b] Contained 10% impurity.

[c] R = Me, Et [29,32] or CH_2Ph [35].

[d] R′ = Ph [36,38], C_6H_4Me-p [37].

[e] R = H, Me, CH_2Ph, Pr^i and CH_2CH_2SMe.



2.2 Cyclodiphosphazanes

There are several methods for the preparation of the cyclodiphosphazanes and this topic has been reviewed [14–16,47]. Of these, the most convenient one is the condensation reaction of primary amines or their hydrochlorides with PCl_3 [21,26,48,49], alkyl and aryl dichlorophosphines [48], phosphoramidodichloridites [50] or alkyl phosphorodichloridites [51]. The first synthesis of a cyclodiphosphazane (viz. $[PhNPCl]_2$) was reported in 1894 by Michaelis and Schroeter [48] who correctly identified the compound as the dimer of [PhNPCl] by molecular weight measurements. A few typical examples of this synthetic route are

$$2PCl_3+2RNH_3Cl \rightarrow [RNPCl]_2+6HCl$$

$(R=Bu^t, Ph, Pr^i)$

$$PCl_3+2RNH_2 \rightarrow [RNPCl]_2+4RNH_2{\cdot}HCl$$

$(R=Pr^i, Bu^t, CH_2Bu^t)$

$$Cl_2PN(R)PCl_2+3Bu^tNH_2 \rightarrow [ClP(NR)(NBu^t)PCl]+2Bu^tNH_2{\cdot}HCl$$

$(R=Me, Et)$

Heptamethyl or phenylhexamethyldisilazane reacts with PCl_3 in 1:1 proportions to form methyl or phenylaminobis(dichlorophosphine) but in the presence of an excess of the disilazanes, the main product is a cyclodiphosphazane [21,22].

$$2PCl_3+PhN(SiMe_3)_2 \rightarrow PhN(PCl_2)_2+2Me_3SiCl$$
$$PhN(PCl_2)_2+PhN(SiMe_3)_2 \rightarrow [PhNPCl]_2+2Me_3SiCl$$

TABLE 2

Experimental details for the synthesis of diphosphinoamines using silylamine precursors[a]

Reactants (amount, mol)	Reaction conditions °C/solvent/time, h	Product (yield%)
PCl$_3$(1.0)+MeN(PPhCl)(SiMe$_3$)(1.0)	25/—/12	MeN(PPhCl)(PCl$_2$)
PCl$_3$(1.0)+MeN(PPh$_2$)(SiMe$_3$)(1.0)	25/—/12	MeN(PPh$_2$)(PCl$_2$)
PCl$_3$(1.0)+MeN(PBr$_2$)(SiMe$_3$)(1.0)	25/—/10	MeN(PBr$_2$)(PCl$_2$)
PPhCl$_2$(2.0)+MeN(SiMe$_3$)$_2$(1.0)	80/—/1	MeN(PPhCl)$_2$ (67)
PPhBr$_2$(2.0)+MeN(SiMe$_3$)$_2$(1.0)	80/—/1	MeN(PPhBr)$_2$ (65)
PMeCl$_2$(1.8)+MeN(SiMe$_3$)$_2$(0.9)	25/—/12	MeN(PMeCl)$_2$
PMe$_2$Cl(2.0)+MeN(SiMe$_3$)$_2$(1.0)	25/C$_6$H$_6$/12	MeN(PMe$_2$)$_2$
PPhCl$_2$(1.0)+MeN(PPh$_2$)(SiMe$_3$)(1.0)	25/—/12	MeN(PPh$_2$)(PPhCl)
P(*p*-MeC$_6$H$_4$)Cl$_2$(2.0)+MeN(SiMe$_3$)$_2$(1.0)	140/—/2	MeN{P(*p*-MeC$_6$H$_4$)Cl}$_2$ (62)
PBrCl$_2$(2.0)+MeN(SiMe$_3$)$_2$(1.0)	25/—/12	MeN(PBrCl)$_2$
PBrCl$_2$(1.0)+MeN(SiMe$_3$)(PBr$_2$)(1.0)	25/—/12	MeN(PBr$_2$)(PBrCl)
PBrCl$_2$(1.0)+MeN(SiMe$_3$)(PCl$_2$)(1.0)	25/—/12	MeN(PCl$_2$)(PBrCl)
PBr$_3$(1.0)+MeN(SiMe$_3$)$_2$(1.0)	0/—/1	MeN(PBr$_2$)$_2$
PBrCl$_2$(1.0)+EtN(SiMe$_3$)PCl$_2$(1.0)	0/—/1	EtN(PCl$_2$)(PBrCl)
PPh$_2$Cl(0.1)+HN(SiMe$_3$)$_2$(0.55)	−5/Et$_2$O/1	HN(PPh$_2$)$_2$ (54)[b]
PMeCl$_2$(0.3)+MeN(SiMe$_3$)$_2$(0.1)	25/—/30	MeN(PMeCl)$_2$ (77)[c]
PCl$_3$(1.0)+MeN(SiMe$_3$)$_2$(1.0)	25/—/12	MeN(PCl$_2$)$_2$[d]

[a] From ref. 25.
[b] Ref. 23.
[c] Ref. 24.
[d] Ref. 39.

An alternate route to the P$_2$N$_2$ ring system takes advantage of reactions which lead to the elimination of metal halides [52–54] or trimethylsilyl halides [55]:

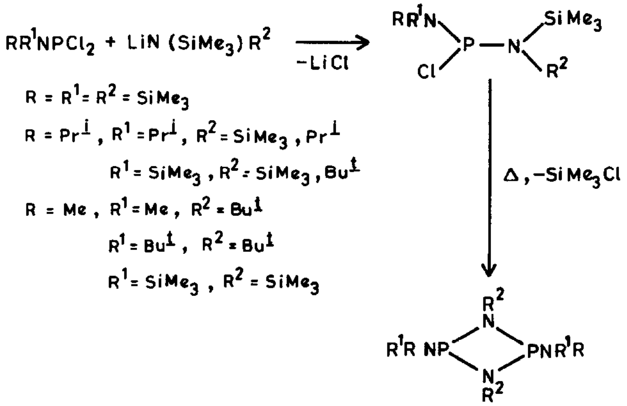


TABLE 3

Experimental details for the derivatization of bis(dichlorophosphino)amines

Reactants (amount, mmol)	Reaction conditions °C/solvent/time, h	Product (yield, %)	Ref.
$MeN(PCl_2)_2(0.1) + SbF_3(0.25)$	120/petrol/1	$MeN(PF_2)_2$ (75)	20
$EtN(PCl_2)_2(0.1) + SbF_3(0.25)$	120/petrol/1	$EtN(PF_2)_2$ (71)	20
$Bu^tN(PCl_2)_2(0.87) + SbF_3(0.123)$	35/pentane/3	$Bu^tN(PF_2)_2$ (48)	11
$PhN(PCl_2)_2(0.72) + SbF_3(2.9)$	170/tht-O_2/4	$PhN(PF_2)_2$ (70)	20
m-$ClC_6H_4N(PCl_2)_2(0.1) + SbF_3(0.25)$	25/pentane/0.5	*m*-$ClC_6H_4N(PF_2)_2$ (54)	22
$MeN(PCl_2)_2(1.0) + MeOH(4.0)/py(4.0)$	25/petrol/0.5	$MeN(P(OMe)_2)_2$	25,43
$MeN(PCl_2)_2(1.0) + EtOH(4.0)/Et_3N(4.0)$	25/Et_2O/3	$EtN(P(OEt)_2)_2$	40
$MeN(PCl_2)_2(1.0) + Pr^iOH(4.0)/Et_3N(4.0)$	25/Et_2O/3	$MeN(P(OPr^i)_2)_2$	40
$MeN(PCl_2)_2(1.0) + CF_3CH_2OH(4.0)/Et_3N(4.0)$	25/Et_2O/10	$MeN[P(OCH_2CF_3)_2]_2$ (62)	41
$MeN(PCl_2)_2(1.0) + PhOH(4.0)/Et_3N(4.0)$	0/Et_2O/10	$MeN[P(OPh)_2]_2$ (72)	41
$EtN(PCl_2)_2(1.0) + PhOH(4.0)/Et_3N(4.0)$	25/Et_2O/3	$EtN(P(OPh)_2)_2$	40
$EtN(PCl_2)_2(1.0) + MeOH(4.0)/Et_3N(4.0)$	25/Et_2O/3	$EtN(P(OMe)_2)_2$	40
$PhN(PCl_2)_2(1.0) + CF_3CH_2OH(4.0)/Et_3N(4.0)$	25/Et_2O/10	$PhN[P(OCH_2CF_3)_2]_2$ (65)	41
$PhN(PCl_2)_2(1.0) + PhOH(4.0)/Et_3N(4.0)$	0/Et_2O/10	$PhN[P(OPh)_2]_2$ (74)	41
$PhN(PCl_2)_2(0.68) +$ *p*-$BrC_6H_4ONa(0.28)$	25/C_6H_6/8	$PhN[P(OC_6H_4Br$-*p*$)_2]_2$ (62)	41
$MeN(PCl_2)_2(1.0) + HNMe_2$(excess)	—	$MeN(P(NMe_2)_2)_2$	25
$MeN(PCl_2)_2 + P(NMe_2)_3$	25/C_6H_6/0.5	$MeN(PCl_2)(P(Cl)NMe_2)$	25
$MeN(P(NMe_2)_2)_2 + PCl_3$	25/C_6H_6/0.5	$MeN\{P(Cl)NMe_2\}_2$	25
$MeN(PCl_2)_2(0.188) + Pr^iOH(0.774) + Et_3N(0.754)$	−78/Et_2O/—	$MeN\{P(OPr^i)_2\}_2$	42
$MeN(PCl_2)_2(0.202) + (CH_2OH)_2(0.376) + Et_3N(0.754)$	−78/Et_2O/—	$MeN\{P(OCH_2)_2\}_2$	42
$Ph_2PN(Pr^i)P(Ph)Cl(0.4) + HOAr(0.40)/Et_3N(0.42)$	25/toluene/4	$Ph_2PN(Pr^i)P(Ph)(OAr)$[a]	46
$Ph_2PN(Pr^i)P(Ph)Cl(0.4) + HN_2C_3HMe_2(0.4)/Et_3N(0.4)$	25/toluene/4	$Ph_2PN(Pr^i)P(Ph)(N_2C_3HMe_2)$[b]	46a

[a] Ar = C_6H_4Me-*p*, C_6H_4Br-*p* or $C_6H_3Me_2$-3,5.

[b] 3,5-Dimethyl pyrazolyl.

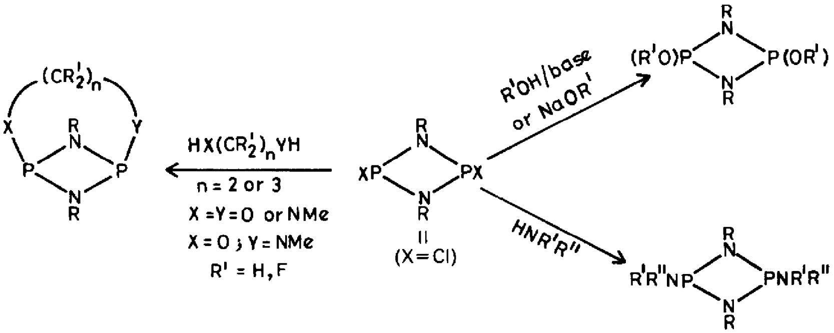
Pure bis(trimethylsilyl)amino trimethylsilylimino phosphane cyclizes slowly under an inert gas at 25°C to give 1,3-bis(trimethylsilyl)- *trans*-2,4-bis[bis(trimethylsilyl)amino]-1,3-2λ^3,4λ^3-diazadiphosphetidine [56].

$$2R_2N{-}P{=}NR \rightarrow trans\text{-}[(R_2N)PNR]_2$$

$$(R = SiMe_3)$$

Other synthetic approaches for cyclodiphosphazanes include, (i) the interaction of *N*,*N*′-dialkylphosphoramidous dichlorides with sulphonamides [57], (ii) the reaction of bis(dichlorophosphino)methylamine with *t*-butylamine [58], (iii) pyrolysis of tris(primary amino)phosphanes [59], (iv) the transamination reactions of tris(diethylamino)phosphine with aniline or *p*-toludine [60], (v) the reaction of sterically shielded dialkyl aminodichlorophosphines with *t*-butylamine [61], and (vi) the reaction of bis-*N*,*N*-dimethylphosphorodiamidous chloride with sodium salt of hexamethyl disilazane [62].

The chlorine atoms in chlorocyclodiphosphazanes (**II**) can be replaced by other substituents to obtain various fluoro [63], alkoxy [64–67], aryloxy [68], alkyl [53] and amino [58,60,70] substituted cyclodiphosphazanes and their bicyclic derivatives [67,71,72]. These reactions are shown below.



The dichlorocyclodiphosphazanes, **II** ($R = Ph$ or Bu^t) have the cis configuration of the chlorine atoms (see Sect. 5.4). The products of alkoxylation or amination reactions can have either cis or trans disposition of the substituents with respect to the P—N ring and often a mixture of isomers is obtained from which one or the other isomer can be isolated in a pure state by fractional crystallization [14,15,66–70].

3. COORDINATION CHEMISTRY OF DIPHOSPHINOAMINES

The versatility of diphosphinoamines as ligands is illustrated by the fluoro derivative, $MeN(PF_2)_2$. Following the work of Johnson and Nixon [73] on the Group 6 metal carbonyl derivatives of $EtN(PF_2)_2$, studies by King have shown that the diphosphazane, $MeN(PF_2)_2$ can bind to transition metals in a monodentate or bidentate mode of coordination giving rise to mononuclear as well as dinuclear complexes [10]. Cotton et al. [74] have found the same ligand capable of stabilizing metal–metal triple bonds and dubbed $[MeN(PF_2)_2]$ the "Nixon" ligand in view of its versatility (vide infra). In the last 4–5 years, Haines and other workers have explored the reactions of alkyl/aryl and alkoxy/aryloxy-substituted diphosphinoamines (diphosphazanes) with various transition metal derivatives. Related ligands with P–O–P [75] or P–C–P [76] backbones have not proved equally versatile on account of the lower flexibility of the backbone (P–O–P) or lower thermal stability (P–C–P).

Though a monodentate mode of coordination of $RN(PX_2)_2$ is feasible, the choice of substituents on nitrogen may favour mutual orientation of the phosphorus lone pairs suitable to allow bidentate ligand behaviour [15,28]. The planar geometry of nitrogen in diphosphazanes [77] would be expected to permit facile incorporation of these ligands into transition metal chelate or bridged structures. The structures of the transition metal complexes of diphosphinoamines also depend on the other ligands present and on the tendency of the particular metal to prefer a particular coordination geometry, e.g. Cr(0) octahedral, Fe(0) trigonal bipyramidal, Ni(0) tetrahedral. Accordingly, diphosphinoamine complexes can display several modes of coordination as shown in Fig. 1.

The coordination chemistry of diphosphinoamines is described in the following sections by classifying the complexes in terms of the various Groups of the Periodic Table of Elements. An asterisk (*) in the schemes and on the structural diagrams indicates that the structure of the compound has been confirmed by X-ray crystallography.

3.1 Group 5

A wide variety of mononuclear complexes of $MeN(PF_2)_2$ has been prepared from thermal and photochemical reactions of substituted Group 5 metal carbonyls. When metal precursors containing an unreactive ligand (e.g. η^5-C_5H_5) and an even number of carbonyl groups, e.g. $[CpM(CO)_4]$ (M = V and Nb) are treated with $MeN(PF_2)_2$ under ultraviolet irradiation, mononuclear complexes **1** and **2** are formed as shown in Scheme 1 [10,78]. These are the first examples of compounds in which all four carbonyl groups of the $[CpM(CO)_4]$ unit have been completely replaced by other ligands. The intermediate dicarbonyl $[CpV(CO)_2\{MeN(PF_2)_2\}]$ can be obtained by carrying out the photochemical irradiation of equimolar quantities of the reactants.

3.2 Group 6

The reactions of diphosphinoamine ligands with Group 6 metal carbonyls were first reported by Payne et al [79,80]. The thermal reactions of $[M(CO)_6]$ (M = Mo or W) with diphosphinoamine ligands afford cis-chelate complexes,

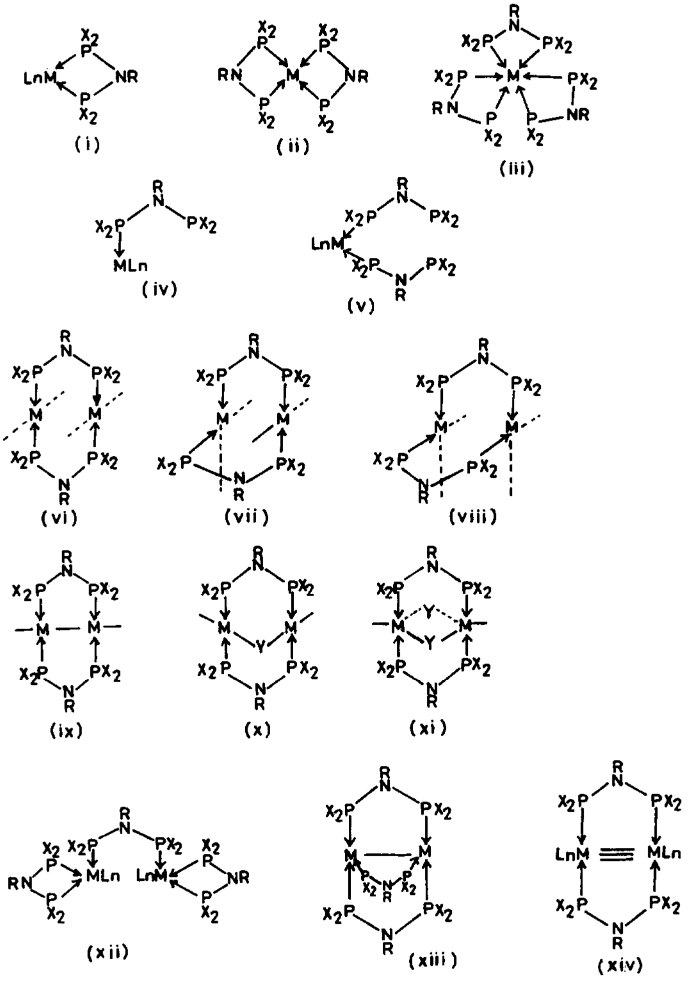
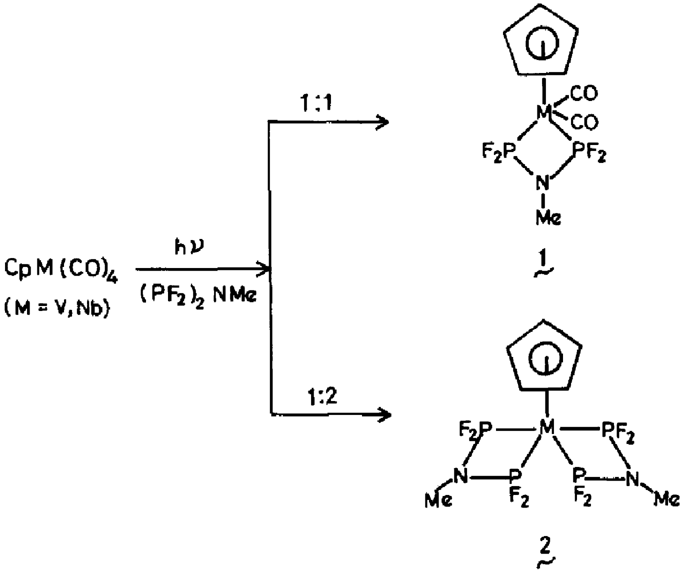


Fig. 1. Possible coordinating modes of diphosphinoamines.

$[M(CO)_4L{-}L]$($L{-}L$ = diphosphinoamine). An X-ray crystallographic study of the complex $[Mo(CO)_4(PPh_2)_2NEt]$ (3) [79] has confirmed that these complexes have the expected cis configuration of the carbonyl ligands. Subsequently, the reactions of $RN(PF_2)_2$ (R = Et, Me or Ph) ligands with Group 6 metal carbonyls have been extensively investigated, first by Johnson and Nixon [73] and later by King et al. [81–85].

The complexes have been prepared by one of three methods: (1) cocondensation of metal vapours with ligands, (2) photochemical reactions and (3) thermal reactions. The range of products formed in the reactions of $RN(PF_2)_2$ with Group 6 metal carbonyls and their derivatives is illustrated in Schemes 2 and 3.

The reactions of $RN(PF_2)_2$ (R = Me or Ph) with $[M(CO)_4NBD]$ (M = Cr, Mo

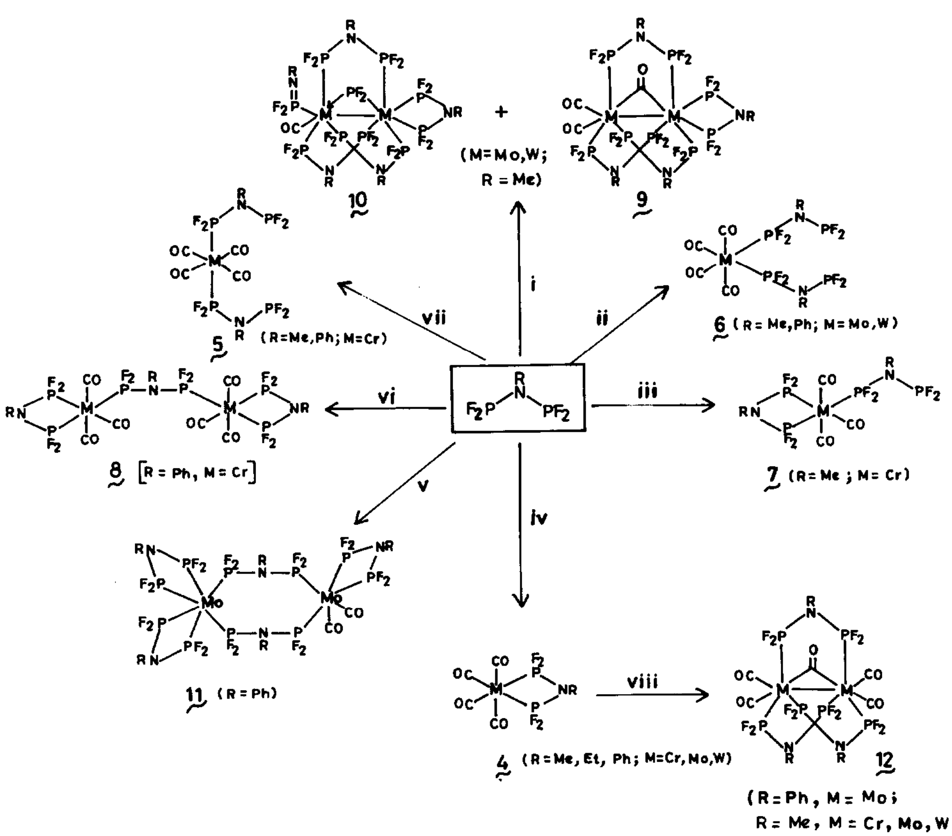


Scheme 1. [78].

or W) give either the chelates $[M(CO)_4(PF_2)_2NR]$ (**4**) or the monoligate monometallic complexes $[M(CO)_4\{(PF_2)_2NR\}_2]$ (**5**, **6**) depending on the reaction conditions.

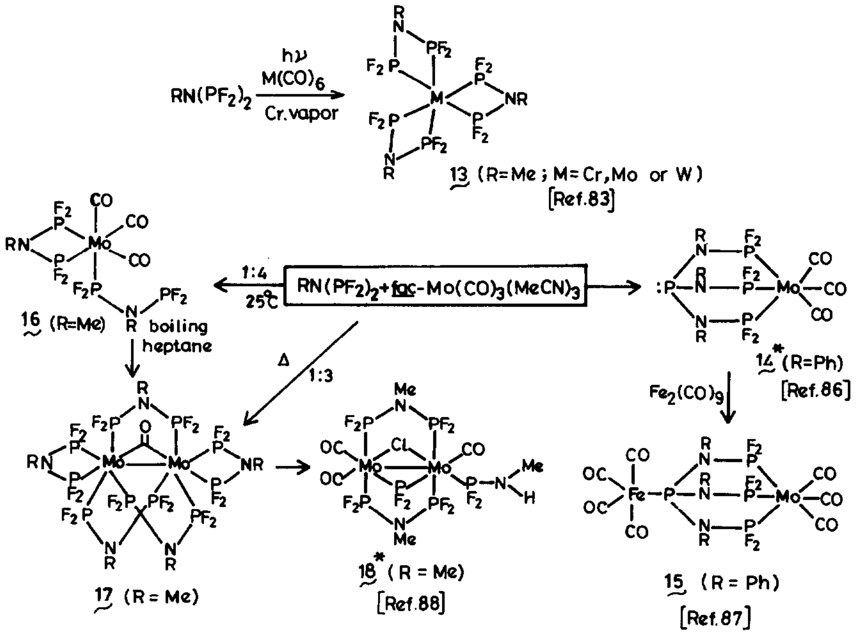
The reactions of the CHT complex, $[Cr(CO)_3(CHT)]$ with $RN(PF_2)_2$ ($R = Me$ and Ph) in a 1:2 molar ratio in boiling hexane gives $[Cr(CO)_3\{(PF_2)_2NR\}_2]$ (**7**), which exists as the meridonial isomer rather than the facial isomer to minimise the number of $RN(PF_2)_2$ ligands in mutual cis positions. The reaction of $PhN(PF_2)_2$ also affords the dinuclear complex, $[Cr_2(CO)_6\{PhN(PF_2)_2\}_3]$ (**8**). Pyrolysis or photolysis of mixtures of the $RN(PF_2)_2$ ligands and the metal carbonyls in a 1:2–2.5 metal–ligand molar ratio gives a mixture of the dinuclear complexes $[M_2(CO)_3\{(PF_2)_2NMe\}_4]$ (**9**) and $[M_2(CO)\{(PF_2)_2NMe\}_4(\mu\text{-}PF_2)(PF_2{=}NR)]$ (**10**) in the case of $MeN(PF_2)_2$ ($M = Mo$ and W) and the dinuclear complexes $[M_2(CO)_3\{(PF_2)_2NPh\}_4]$ (**9**) and $[M_2(CO)_2\{(PF_2)_2NPh\}_5]$ (**11**) in the case of $PhN(PF_2)_2$ ($M = Mo$). Pyrolysis of the molybdenum complexes $[Mo(CO)_4RN(PF_2)_2]$ (**4**) at 100–120°C results in extensive rearrangement to give the dinuclear complexes $[Mo_2(CO)_5\{RN(PF_2)_2\}_3]$ (**12**) ($R = Me$ or Ph) containing three biligate $RN(PF_2)_2$ ligands. The chromium and tungsten analogues $[M_2(CO)_5\{CH_3N(PF_2)_2\}_3]$ ($M = Cr$ or W) can be obtained by photolysis of the corresponding metal hexacarbonyls and $MeN(PF_2)_2$ in a 1:1–1.5 metal–ligand mole ratio [81,82].

Co-condensation of $MeN(PF_2)_2$ with Cr vapours affords $[Cr\{(PF_2)_2NMe\}_3]$ (**13**) in 48% yield [83]. Photochemical reactions of $[M(CO)_6]$ ($M = Cr$, Mo or W) with an excess of $MeN(PF_2)_2$ give completely substituted complexes, $[M\{(PF_2)_2NMe\}_3]$, which are the first known carbonyl free chelate complexes of Group 6 metals [84,85]. They are volatile and stable to air oxidation. Such complete



Scheme 2. (i) [Mo(CO)$_3$CHT]/thermal (1:2.2 M/L ratio) or W(CO)$_6$ (1:2.5 M/L ratio); (ii) [M(CO)$_4$NBD] (1:4 M/L ratio); (iii) M(CO)$_3$CHT (1:3 M/L ratio); (iv) [M(CO)$_4$NBD] (1:1 M/L ratio); (v) Mo(CO)$_6$ (1:2.5 M/L ratio)/thermal; (vi) M(CO)$_3$CHT (1:2 M/L ratio); (vii) [Cr(CO)$_4$NBD] (1:2 M/L ratio; sealed tube); (viii) pyrolysis in hydrocarbon solvents at 100–120°C [81,82].

substitution of CO groups from Group 6 metal carbonyls by diphosphino alkanes $Ph_2P(CH_2)_nPPh_2$ ($n = 2$–4) has not been achieved either thermally or photochemically. Reaction of fac-$[Mo(CO)_3(CH_3CN)_3]$ with $PhN(PF_2)_2$ gives a novel bicyclo[2.2.2]octane-like cage chelate $[Mo(CO)_3\{PF_2NPh\}_3P]$ (**14**) by condensation of three $PhN(PF_2)_2$ ligands [86]. Reaction of **14** with an excess of $Fe_2(CO)_9$ in boiling diethyl ether results in complexation of the free phosphorus atom to give the heterobimetallic complex $[(CO)_4Fe\{P(PhNPF_2)_3\}Mo(CO)_3]$ (**15**) [87]. Unexpectedly, a subtle change in the R group of the ligand, $(PF_2)_2NR$ from Ph to Me is sufficient to prevent PF_3 elimination to give a complex analogous to **14**. Instead, the reaction of fac-$[Mo(CO)_3(CH_3CN)_3]$ with $MeN(PF_2)_2$ yields either mononuclear fac-$[Mo(CO)_3\{(PF_2)_2NMe\}_2]$ (**16**) or dinuclear $[Mo_2(CO)\{(PF_2)_2NMe\}_5]$ (**17**) depending on the experimental conditions. Another unusual compound $[Mo(CO)_2\{\mu\text{-}MeN(PF_2)_2\}_2(\mu\text{-}PF_2)(\mu\text{-}Cl)Mo(CO)(PF_2NHMe)]$ (**18**) is obtained in trace amounts

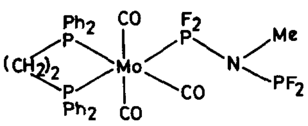


Scheme 3.

from the above reaction, apparently because of the presence of trace amounts of HCl as an impurity in the reaction mixture. This novel quadruply bridged dinuclear complex **18** is obtained in considerably higher yield from the reaction of $[Mo_2(CO)_5\{MeN(PF_2)_2\}_3]$ (**12**) with $Et_3N{\cdot}HCl$ in acetonitrile [88].

The photochemical reaction of $[Mo(CO)_4(dppe)]$ with $MeN(PF_2)_2$ affords complexes of the type fac-$[Mo(CO)_3(dppe)(PF_2)_2NMe]$ (**19**) and $[Mo(CO)_2(dppe)(PF_2)_2NMe]$ (**20**) in which the $MeN(PF_2)_2$ ligand exhibits monodentate or bidentate coordination behaviour, respectively [89]. The reaction of $[CpMo(CO)_2(NO)]$ with $MeN(PF_2)_2$ in boiling benzene gives the yellow-orange solid $[CpMo(CO)(NO)(PF_2)_2NMe]$ (**21**) in low yield. The thermal reaction of $[CpM(CO)_3Cl]$ (M = Mo or W) with $MeN(PF_2)_2$ results in the formation of an orange complex, $[CpM(CO)_2(PF_2)_2NMe(Cl)]$ (**22**); however, ultraviolet irradiation of $[CpM(CO)_3Cl]$ in the presence of an excess of $MeN(PF_2)_2$ in diethylether affords the yellow carbonyl-free complexes $[CpM\{(PF_2)_2NMe\}_2Cl]$ (**23**) [90,91].

Fischer et al. have demonstrated that the photochemical reaction of the carbyne complex, $[Br(CO)_4W{\equiv}C(C_6H_4Me\text{-}p)]$ with $MeN(PF_2)_2$ gives the violet diamagnetic ditungsten double-bonded complex **24** containing two bridged bidentate $MeN(PF_2)_2$ ligands [92]. Cotton et al., have reported a low-yield synthesis of the triply bonded dimolybdenum complex **25** starting from $[Mo_2Cl_8]^{2-}$ and $MeN(PF_2)_2$ [74]. Paine and co-workers have reported complexes of the type **26** and **27**, which may be regarded as being derived from a mono- and di-cationic diphosphinoamine ligand [93].



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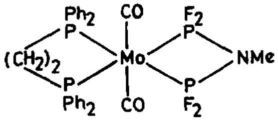

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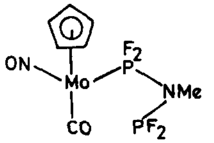

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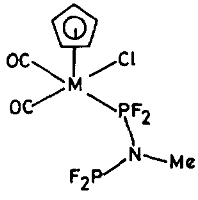

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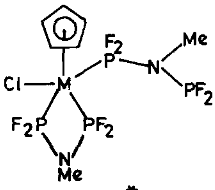

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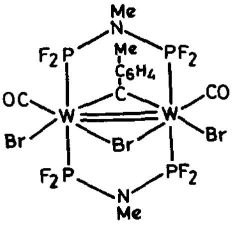

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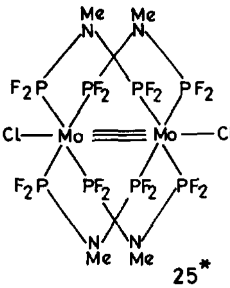

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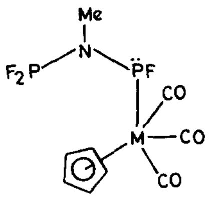

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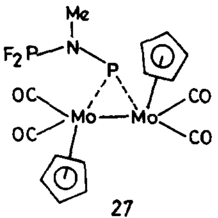
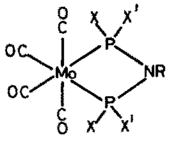


27

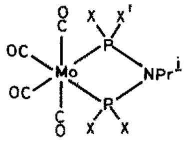
Thermal reactions of $PhN(PX_2)_2$ (X = Cl, NHPh) with $[Mo(CO)_4(C_7H_8)]$ afford the chelate complexes, *cis*-$[M(CO)_4(PX_2)_2NR]$ (**28**) in moderate yields. The complex, $[Mo(CO)_4(PCl_2)_2NPh]$ reacts with $PhNH_2/Et_3N$ or Pr^iNH_2/Et_3N to form $[Mo(CO)_4\{P(NHPh)_2)\}_2NPh]$ or $[Mo(CO)_4\{(NHPr^i)_2PN(Pr^i)P(NHPh)(NHPr^i)\}]$ (**29**), respectively [94]. The latter complex is formed, apparently as a result of a transamination reaction. An analogous complex, $[Mo(CO)_4\{(Pr^iNH)(Ph)PN(Pr^i)P(Ph)(NHPr^i)\}]$ (**30**) has also been reported [95].

Diphosphinoamine ligands of the type $RN(PX_2)_2$ (R = Me, X = OMe, OCH_2CF_3 or OPh; R = Ph, X = OPh, OCH_2CF_3 or OC_6H_4Br-p; R = Pr^i, X = Ph) react with the tetracarbonyl derivatives, *cis*-$[M(CO)_4(C_7H_8)]$ (M = Cr, Mo) or *cis*-$[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W) to form the chelate complexes, *cis*-$[M(CO)_4(PX_2)_2NR]$ (**31**) [96]. Pyrolysis or thermal decarbonylation of these chelated



28 R = Ph; X = X' = Cl or NHPh*

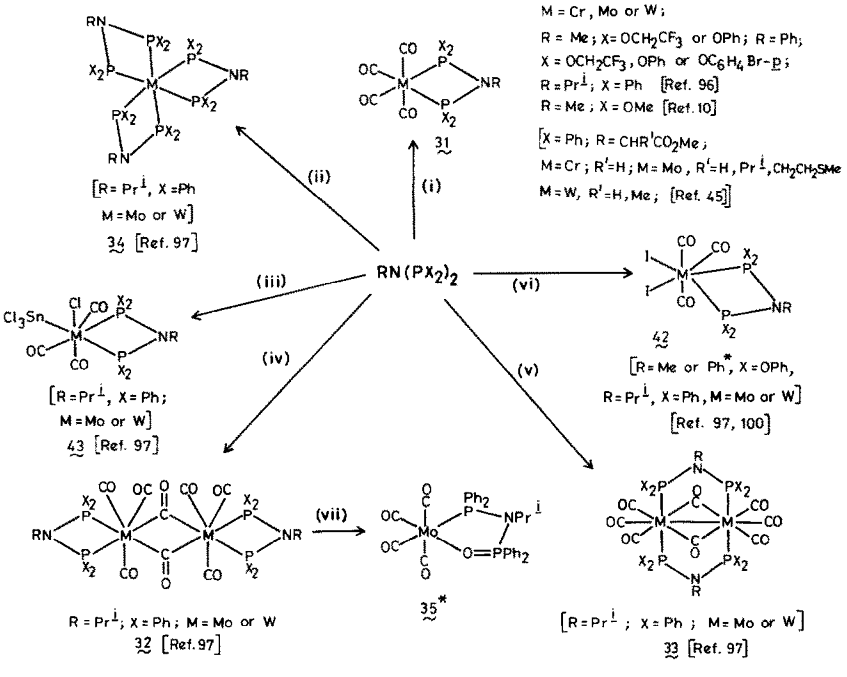
30* R = Pr^i; X = Ph; X' = NHPr^i



29* X = NHPr^i; X' = NHPh

complexes with an excess of the ligand does not lead to any further change. Attempts to substitute additional CO groups by using trimethylamine-*N*-oxide have also been unsuccessful. However, in the reactions of Group 6 metal carbonyls or their derivatives with $Pr^iN(PPh_2)_2$, binuclear complexes of the type **32** and **33** have been isolated. With this ligand, it has also been possible to effect complete substitution of the carbonyl groups thermally to obtain tris-chelated $[M\{(PX_2)_2NR\}_3]$ (**34**) [97] (see Scheme 4). The dinuclear complexes **32** and **33** are highly sensitive to air and moisture. Recrystallization of **32** from diethyl ether has led to the isolation of the novel heterofunctional chelate derivative **35** due to the adventitious entry of dioxygen [97].

Recently, Mague and Johnson [42] have investigated the reactions of

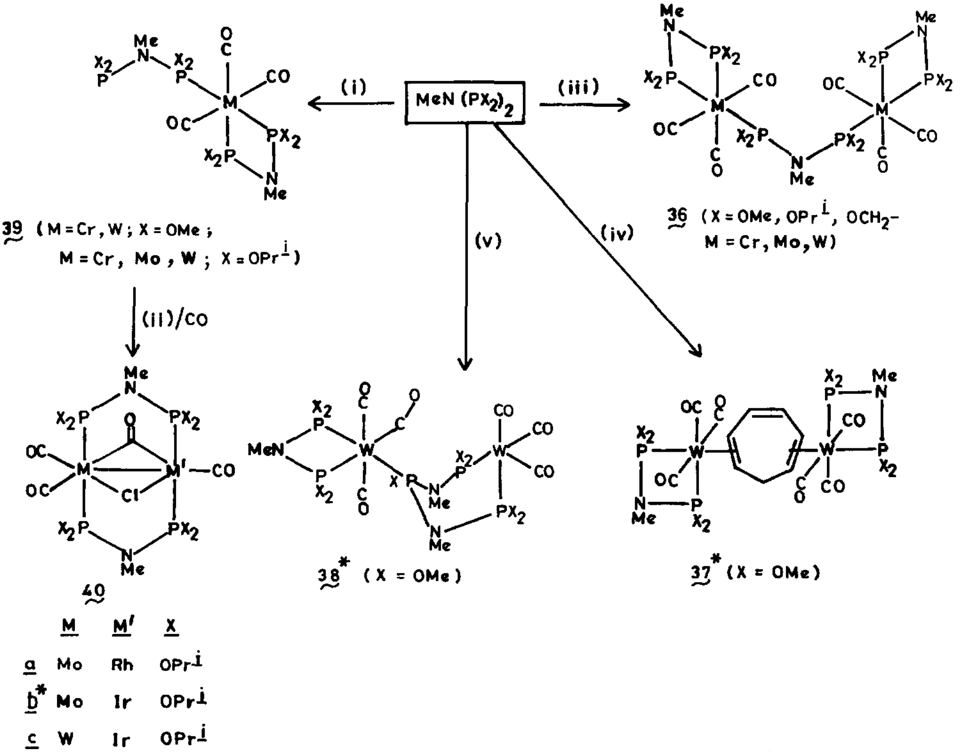


Scheme 4. (i) $[M(CO)_4NBD]$(M = Cr or Mo) or $[M(CO)_4(NHC_5H_{10})_2]$(M = Mo or W); (ii) $[M(CO)_3(NCMe)_3]$ (M = Mo or W); (iii) $[MCl(SnCl_3)(CO)_3(NCMe)_3]$ (M = Mo or W); (iv) and (v) $[M(CO)_3(NCMe)_3]$ (1:3 M/L ratio); (vi) $[M(I)_2(CO)_3(NCMe)_2]$ (M = Mo or W); (vii) recrystallization from Et_2O.

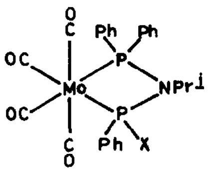
$MeN(P(OR)_2)_2$ (R = Me, Pr^i, CH_2–) ligands with $M(CO)_3(CHT)$, and the products isolated (**36**–**39**) are shown in Scheme 5. The ligand-bridged dimers (**36**) are obtained as all-mer, all-fac and mer-fac isomers, depending on the experimental conditions. Two minor products of the reaction of $[W(CO)_3(CHT)]$ and $MeN(P(OMe)_2)_2$ are the novel cycloheptatriene bridged dimer **37** [98] and the dinuclear complex $[W_2(CO)_6\{MeN(P(OMe)_2)_2\}(MeOP\{NMeP(OMe)_2\}_2)]$ **38** in which the conversion of the diphosphinoamine ligand into a triphosphazane ligand has occurred either during the original reaction or at the time of chromatographic work-up of the crude reaction mixture.

The reaction of **39** with $[Rh(Cl)(COD)]_2$ in diethylether under CO atmosphere gives the hetero-bimetallic complex $[RhMoCl(CO)_4\{MeN[P(OPr^i)_2]_2\}_2]$ (**40**). An iridium analogue of **40** could be obtained similarly as air-stable orange crystals from **39** and $[IrCl(COD)]_2$ followed by reaction with carbon monoxide [42].

The reactions of $Mo(CO)_4(NHC_5H_{10})_2$ with the heterofunctional diphosphazanes $[Ph_2PN(Pr^i)P(Ph)(X)]$ (X = OC_6H_4Me-*p*, OC_6H_4Br-*p*, $OC_6H_3Me_2$, 3,5-dimethyl pyrazolyl) in dichloromethane give the chelate complexes of the type **41**. The reaction of dimethyl pyrazolyl-substituted diphosphinoamine with fac-

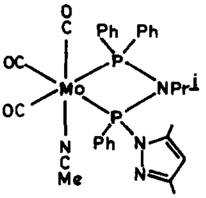


Scheme 5. [42,98]. (i) $M(CO)_3CHT$ (1.5 : 1 L/M ratio). (ii) $[M'Cl(COD)]_2$. (iii) $M(CO)_3CHT$ (2 : 1 L/M ratio). (iv) $W(CO)_3CHT$. (v) $W(CO)_3CHT$ (1.5 : 1 L/M ratio).

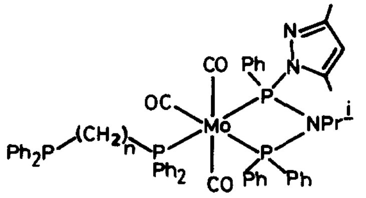


41

X = OC_6H_4Me-*p*,
OC_6H_4Br-*p*,
$OC_6H_3Me_2$-2,6



41a*



41b n = 1

41c n = 2

$[Mo(CO)_3(MeCN)_3]$ in acetonitrile gives the yellow complex fac-$[Mo(CO)_3(NCMe)$-$\{Ph_2PN(Pr^i)PPh(3,5$-dimethyl pyrazolyl$)\}]$ (**41a**) in which the pyrazolyl-substituted diphosphinoamine acts as a chelating ligand with its two phosphorus centres and a MeCN molecule remains coordinated to the metal. The acetonitrile complex **41a** reacts with PPh_3 or $P(OPh)_3$ to yield at first fac-$[Mo(CO)_3(PX)_3(L)]$, which in turn undergoes intramolecular rearrangement to give the mer isomer [46a]. Treatment of **41a** with dppm or dppe yields mer isomers of dppm or dppe complexes of the types **41b** and **41c**, respectively [46]. This behaviour provides a contrast to the analogous reaction of $[Mo(CO)_3(MeCN)(dppm)]$ with dppe wherein the dppe ligand replaces the chelating dppm which is coordinated in monodentate fashion [99]. The strong tendency of diphosphinoamine to form chelate complexes is evident from these results.

The reactions of $[MI_2(CO)_3(NCCH_3)_2]$ (M = Mo, W) with $RN(PX_2)_2$ (R = Me or Ph, X = OPh; R = Pr^i, X = Ph) in dichloromethane at 25°C give new seven-coordinated Mo(II) and W(II) complexes of the type $[MI_2(CO)_3(PX_2)_2NR]$ (**42**) [97,100] (Scheme 4). These are the first examples of seven-coordinated Group 6 metal carbonyl derivatives containing diphosphinoamine ligands. The structure of the tungsten complex, $[WI_2(CO)_3(P(OPh)_2)_2NPh]$ has been determined by single-crystal X-ray diffraction which reveals a pentagonal bipyramidal geometry around the metal centre akin to that of the analogous dppm complex [101]. [(Trichlorostannyl)(chloro)tricarbonyl] M(II) (**43**) (M = Mo or W) derivatives of $RN(PX_2)_2$ (R = Pr^i; X = Ph) have also been isolated [97] (see Scheme 4).

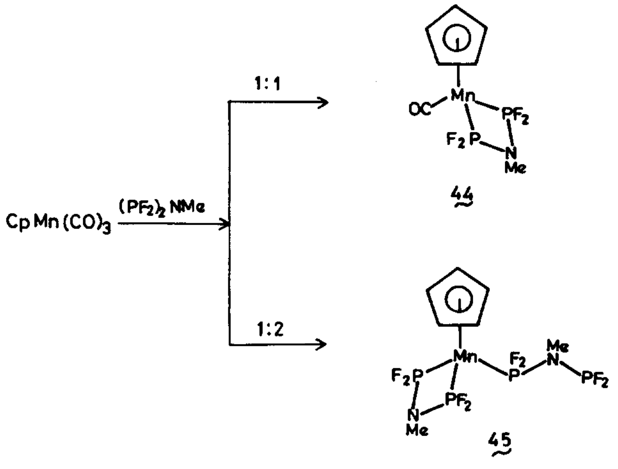
3.3 Group 7

Only a few diphosphinoamine complexes of Mn are known. Ultraviolet irradiation of [$CpMn(CO)_3$] with $MeN(PF_2)_2$ gives [$CpMn(CO)(PF_2)_2NMe$] (**44**) containing a chelating $MeN(PF_2)_2$ ligand and the carbonyl-free complex [$CpMn\{(PF_2)_2NMe\}_2$] (**45**) containing one bidentate and one monodentate $MeN(PF_2)_2$ ligand [90] (see Scheme 6). These complexes are yellow liquids and are highly air-sensitive. A carbene complex of the type [$(MeC_5H_4)Mn(PF_2)_2NMe\{C(OMe)Me\}$] (**46**) has been isolated in 82% yield from the reaction of [$(MeC_5H_4)Mn(CO)_2C(OMe)Me$] with $MeN(PF_2)_2$ under UV irradiation [102].

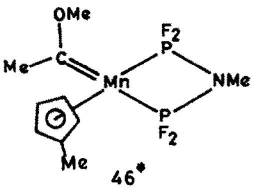
Recently, Walton and co-workers reported the triply bonded dirhenium complexes of $NH(PPh_2)_2$ (dppa). The reactions of dirhenium(III) carboxylates of the type [$Re_2(O_2CMe)_2X_4(H_2O)_2$] (X = Cl, Br) with dppa in hot ethanol gives mixed halide–phosphine complexes with two, one or zero bridging acetato ligands. The yellow paramagnetic dirhenium complex [$Re_2(O_2CMe)X_4(dppa)_2$] (**47**) is obtained when the duration of the reaction is kept short (ca. < 3 min). A longer reaction time (> 15 min) favours the formation of *trans*-[$Re_2(O_2CMe)_2X_2(dppa)_2$] (**48**) containing two bridged acetato ligands. The trans complex **48** is converted into *cis*-[$Re_2(O_2CMe)_2X_2(dppa)_2$] (**49**) after several days. Reductive decarboxylation of **47** gives [$Re_2X_4(dppa)_2$] (**50**), which on electrolysis in the presence of $Bu^n_4NPF_6$ in CH_2Cl_2 yields a red monocation [$Re_2Cl_4(dppa)_2$]$^+$ in solution. Oxidation of **49** (X = Cl) with [η^5-Cp_2Fe]PF_6 gives paramagnetic *cis*-[$Re_2(O_2CMe)_2Cl_2(dppa)_2$]$PF_6$ which is structurally characterized [103–105].

3.4 Group 8

Co-condensation of iron vapours with $MeN(PF_2)_2$ gives yellow air-stable crystals of [$Fe\{(PF_2)_2NMe\}_4$] (**51**) in very low yields. This complex contains one bidentate



Scheme 6. [90].



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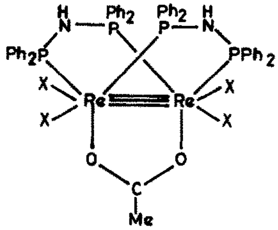

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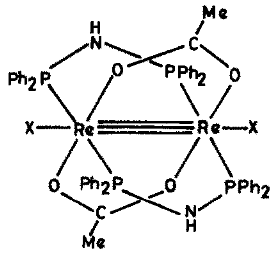
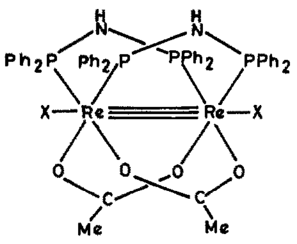
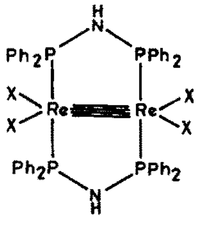


(X = Cl, Br) 48*



(X = Cl*, Br) 49



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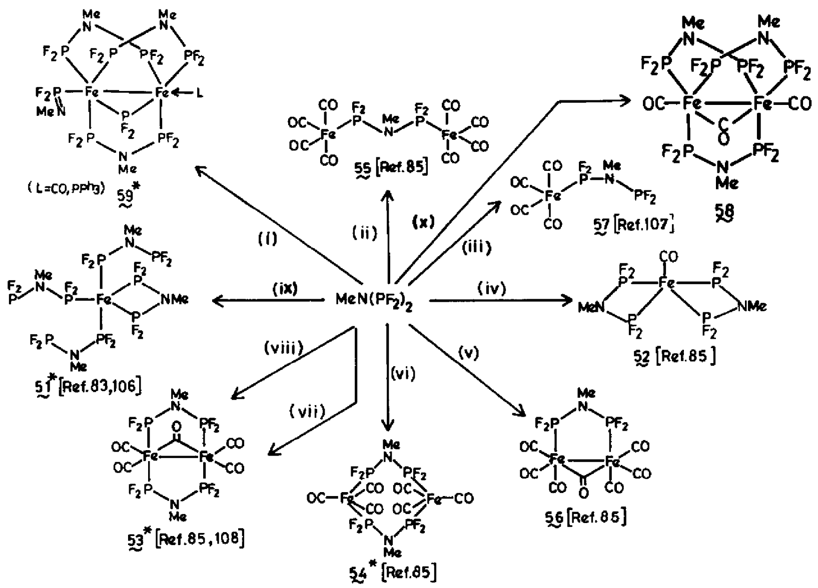
(X = Cl*, Br)

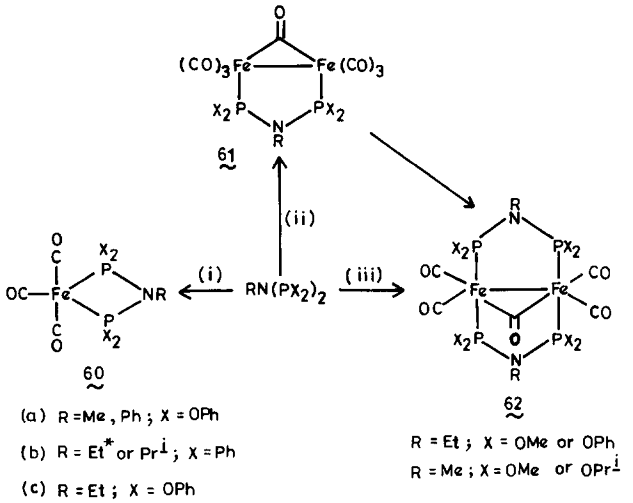
and three monodentate $MeN(PF_2)_2$ ligands. Co-condensation of a 1:4 mixture of $MeN(PF_2)_2$ and Me_2NPF_2 with iron vapours gives the red-yellow mixed-ligand complex $[Fe(PF_2NMe_2)_3\{(PF_2)_2NMe\}]$ which is assigned a structure similar to that of **51** with the three monodentate $MeN(PF_2)_2$ ligands replaced by Me_2NPF_2 ligands [83,106].

Photochemical reactions of $MeN(PF_2)_2$ with $[Fe(CO)_5]$, $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ afford a variety of complexes (**52**–**59**), depending on the reaction conditions and the stoichiometry of the reactants [85,107–110]. Some typical reactions are shown in Scheme 7. Solvent plays a vital role in the reaction between iron carbonyls and diphosphinoamine ligands under UV irradiation. Ultraviolet irradiation of $[Fe(CO)_5]$ with an excess of $MeN(PF_2)_2$ in a polar solvent such as tetrahydrofuran gives the mononuclear yellow volatile complex $[Fe(CO)\{MeN(PF_2)_2\}_2]$ (**52**) but in a less polar solvent such as pentane, an orange crystalline biligate bimetallic



Scheme 7. (i) $Fe_3(CO)_{12}/Et_2O/h\nu$ (1:6 M/L ratio); (ii) $Fe_2(CO)_9/Et_2O/25°C$ (1:1 M/L ratio); (iii) $Fe_2(CO)_9/Et_2O/25°C$/excess ligand; (iv) $Fe(CO)_5/THF/h\nu$ (1:4 M/L ratio); (v) $Fe_2(CO)_9/Et_2O/25°C$; (vi) $Fe_3(CO)_{12}/THF/h\nu/$ (1:2.5 M/L ratio); (vii) $Fe_3(CO)_{12}$/THF/reflux/ (1:4 M/L ratio); (viii) $Fe(CO)_5/pentane/h\nu$ (1:1 M/L ratio); (ix) Fe vapours (x) $Fe_3(CO)_{12}/h\nu/$ (2.1:1 M/L ratio).

complex $[Fe_2(CO)_5\{MeN(PF_2)_2\}_2]$ (**53**) is obtained. The dinuclear complex **53** can also be obtained from a thermal reaction between $[Fe_3(CO)_{12}]$ and $MeN(PF_2)_2$ in boiling THF; a second yellow bimetallic product $[Fe(CO)_3\{MeN(PF_2)_2\}]_2$ (**54**) is also formed in this reaction. Complex **54** loses carbon monoxide in solution to form the pentacarbonyl derivative **53**. The reaction of $[Fe_2(CO)_9]$ with $MeN(PF_2)_2$ in THF at room temperature gives **55** in addition to $[Fe_2(CO)_7\{MeN(PF_2)_2\}]$ (**56**) as a minor product [85]. Reaction of an excess of $MeN(PF_2)_2$ with $[Fe_2(CO)_9]$ in diethyl ether at room temperature gives the monoligate monometallic complex $[Fe(CO)_4\{MeN(PF_2)_2\}]$ (**57**) as a yellow distillable product [107]. Complexes analogous to **53** and **56** are obtained from the reaction between $MeN\{P(OMe)_2\}_2$ and $[Fe_2(CO)_9]$ in boiling hexane [108]. The photochemical reaction of $[Fe_3(CO)_{12}]$ with $MeN(PF_2)_2$ (molar ratio 1:2.5) gives $[Fe_2(CO)_3\{\mu\text{-}(MeN(PF_2)_2)\}_3]$ (**58**); when an excess of the ligand (metal–ligand ratio 1:6) is used, an unusual complex, $[Fe_2(\mu\text{-}CO)(\mu\text{-}PF_2)(MeNPF_2)\{\mu\text{-}(MeN(PF_2)_2\}_3]$ (**59**) is obtained. The CO group in **59** can be substituted further by PPh_3 [109,110]. Photochemical reactions of $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$ with $RN(PX_2)_2$ afford both mononuclear and dinuclear complexes of the type $[Fe(CO)_3(PX_2)_2NR]$ (**60a**), $[Fe_2(CO)_7\{(PX_2)_2NR\}]$ (**61**) and $[Fe_2(CO)_5\{\mu\text{-}(PX_2)_2NR\}_2]$ (**62**), depending on the reaction conditions. The former complex, **61**, is structurally similar to the dppm complex $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}dppm\}]$ [111].

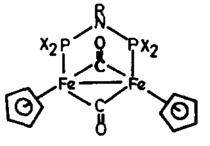


Scheme 8. (i) (a) $Fe(CO)_5/h\nu$, (b) $Fe(CO)_5/Me_3NO\cdot 2H_2O$, (c) $Fe_2(CO)_9$/reflux; (ii) $Fe_2(CO)_9/h\nu$ (1 : 2 L/M ratio); (iii) $Fe_2(CO)_9/h\nu$ (excess ligand) [96,97,111,112].

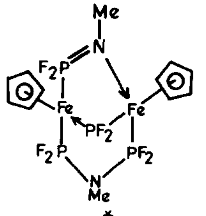
Treatment of $[Fe(CO)_5]$ with $Pr^iN(PPh_2)_2$ in the presence of trimethylamine *N*-oxide gives the chelate complex **60b** [97] (Scheme 8). The crystal structure of the analogous *N*-ethyl compound, $[Fe(CO)_3(PPh_2)_2NEt]$ has been reported [112].

Photochemical reaction of $MeN(PF_2)_2$ with $[FeCp(CO)_2]_2$ in THF or pentane yields the complex (**63a**) as the major product along with **64** (yield <10%). The latter complex, **64**, contains a bridging $MeN(PF)_2)_2$ ligand in addition to $MeN(PF_2)$ and PF_2 units which arise from the cleavage of one of the P—N bonds of the $MeN(PF_2)_2$ molecule. The $MeNPF_2$ unit acts as a bridging bidentate ligand through both phosphorus and nitrogen and the PF_2 unit also bridges the two metal centres [113]. A similar cleavage of $MeN(PF_2)_2$ ligand was also noted in the reaction of $Fe_3(CO)_{12}$ but the resulting complex **59** (Scheme 7) contains an $MeN{=}PF_2$ ligand which acts as a monodentate ligand through phosphorus [109]. A similar behaviour is observed in the reaction of $[FeCp(CO)_2]_2$ with the diphosphinoamine ligand, $PhN\{P(OPh)_2\}_2$ in boiling benzene and compounds **63b** and **65** have been isolated [114]. Treatment of $[FeCp(CO)_2Cl]$ with $MeN(PF_2)_2$ results in the successive replacement of the two carbonyl groups to afford the mononuclear complexes $[FeCp(CO)\{MeN(PF_2)_2\}Cl]$ (**66**) and $[FeCp\{MeN(PF_2)_2\}_2Cl]$ (**67**), respectively containing monoligated diphosphinoamine ligands [90,91].

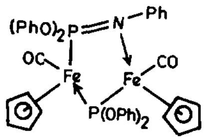
An interesting yellow complex, $[PhCH{=}CHC(Me){=}C\{P(O)F_2\}(NMePF_2)Fe(CO)(PF_2)_2NMe]$ (**68**) is obtained in low yield (11.6%) when $[\{PhCH{=}CHCOMe\}Fe(CO)_3]$ is treated with $MeN(PF_2)_2$ in boiling hexane. Single-crystal X-ray diffraction reveals an unexpected structure containing a novel chelate ligand bonding through both tetrahapto-1,3-diene and aminodifluorophosphino units [115]. The formation



63 a R = Me, X = F
b R = Ph, X = OPh
c R = Et, X = Ph



64*



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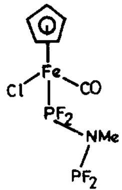

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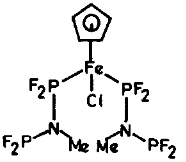
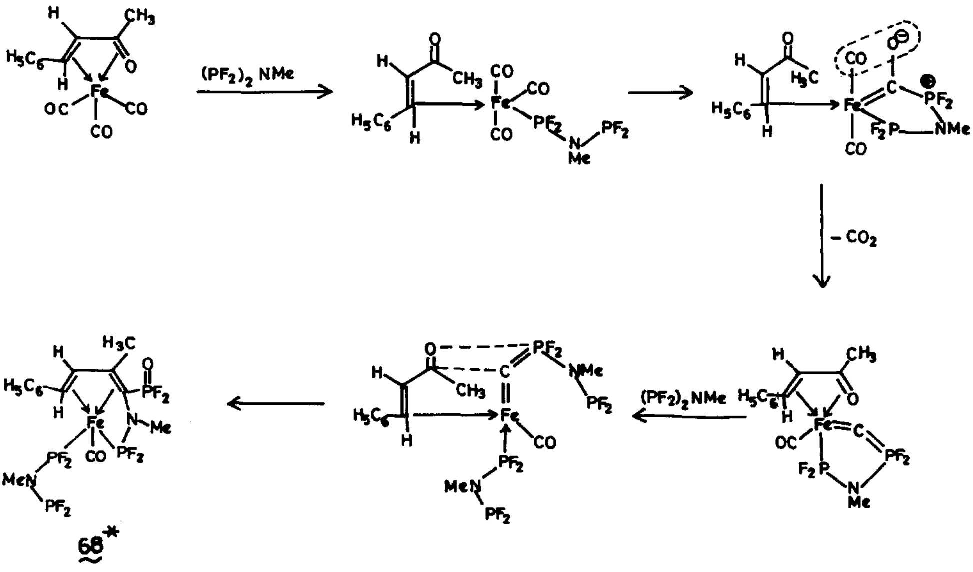


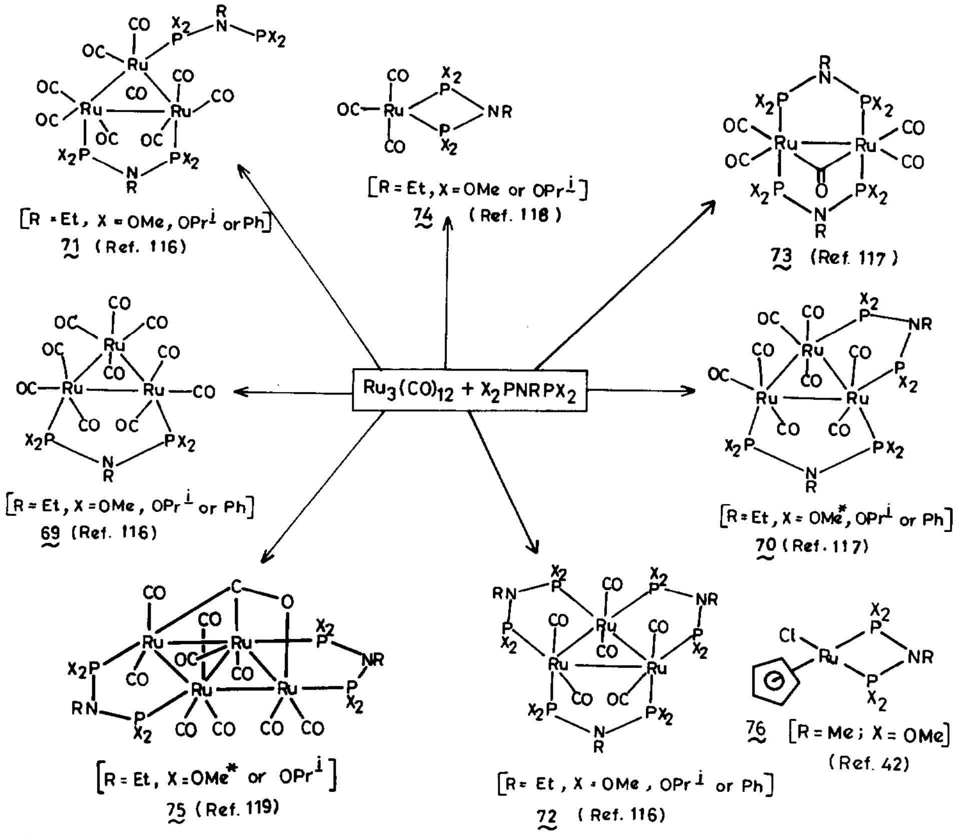
67

of this complex can be rationalised by a pathway that involves an intramolecular Wittig type reaction as a key step as shown in Scheme 9.

Haines and co-workers have investigated in detail the reactions of $[Ru_3(CO)_{12}]$ with diphosphazanes $RN(PX_2)_2$ (R = Et, X = OCH_2–, OMe, OEt, OPr^i or OPh, R = Me, X = OEt or OPr^i) and isolated mono-, di-, tri- and tetranuclear complexes, depending on the reaction conditions and the nature of the ligand. The results are summarized in Scheme 10 [13,116–118].



Scheme 9. [115].



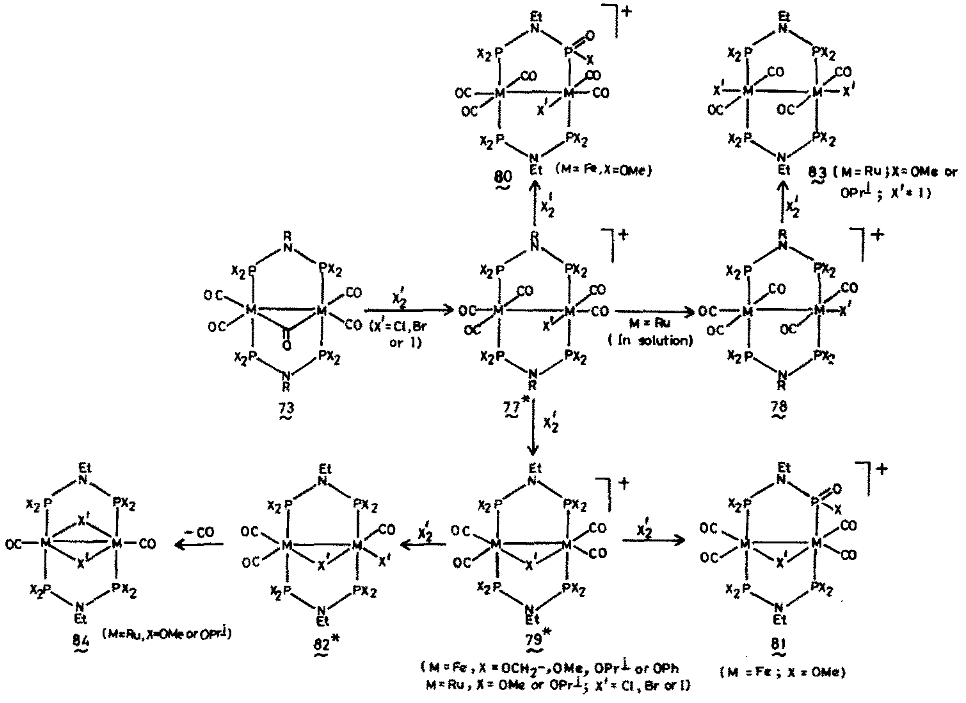
Scheme 10.

Irradiation of equimolar amounts of $[Ru_3(CO)_{12}]$ and the diphosphazane ligands, $RN(PX_2)_2$ (R = Et, X = OMe, OPr^i or OPh; R = Me, X = OMe or OPr^i) results in the simple replacement of two carbonyl groups and formation of **69–72**. However, in the presence of two- or three-fold molar equivalents of the ligand, the same reaction yields both dinuclear $[Ru_2(\mu\text{-}CO)(CO)_5\{\mu\text{-}(PX_2)_2NR\}_2]$ (**73**) and mononuclear $[Ru(CO)_3\{(PX_2)_2NR\}]$ (**74**) complexes [116–118]. On the other hand, the thermal reactions of $Ru_3(CO)_{12}$ with diphosphinoamine ligands follows a more complex course and yields a variety of products (**69–74**), including an interesting tetranuclear complex **75**. The Ru_3 framework remains intact and substitution of only carbonyl groups occurs when the diphosphinoamine ligand is $Ph_2PN(Et)PPh_2$; when the substituents on the phosphorus are OMe or OPr^i, the tetranuclear complex **75** is obtained as the major product. Treatment of the trinuclear complex $[Ru_3(CO)_8\{\mu\text{-}(PX_2)_2NEt\}]$ (**69**) with $Me_3NO{\cdot}2H_2O$ in MeCN in the presence of diphosphinoamine leads to the breakdown of the Ru_3 framework to afford diruthenium (**73**) and monoruthenium (**74**) complexes in addition to the triruthenium complex **70** as a minor product [119].

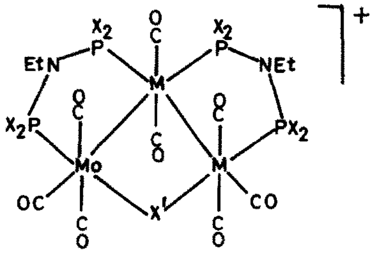
Mague and Johnson have isolated a mononuclear ruthenium complex, $[CpRuCl\{(P(OMe)_2)_2NMe\}_2]$ (**76**) from the reaction of the diphosphinoamine with [CpRu(COD)Cl] in acetone at room temperature [42].

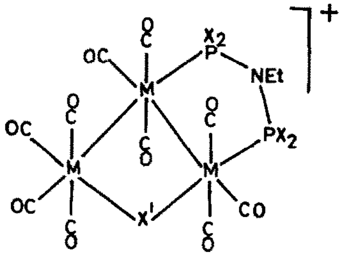
The tetrasubstituted diphosphinoamine bridged species $[M_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PX_2)_2NR\}_2]$ (**73**) are susceptible to electrophilic attack. They react with halogens to form $[M_2X'(CO)_5\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (M = Fe, R = Me or Et, X = OCH_2–, OMe, OPr^i or OPh; M = Ru, R = Me or Et, X = OMe, OPr^i or OPh; X′ = Cl, Br or I) (**77**) in which the halogen atom coordinates terminally; these pentacarbonyl species have been isolated as their BF_4 or PF_6 salts. The ruthenium pentacarbonyl species $(M_2X'(CO)_5\{\mu\text{-}(PX_2)_2NR\}_2]^+$ exist in two isomeric forms (**77** and **78**) in which the halogen is bonded either axially (**77**) or equatorially (**78**). This is in contrast to the iron analogue in which only one isomer is observed [116,120–122]. The isomer with an equatorially oriented halogen (**77**) decarbonylates more readily in solution to give a tetracarbonyl species $[M_2(\mu\text{-}X')(CO)_4\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (M = Fe or Ru; X = OCH_2–, OMe, OPr^i or OPh; X′ = Cl, Br or I) (**79**); the rate of decarbonylation increases slightly along the series $X' = Cl < Br < I$ and to some extent varies with alkoxy groups present on the phosphorus atoms ($OMe \ll OPr^i < OPh$). The decarbonylation can be accelarated in donor solvents such as dimethyl sulphoxide or acetone or in the presence of a decarbonylating agent such as trimethylamine *N*-oxide dihydrate [120]. The iron analogues of both pentacarbonyl species $[Fe_2X'(CO)_5\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (**77**) and tetracarbonyl species $[Fe_2(\mu\text{-}X')(CO)_4\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (**79**) are susceptible to halide ion attack at the phosphorus, affording the products $[Fe_2X'(CO)_5\{\mu\text{-}(PX_2)_2NR\}\{\mu\text{-}(X_2PN(R)P(O)X\}]^+$ (**80**) and $[Fe_2(\mu\text{-}X')(CO)_4\{\mu\text{-}(PX_2)_2NR\}\{\mu\text{-}(X_2PN(R)P(O)X\}]^+$ (X = OMe, R = Et, X′ = Cl, Br or I) (**81**), respectively, which arise as a result of a Michaelis-Arbuzov-type rearrangement [13] (Scheme 11). In contrast, the diruthenium species (**79**, M = Ru) reacts with halide ions to yield tricarbonyl species $[Ru_2(\mu\text{-}X')(X')(CO)_3\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (**82**). Treatment of diruthenium pentacarbonyl species (**77** or **78**, M = Ru) with iodide ions in the presence of an excess of $Me_3NO{\cdot}2H_2O$ gives a neutral tetracarbonyl dihalide derivative $[Ru_2(I)_2(CO)_4\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (**83**), which is stable in both polar and non-polar solvents and cannot be decarbonylated to tricarbonyl species **82** [121]. The tricarbonyl ruthenium derivative **82** undergoes further decarbonylation when treated with $Me_3NO{\cdot}2H_2O$ in acetone to give the dihalobridged dicarbonyl derivative $[Ru_2(\mu\text{-}X')_2(CO)_2\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (X = Cl or Br) (**84**) [120].

Recently, Haines and co-workers have investigated the halogenation behaviour of triruthenium complexes **69** and **70** (X = OMe or OPr^i) and their triosmium analogues. Thus, treatment of $[M_3(CO)_8\{\mu\text{-}(PX_2)_2NR\}_2]$ (**70**) and $[M_3(CO)_{10}\{\mu\text{-}(PX_2)_2NR\}]$ (**69**) with halogens in the presence of NH_4PF_6 or $NaBPh_4$ leads to the formation of cationic complexes $[M_3(\mu\text{-}X')(CO)_8\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (**85**) and $[M_3(\mu\text{-}X')(CO)_{10}\{\mu\text{-}(PX_2)_2NR\}_2]^+$ (**86**), respectively, in which the halogen bridges an open edge of the metal frame. In an attempt to synthesize the di-iodo species $[M_3X'_2(CO)_8\{\mu\text{-}(PX_2)_2NR\}]$, the authors have carried out the reaction of $[M_3(\mu\text{-}$



Scheme 11. [116,120–122].



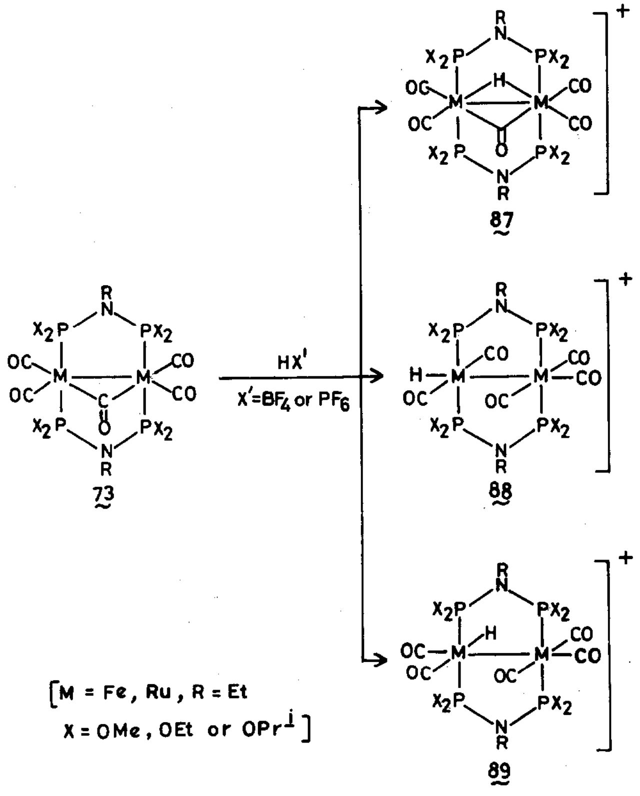


85 (M = Ru, Os; X = OMe, OPr^i; X' = Cl, Br, I) 86

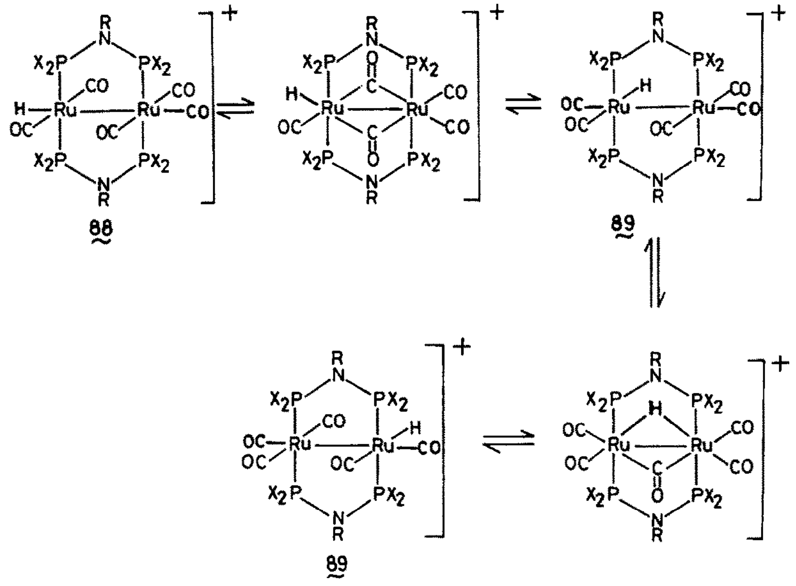
X')(CO)$_8${μ-(PX$_2$)$_2$NR}$_2$]$^+$ (**85**) (M = Os, X = OMe) with an excess of iodide ions; the reaction does occur, but the iodide ion further acts as reducing agent to give the parent species [M$_3$(CO)$_8${μ-(PX$_2$)$_2$NR}$_2$] (**70**) [122].

Haines and co-workers have also investigated the protonation reactions of diruthenium and di-iron complexes of the type **73**. The products obtained again depend on both the metal as well as the ligand bridging the two metal centres. Treatment of the diruthenium complex (**73**) with HBF$_4$ or HPF$_6$ yields crystalline cationic hydrido complexes $[M_2H(CO)_5\{\mu\text{-}(PX_2)_2NR\}_2{}'X]$ (**87**–**89**) ($X'=BF_4$ or PF_6) in which hydride ligand is terminal in **88** and **89** (M = Ru; R = Et, X = OMe or OPr^i) and bridging in **87** (M = Fe; R = Et, X = OMe, OEt or OPr^i) (Scheme 12). This protonation is reversible, unlike the case with ditertiary phosphine complexes which can be deprotonated only by strong bases such as $NaBH_4$. It may be noted that the analogous dppm complex, $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-dppm})_2]$ affords a protonated product in which the proton has effectively added across the two ruthenium atoms [123]. In contrast, the diphosphinoamine iron complexes are found to be readily deprotonated by solvents even in the absence of an excess of an acid. The ease of deprotonation increases along the series X = OEt < OPr^i < OMe < OPh [123].

The variable-temperature $^{31}P\{^1H\}$ NMR spectrum of $[Ru_2H(CO)_5\{\mu\text{-}(PX_2)_2NEt\}_2]X'$ (**88**) (X = OMe or OPr^i; $X'=BF_4$ or PF_6) reveals the presence of predominantly two isomers in solution (**88** and **89**) and the possible intermediates involved in the fluxional process are illustrated in Scheme 13. The rate of protonation of **73** has also been studied and can be markedly increased by the addition of water to the reaction mixture. The authors propose that initial attack of a proton at the



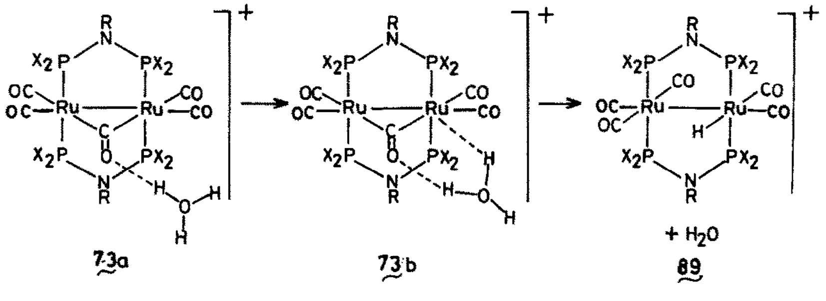
Scheme 12. [123].



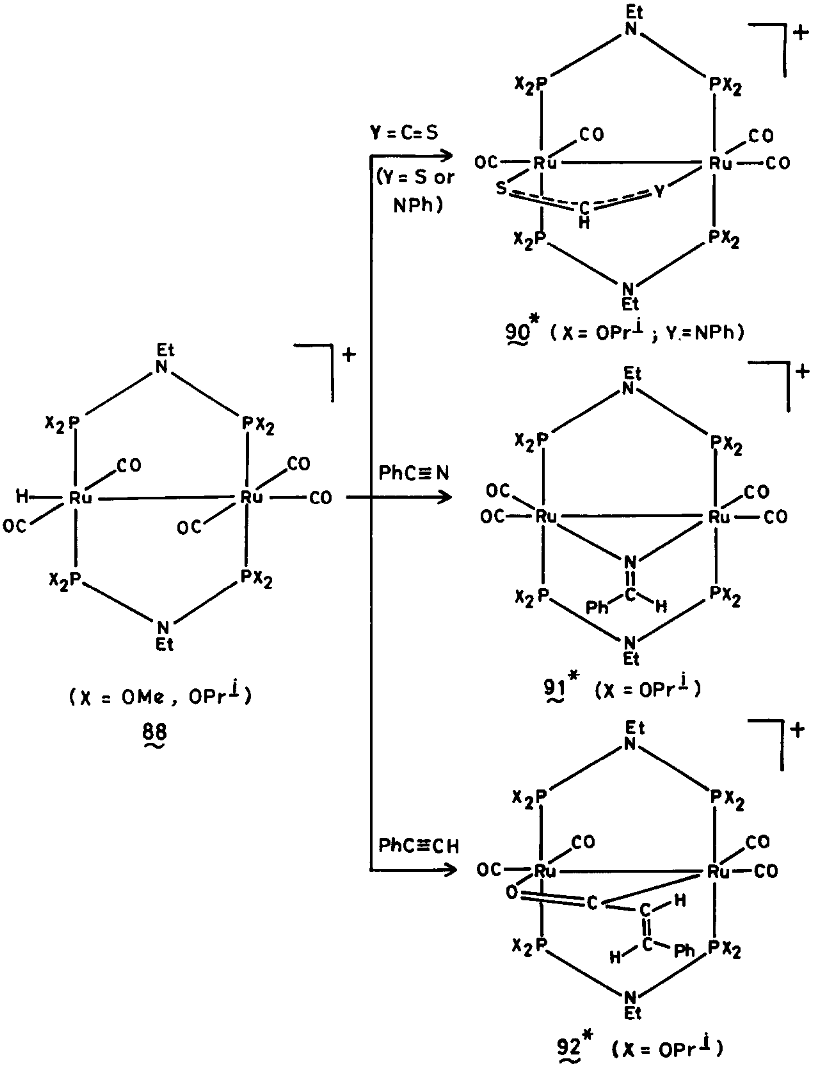
Scheme 13. [123].

bridging carbonyl group is followed by its transfer to ruthenium via a six-membered transition state (**73b**) as shown in Scheme 14. Apparently, water catalyses the transfer of the proton from a bridging carbonyl oxygen to ruthenium [123].

Di-iron and diruthenium species of the type $[M_2(\mu\text{-CO})(CO)_4\{\mu\text{-}(PX_2)_2NEt\}_2]$ (M = Fe, Ru; X = OMe or OPr^i) (**73**) containing bridging diphosphinoamine ligands, have been subjected to cyclic voltametric studies in acetone and benzonitrile. The oxidation of $[Fe_2(\mu\text{-CO})(CO)_4\{\mu\text{-}(PX_2)_2NEt\}_2]$ generally proceeds via an EEC mechanism (E = electron transfer, C = chemical step), whereas oxidation of $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-}(PX_2)_2NEt\}_2]$ proceeds via an ECE mechanism, for which removal of the second electron is easier than the first, giving rise to an overall two-electron transfer reaction. In both the mechanisms, the chemical step involves solvent attack [124].

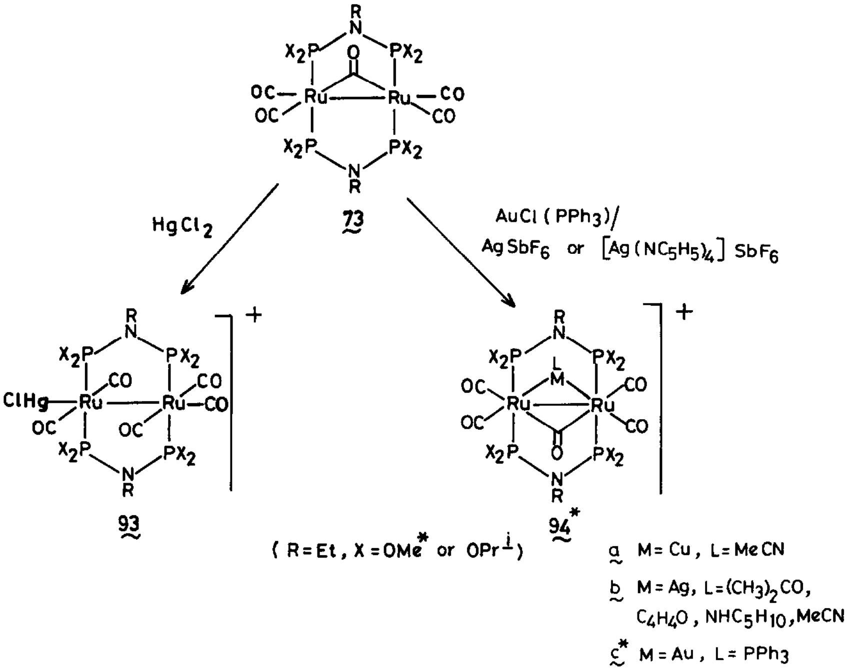


Scheme 14. [123].



Scheme 15. [125].

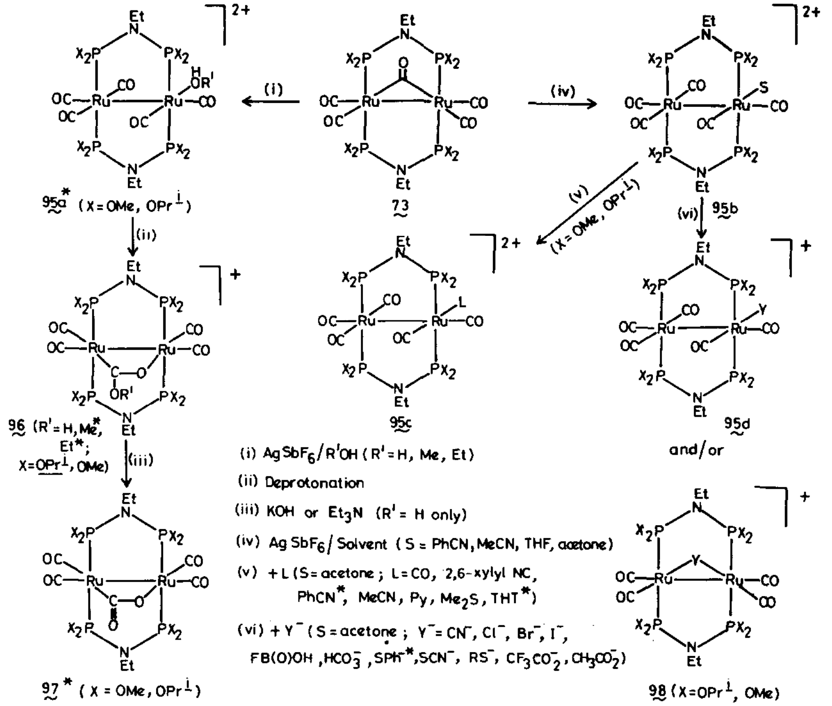
The reactions of **88** with unsaturated compounds such as alkynes, nitriles and carbon disulphide give three-, four- or five-membered dimetallocyclic species (**90–92**), depending on the nature of the unsaturated system as shown in Scheme 15 [125]. The diruthenium species $[Ru_2(\mu\text{-}CO)(CO)_4\{(PX_2)_2NEt\}_2]$ (**73**) (X = OMe, OPr^i) react readily with $HgCl_2$ to give a cationic cluster complex $[Ru_2(HgCl)(CO)_5\{\mu\text{-}(P(OR)_2)_2NEt\}_2]^+$ (**93**), in which the HgCl fragment is coordinated terminally to ruthenium. On the other hand, reaction of **73** with $[Cu(MeCN)_4]^+$, $[Ag(NHC_5H_{10})_4]SbF_6$ or $[AuCl(PPh_3)]$ affords $[Ru_2(\mu\text{-}ML)(\mu\text{-}CO)(CO)_4\text{-}\{\mu\text{-}$



Scheme 16. [126].

$(PX_2)_2NEt\}_2]^+$ (L = acetone, MeCN, THF or C_5H_5N) (**94**) in which the metal substrate is coordinated to the ruthenium centres in the bridging mode (Scheme 16). The silver(I) adducts (**94b**) degrade to elemental silver and the radical cation of **73**, which in turn disproportionates in solution to the parent compound **73** and the dicationic solvento species, $[Ru_2(CO)_5\,(solvent)\{\mu\text{-}(PX_2)_2NR\}_2]^{2+}$ (**95b**) (Scheme 17) [126,127].

A different reactivity pattern is observed when the oxidation by silver salts is carried out in the presence of protic solvents of the type R'OH. Thus, treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PX_2)_2NEt\}_2]$ (**73**) (X = OMe or OPr^i) with silver(I) salts in the presence of R'OH (R' = H, Me or Et) yields the solvento species of the type **95a**, which undergo deprotonation by weak bases such as pyridine or an equimolar amount of triethylamine and rearranges to give $[Ru_2\{\mu\text{-}OC(OR')\}(CO)_4\{\mu\text{-}(PX_2)_2NEt\}_2]^+$ (**96**). The carboxylic acid derivative $[Ru_2\{\mu\text{-}OC(OR')\}(CO)_4\{\mu\text{-}\{(PX_2)_2NEt\}_2]SbF_6$ (**96**, R' = H) can be further deprotonated by stronger bases such as KOH or an excess of triethylamine to give a neutral product, $[Ru_2\{\mu\text{-}OC(O)\}(CO)_4\{\mu\text{-}(PX_2)_2NEt\}_2]$ (**97**) containing a bridging carbon dioxide group confirmed by X-ray crystallography [128]. The acetone molecule in $[Ru_2(CO)_5(OCMe_2)\{\mu\text{-}(P(OR)_2)_2NEt\}_2]^{2+}$ (**95b**) is readily replaced by various nucleophiles to afford products of the type $[Ru_2(CO)_5(L)\{\mu\text{-}(P(OR)_2)_2NEt\}_2]^{2+}$ (**95c**), where L is a neutral ligand such as CO, $Me_2C_6H_3NC$, PhCN, C_5H_5N, H_2O, Me_2S

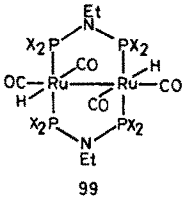


Scheme 17. [127, 128, 128a].

or SC_4H_8. A detailed spectroscopic study of these species reveals that the coordinated acetone is readily and reversibly displaced by water such that the aquo species is present in significant quantities, even in conventionally dried acetone. Anionic ligands also readily displace acetone from **95b** affording monocationic products of the type $[Ru_2Y(CO)_5\{\mu\text{-}(P(OR)_2)_2NEt\}_2]^+$ (**95d**) where Y is Cl^-, Br^-, I^-, NO_3^-, $FB(O)OH^-$, CN^-, SCN^-, $S_2CNEt_2^-$, RS^- or CF_3COO^-. Those ligands which are capable of effecting further substitution, give tetracarbonyl anion-bridged diruthenium species of the type $[Ru_2(\mu\text{-}Y)(CO)_4\{\mu\text{-}(P(OR)_2)_2NEt\}_2]^+$ (**98**) ($Y = CN^-$, SCN^-, Cl^-, Br^-, I^-, SR^-, $S_2CNEt_2^-$, HCO_3^-, $FB(O)OH^-$ or CF_3COO^-). Acetic acid effects only the displacement of acetone from the solvento species **95b** to afford $[Ru_2(CO)_5(MeCOOH)\{\mu\text{-}(P(OR)_2)NEt\}_2]^{2+}$, which is readily deprotonated to **95d**. The phenyl mercaptide derivative **95d** has been identified only spectroscopically; it readily decarbonylates to $[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}(P(OR)_2)_2NEt\}_2]^+$ (**98**) [127,128,128a] (see Scheme 17).

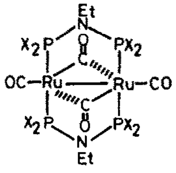
Reaction of the electron-rich dinuclear complexes **73** (M = Ru; R = Et, X = OMe or OPr^i) with the electron-acceptor ligands 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) or tetracyanoethylene (TCNE) leads to electron transfer with the formation of the charge transfer salts $[Ru_2(CO)_5(A)\{\mu\text{-}(PX_2)_2NEt\}_2]A$ (A = TCNQ or TCNE) which contains the radical anion of the electron-acceptor ligand in both inner and outer coordination spheres [129].

The dihydride, $[Ru_2H_2(CO)_4\{\mu\text{-}\{(P(OR)_2)_2NEt\}_2]$ (R = Me or Pr^i) (**99**) has been obtained in high yield by the passage of dihydrogen through a toluene solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}\{(P(OR)_2)_2NEt\}_2]$ (**73**) at 80°C. Thermolysis of **73** or **99** under vacuum at 80°C or passage of argon through a toluene solution of **99** at 80°C affords the formally unsaturated species $[Ru_2(CO)_4\{\mu\text{-}(P(OR)_2)_2NEt\}_2]$ (**99a**), which are highly reactive and react spontaneously with both nucleophiles and electrophiles such as H^+, H_2, CO, halogens, alkynes, and silver(I) salts. Reaction with CO gives the parent pentacarbonyl derivative **73** whereas that with alkynes gives the vinylidene-bridged derivative $[Ru_2\{\mu\text{-}\eta^1\text{-}C{=}C(R')R''\}(CO)_4\{\mu\text{-}(P(OR)_2)_2NEt\}_2]$ (**100b**) and/or alkenediyl-bridged derivatives $[Ru_2\{\mu\text{-}\sigma^2\text{-}R'C{=}CR''\}(CO)_4\{\mu\text{-}(P(OR)_2)_2NEt\}_2]$ (**100a**), depending on the nature of the alkyne [130].



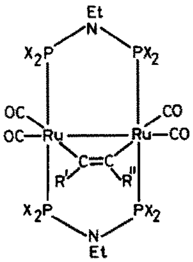
99

(X = OMe or OPr^{i*})

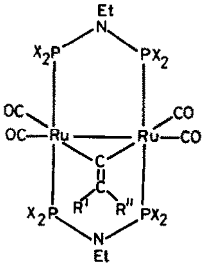


99a

(X = OMe or OPr^{i*})



100a (X = OPr^i)



100b (X = OPr^i)

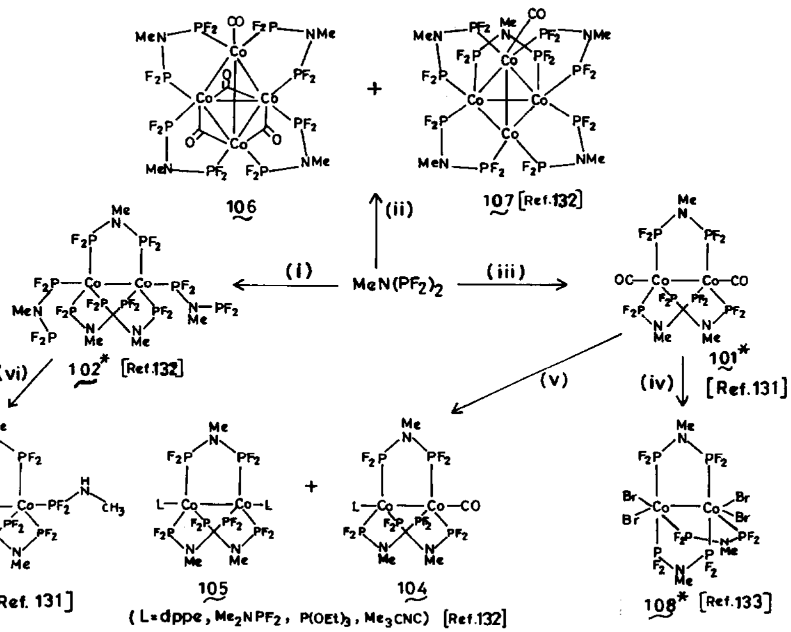
3.5 *Group 9*

Cobalt carbonyl chemistry of the $MeN(PF_2)_2$ ligand has been investigated by King and co-workers and others. With other diphosphinoamine ligands, $RN(PX_2)_2$ (R = Me, Et, Ph; X = OMe, OPr^i or OPh), rhodium chemistry has been explored in detail; cobalt and iridium chemistry has been studied only to a limited extent.

3.5.1 Cobalt chemistry

Some typical reactions of $MeN(PF_2)_2$ with $[Co_2(CO)_8]$ are shown in Scheme 18. Reaction of $[Co_2(CO)_8]$ with $MeN(PF_2)_2$ at room temperature gives the purple complex, $[Co_2(CO)_2\{(PF_2)_2NMe\}_3]$ (**101**). Ultraviolet irradiation of $[Co_2(CO)_8]$ with an excess of the ligand results in complete displacement of all carbonyl groups to give the black complex, $[Co_2\{(PF_2)_2NMe\}_5]$ (**102**) containing three biligate and two monoligate $MeN(PF_2)_2$ ligands. Chromatography of complex **102** on fluorosil results in the hydrolysis of the two monoligate ligands to give the purple complex, $[Co_2\{(PF_2)_2NMe\}_3\{PF_2NHMe\}_2]$ (**103**). The monocarbonyl complex $[Co_2(CO)(PF_2NHMe)\{\mu\text{-}(PF_2)_2NMe\}_3]$ (**104**) has also been isolated from this reaction. Ultraviolet irradiation of $[Co_2(CO)_2\{(PF_2)_2NMe\}_3]$ (**101**) with the ligands, L ($L = Me_2NPF_2$, $P(OEt)_3$, PPh_3, dppe or Me_3CNC) results in the stepwise replacement of the two carbonyl groups to give complexes of the type $[Co_2(CO)L\{(PF_2)_2NMe\}_3]$ (**104**) and $[Co_2L_2\{(PF_2)_2NMe\}_3]$ (**105**), respectively [131,132].

The reaction of $[Co_4(CO)_{12}]$ with $MeN(PF_2)_2$ results in the pairwise replacement of CO groups by the diphosphinoamine ligand to give products of the type, $[Co_4(CO)_{12-2n}\{(PF_2)_2NMe\}_n]$ ($n = 1$–5) [132]. These complexes have structures in which 2–5 of the six edges in the Co_4 tetrahedron of $[Co_4(CO)_{12}]$ are bridged by the biligate diphosphinoamine ligands (e.g. **106** and **107**). Treatment of $[Co_2(CO)_4\{(PF_2)_2NMe\}_3]$ (**101**) with bromine in diethylether gives the brown com-



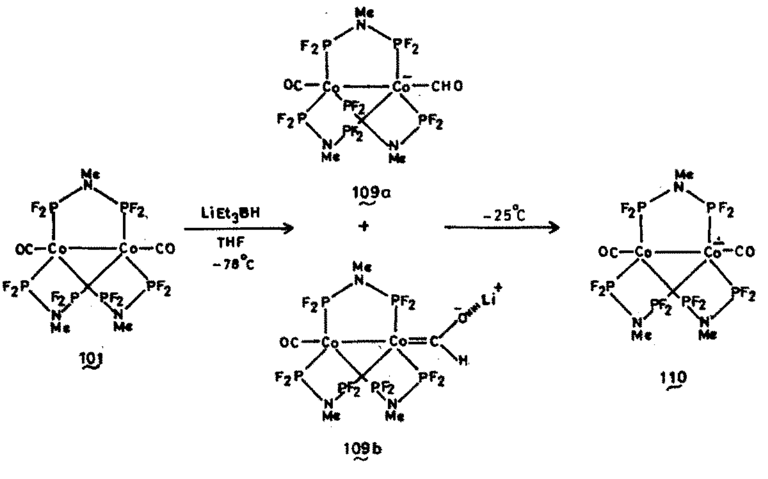
Scheme 18. (i) $Co_2(CO)_8/h\nu$; (ii) $Co_4(CO)_{12}$/reflux; (iii) $Co_2(CO)_8$ (1:5 M/L ratio) at 0°C; (iv) $Br_2/Et_2O/25°C$; (v) ligand/$h\nu$; (vi) hydrolysis.

plex, $[Co_2Br_4\{(PF_2)_2NMe\}_3]$ (**108**) in high yield (84%). This complex retains a formal Co··Co bond, with a bond distance close to that in the parent compound (**101**) and its derivatives **105** ($L = PF_2NHMe$ or PF_2NMe_2) (2.71–2.77 Å). This observation indicates that the dimensions of the very stable $[Co_2\{(PF_2)_2NMe\}_3]$ unit are not appreciably affected by an increase in the formal oxidation state of cobalt from 0 to +2 when the CO group is replaced by two bromines [133].

Reduction of **101** with $LiEt_3BH$ (2 equiv.) in THF affords an orange solution containing the cobalt formyl complex which exists as a mixture of solvent separated and ion-paired species ($[Co_2\{MeN(PF_2)_2\}_3(CO)(CHO)]^-$ (**109a**) and $[Co_2\{MeN(PF_2)_2\}_3(CO)(CHO)]^-Li^+$ (**109b**), respectively). This complex is stable for a period of at least one week when kept at −70°C. Upon raising the temperature to −25°C, the orange colour quickly changes to green. This product is identified as a mixed valance d^9–d^{10} radical anion $[Co_2\{MeN(PF_2)_2\}_3(CO)_2]^-$ (**110**) (Scheme 19) which is chemically and electrochemically stable. The fate of the formyl derived hydrogen atom is not known [134].

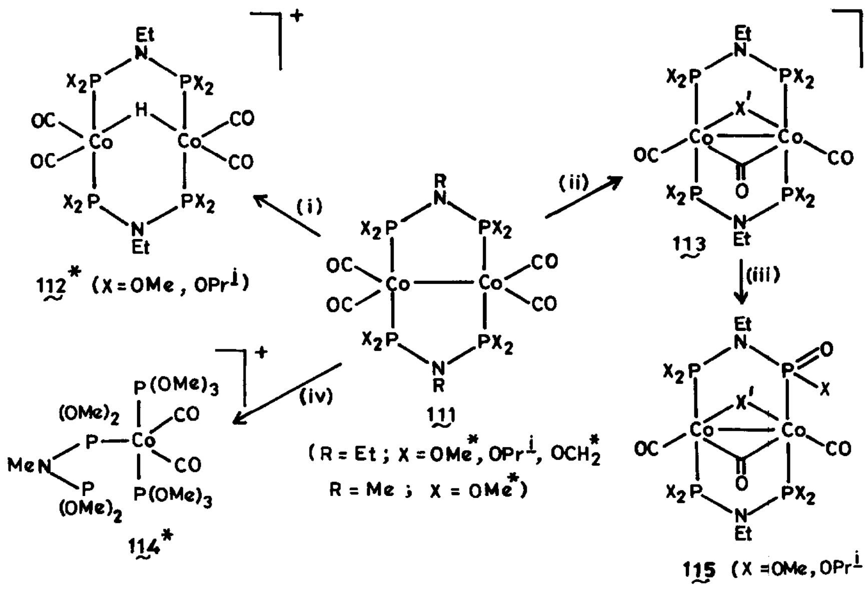
The reaction of $MeN(P(OMe)_2)_2$ with $[Co_4(CO)_{12}]$ in THF at 0°C gives the violet brown complex, $[Co_2(CO)_4\{(P(OR)_2)_2NR'\}_2]$ (**111**) (R = Me, X = OMe) [43]. The analogous complexes of $EtN\{P(OR)_2\}_2$ ($R = CH_2-$, Me or Pr^i) have been reported by Haines and co-workers. An ionic intermediate, $[Co_2(CO)_4\{P(OR)_2\}_2NEt][Co(CO)_6]_2$ has been identified in these reactions. When the reaction of $Co_2(CO)_8$ with $EtN\{P(OPr^i)_2\}_2$ is carried out with a low ligand : metal molar ratio, the product is $[Co_2(CO)_6\{\mu\text{-}(P(Pr^iO)_2)_2NEt\}]$. An ionic mononuclear species $[Co(CO)\{P(Pr^iO)_2)_2NEt\}_2]^+$ containing two chelating diphosphazanes (which has an irregular trigonal bipyramidal geometry around the metal centre) is also formed in the reaction and has been isolated as its BPh_4^- salt [135,136].

The protonation of $[Co_2(CO)_4\{\mu\text{-}(P(OR)_2)_2NEt\}_2]$ (**111**) (R = Me or Pr^i) in



Scheme 19. [134].

methanol with acids such as HPF_6, HBF_4 or HCl proceeds rapidly without loss of CO to afford a new hydrido-bridged compound $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(P(OR)_2)_2NEt\}_2]^+$ (**112**), which is characterized structurally as its BPh_4^- salt. Attempts to form a dihydride species by addition of H^- merely results in the deprotonation of the cation with formation of the starting complex and H_2 [137] (Scheme 20). Halogenation of **111** by I_2, Br_2 or freshly distilled CCl_4 affords the cations $[Co_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2\{\mu\text{-}(P(OR)_2)_2NEt\}_2]^+$ (**113**) (X = I, Br or Cl, respectively). These cations have an "A-frame" structure with a neutral CO ligand occupying a bridging site in addition to a bridging halogen atom. In contrast, when **111** is treated with undistilled CCl_4, an unexpected product $[Co\{P(OMe)_3\}_2(CO)_2\{(OMe)_2PN(Et)P(OMe)_2\text{-}\eta^1\}]BPh_4$ (**114**) is isolated. A single-crystal X-ray diffraction study of **114** reveals a trigonal bipyramidal geometry at the cobalt centre; the axial positions are occupied by $P(OMe)_3$ groups and the equatorial positions by two carbonyl groups and a pendant diphosphinoamine ligand. Apparently, an unidentified impurity in undistilled CCl_4 causes cleavages of Co—Co, Co—P and P—N bonds. The halogenation reactions of the complexes **111** proceed with loss of CO and thus provide a contrast to protonation reactions in which there is no loss of CO. In solution, $[Co_2(\mu\text{-}X')(\mu\text{-}CO)(CO)_2\{\mu\text{-}[P(OR)_2]_2NEt\}_2]X'$ (**113**) (X' = Cl, Br or I) cations slowly undergo a Michaelis–Arbuzov type rearrangement (initiated by attack of halide ions at a coordinated phosphorus atom) to give a neutral complex, $[Co_2(\mu\text{-}X')(\mu\text{-}CO)(CO)_2\{\mu\text{-}[P(OR)_2]_2NEt\}\{\mu\text{-}(OR)_2PN(Et)P(O)(OR)\}]$ (**115**). The methyl analogue of **115** could



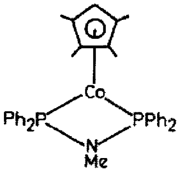
Scheme 20. (i) HX' (X' = PF_6^-, BF_4^- or Cl^-); (ii) X' or freshly distilled CCl_4(X' = Cl, Br or I); (iii) in solution (X = OMe, X' = Cl, Br, I) or $NaBH_4$ (X' = I, X = OPr^i; (iv) undistilled CCl_4 [43,135–138].

not be isolated but the isopropyl analogue (X′ = I) is readily isolated by chromatography of the reaction mixture [138] (Scheme 20).

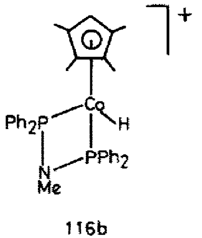
Recently, Werner et al. have reported that the displacement of two PMe_3 ligands from $[Co(\eta^5\text{-}C_5Me_4H)(PMe_3)_2]$ by $MeN(PPh_2)_2$ affords the unstable chelate complex, $[Co(\eta^5\text{-}C_5Me_4H)\{(Ph_2P)_2NMe\}]$ (**116a**), which has been isolated as a stable hydrido complex $[Co(H)(\eta^5\text{-}C_5Me_4H)\{(Ph_2P)_2NMe\}]^+PF_6^-$ (**116b**), upon treatment with NH_4PF_6 [139].

3.5.2 Rhodium and iridium chemistry

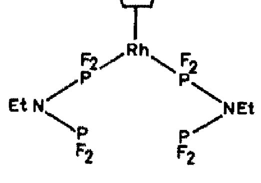
The reaction of $[RhCp(C_2H_4)_2]$ with an excess of $EtN(PF_2)_2$ at 25°C gives $[RhCp\{\eta^1\text{-}(PF_2)_2NEt\}_2]$ (**117**) in which $EtN(PF_2)_2$ acts a monodentate ligand [140]. The reaction of $RN(PX_2)_2$ (R = Et, Ph; X = OPh; R = Me, X = F) with $[RhX'diene]_2$ (diene = COD or NBD; X′ = Cl, Br or I) in 1 : 1 and 1 : 2 mole ratio in benzene leads to the successive replacement of the diene ligands and the formation of complexes, of the type $[Rh_2X'_2(diene)\{(PX_2)_2NR\}]$ (e.g. **118a**) and $[Rh\{(PX_2)_2NR\}X']_2$ (**118b**) [41,141]. Reaction of $[Rh(COD)Cl]_2$ with an excess of $EtN(P(OPh)_2)_2$ in ethanol or methanol in the presence of a suitable counter ion effects not only the displacement of dienes but also the halogens as halide ions to afford $[Rh\{(P(OPh)_2)_2NEt\}_2]X'$ (**119**) and $[Rh(C_8H_{12})\{(P(OPh)_2)_2NEt\}]X'$ (**120**) (X′ = BPh_4 or SbF_6). Carbon monoxide reacts reversibly with **119** and **120** to yield $[Rh\{(P(OPh)_2)_2NEt\}_2(CO)]^+$ (**121**) and $[Rh(COD)\{(P(OPh)_2)_2NEt\}(CO)]^+$ (**122**), respectively. Reaction of $[Rh\{(P(OPh)_2)_2NEt\}_2]^+$ (**119**) with HBr and Br_2 gives *trans*-$[Rh\{(P(OPh)_2)_2NEt\}_2(H)(Br)]^+$ (**123a**) and $[Rh\{(P(OPh)_2)_2NEt\}_2Br_2]^+$ (**123b**), respectively [141].



116a



116b



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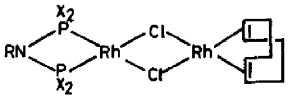
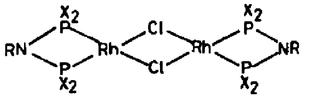
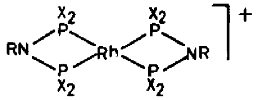


118a



118b

R = Et, Ph ; X = OPh ; OC_6H_4Br-p
R = Me, X = F or OPh



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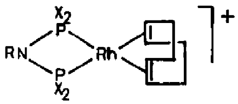
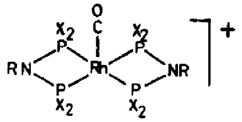


120

R = Et ; X = OPh



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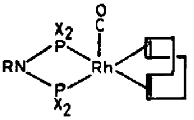
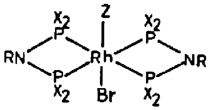


122

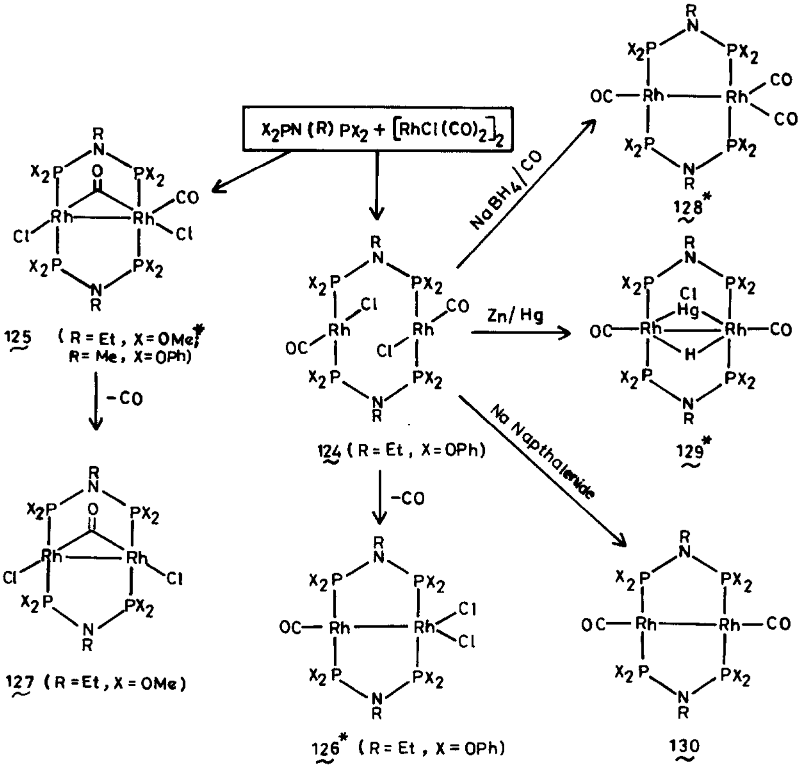
R = Et ; X = OPh



123 (a) Z = H ; (b) Z = Br

Reactions of $RN(PX_2)_2$ with $[RhCl(CO)_2]_2$ give a variety of products depending on the reaction conditions and the ligands used (see Scheme 21). Reactions of $RN(P(OPh)_2)_2$ (R = Et or Ph) with $[RhCl(CO)_2]_2$ in benzene at room temperature affords the symmetric complex. $[RhCl(CO)\{\mu\text{-}(P(OPh)_2)_2NR\}]_2$ (**124**) whose structure is analogous to that of the dppm complex [142,143], whereas the ligands $RN(PX_2)_2$ (R = Et, X = OMe; R = Me, X = OPh) afford the asymmetric complexes $[Rh_2(\mu\text{-}CO)(CO)(Cl)_2\{\mu\text{-}(P(OPh)_2)_2NR\}_2]$ (**125**) containing both bridging as well as terminal carbonyl groups [144,145]. The diphosphazane, $PhN\{P(OC_6H_4Br\text{-}p)_2\}_2$ behaves somewhat differently. The reaction of $PhN\{P(OC_6H_4Br\text{-}p)_2\}_2$ with either $[RhCl(CO)_2]_2$ or $[RhCl(COD)]_2$ leads to the formation of only the chloro-bridged bischelate complex (**118b**). The same product is obtained when the reaction is carried out under CO atmosphere [41,145].

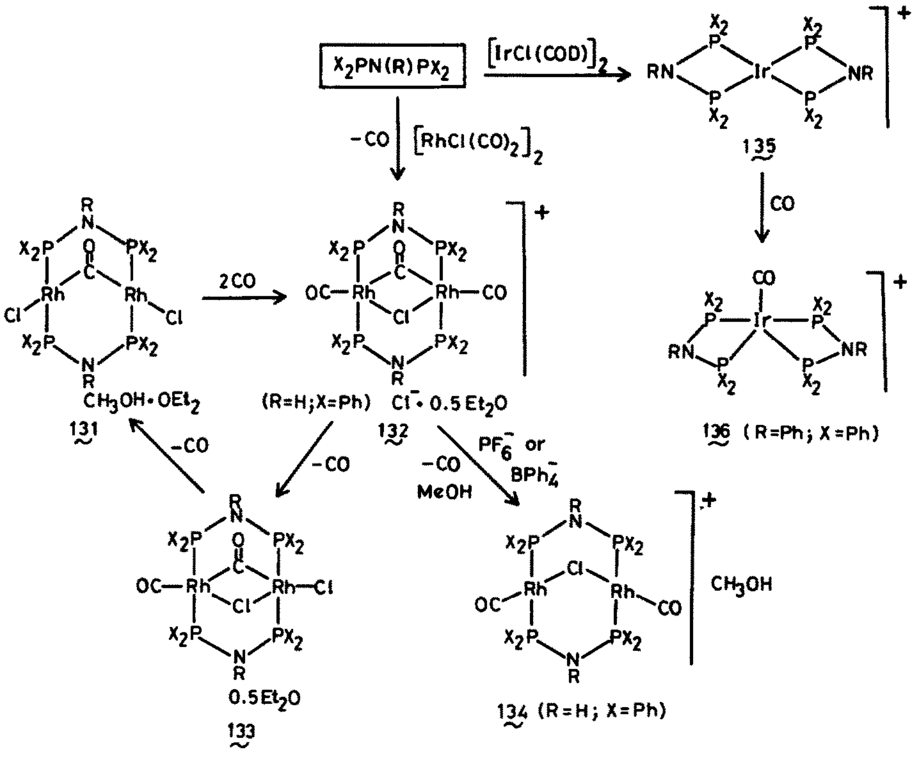
Decarbonylation of **124** occurs readily in chloroform to give the mixed Rh(0)–Rh(II) complex $[Rh_2(Cl)_2(CO)\{\mu\text{-}(PX_2)_2NR\}_2]$ (R = Et, X = OPh) (**126**), whereas **125** undergoes decarbonylation to yield the Rh(I)–Rh(I) derivative $[Rh_2(\mu\text{-}CO)(Cl)_2\{\mu\text{-}(PX_2)_2NR\}_2]$ (R = Et, X = OMe) (**127**). Reduction of **124** with zinc amalgam yields three products $[Rh_2(CO)_3\{\mu\text{-}(PX_2)_2NR\}_2]$ (**128**), $[Rh_2(\mu\text{-}H)(\mu\text{-}$



Scheme 21. [144–148].

HgCl)(CO)$_2${μ-(PX$_2$)$_2$NR}$_2$] (**129**) and [Rh$_2$(CO)$_2${μ-(PX$_2$)$_2$NR}$_2$] (**130**) of which **129** is the major product. The tricarbonyl complex **128** can also be obtained by the treatment of **124** with $NaBH_4$ under CO atmosphere; however, reduction with sodium naphthalenide yields the Rh(0)–Rh(0) complex **130**, which can also be prepared by the decarbonylation of **128** in the presence of $Me_3NO{\cdot}2H_2O$ [146–148].

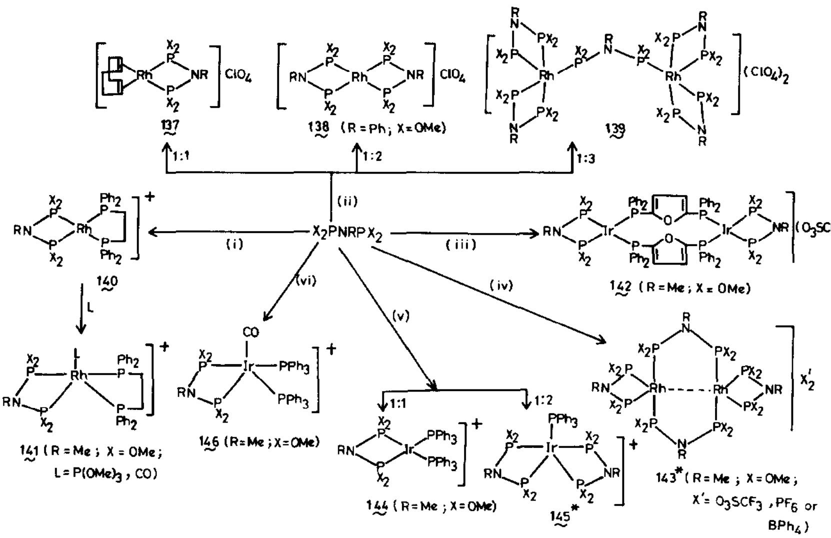
The reaction of [RhCl(CO)$_2$]$_2$ with dppa in benzene (1 : 4 mole ratio) gives the bis-chelate complex [Rh(CO)(dppa)$_2$]Cl, which in hot methanol loses CO and dppa to yield [Rh(dppa)$_2$]Cl and the "A-frame" complex [Rh$_2$(μ-CO)(μ-dppa)$_2$Cl$_2$]·CH$_3$OH·OEt$_2$ (**131**) [149]. The "A-frame" complex **131** can be isolated as its methanol–Et$_2$O solvate from the direct reaction of [RhCl(CO)$_2$] with dppa in a 2 : 1 molar ratio. The intermediates formed in this reaction, viz. [Rh$_2$(μ-CO)(μ-Cl)(μ-dppa)$_2$(CO)$_2$]Cl·0.5OEt$_2$ (**132**) and [Rh$_2$(μ-CO)(μ-Cl)(μ-dppa)$_2$(CO)Cl]·0.5OEt$_2$ (**133**) have been isolated and characterized. The BPh$_4$ salt of **132** loses CO in methanol to give [Rh$_2$(μ-Cl)(CO)$_2$(μ-dppa)$_2$]BPh$_4$·MeOH (**134**). Addition of diethyl ether to **134** in CH$_2$Cl$_2$ gives the red complex, [Rh$_2$(μ-Cl)(μ-X')(CO)$_2$(μ-dppa)$_2$]BPh$_4$ (X' = CH$_2$Cl$_2$) which in methanolic solution reverts back to the yellow **134** [150] (see Scheme 22). The crystal structure of the methanol solvate of **132** reveals a



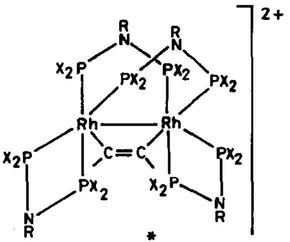
Scheme 22. [149–152].

complicated hydrogen bridge linkage system [151]. The diphosphinoamines, $(Ph_2P)_2NR$ (R = Me, Ph, C_6H_4Me-*p*) react with $[Ir(\mu\text{-}Cl)COD]_2$ to give the ionic square planar complexes $[Ir\{(Ph_2P)_2NR\}_2]Cl$·(solvent) (**135**). Five-coordinated $[Ir(CO)(Ph_2P)_2NR\}_2]X$ (X = Cl or BPh_4) (**136**) have been synthesized by treatment of **135** with CO in CH_2Cl_2 or by the reaction of the diphosphinoamine with $[Ir(CO)_2$(*p*-toludine)Cl] or $[Ir(CO)(PPh_3)_2Cl]$ in benzene [152]. Similarly, $[Rh(dppa)_2]X$ (X = Cl or PF_6) reacts with CO, O_2 or S_8 to yield $[Rh(Y)(dppa)_2]X$ (Y = CO, O_2 or S_2). The structure $[Rh(O_2)(dppa)_2]PF_6$ has been determined by X-ray crystallography; it reacts with SO_2 to form the rhodium(III) derivative, $[Rh(\eta^2\text{-}SO_4)(dppa)_2]PF_6$. Treatment of $[Rh(dppa)_2]Cl$ with CS_2 leads to $[Rh(\eta^2\text{-}CS_2)(dppa)_2]Cl$ [149].

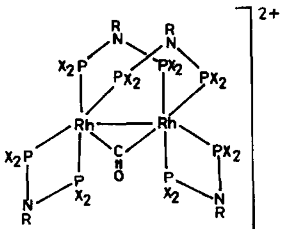
Recently, Mague [154] has reported several mono-, di- and trimetallic rhodium and iridium complexes with diphosphinoamine ligands. The reactions of alkoxy diphosphazanes, $RN\{P(OR')_2\}_2$ with rhodium and iridium derivatives afford a range of mono- and bimetallic complexes (**137**–**146**) as shown in Scheme 23 [153]. The dinuclear rhodium complex **143** (X′ = BPh_4 or ClO_4) reacts with dimethyl acetylene dicarboxylate (DMAD) or carbon monoxide to give $[Rh_2\{MeN(P(OMe)_2)_2\}_2\{\mu\text{-}(MeN(P(OMe)_2)_2\}_2(\mu\text{-}H_3COOCC{=}CCOOCH_3)]^{2+}$ (**147**) and $[Rh_2\{MeN\text{-}$



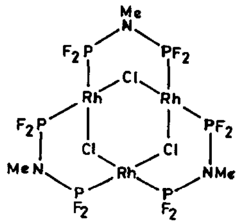
Scheme 23. (i) [Rh(COD)(dppe)]ClO_4; (ii) [Rh(COD)(acetone)$_x$]ClO_4; (iii) [Ir_2(COD)-(dppf)$_2$]ClO_4/AgO_3SCF_3; (iv) [Rh(COD)Cl]$_2$/AgO_3SCF_3 (X' = O_3SCF_3) or [RhCl(COD)]$_2$/MX' (MX' = NH_4PF_6, $NaBPh_4$); (v) [Ir(COD)(PPh_3)$_2$]ClO_4; (vi) [Ir(CO)$_3$(PPh_3)$_2$]ClO_4 [153].



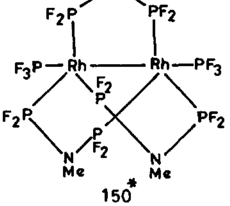
147*
(R = Me, X = OMe)



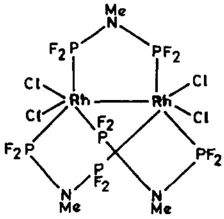
148
(R = Me, X = OMe)



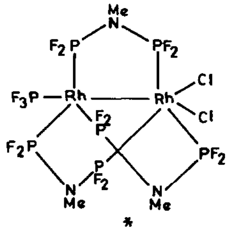
149*



150*



151*



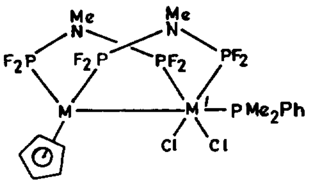
152*

$(P(OMe)_2)_2\}_2\{\mu\text{-}MeN(P(OMe)_2)_2\}_2(\mu\text{-}CO)]^{2+}$ (**148**), respectively. The acetylene or the CO ligand forms a bridge between the two metal centres and there is an indication of the formation of a metal–metal bond (Rh–Rh distance is 2.76 Å in **147** compared with 3.27 Å in the parent compound **143** ($X' = O_3SCF_3$)) [154].

The reaction of $MeN(PF_2)_2$ with $[RhCl(CO)_2]_2$ affords a novel trimetallic complex $[Rh(\mu\text{-}Cl)_3(\mu\text{-}(PF_2)_2NMe)_3]$ (**149**) unlike alkoxy derivatives, which give dinuclear complexes of the type **124** or **125** [155,156].

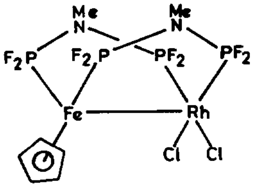
A novel homologous series of $Rh_2(0,0)$, $Rh_2(0,II)$ and $Rh_2(II,II)$ bis(difluorophosphino)methylamine complexes have been prepared from the reaction of $[RhCl(PF_3)_2]_2$ with $MeN(PF_2)_2$. Under reducing conditions, $[Rh_2\{MeN(PF_2)_2\}_3(PF_3)_2]$ (**150**) is isolated in moderate yields; conversely, in the presence of the oxidant $Cl_2IC_6H_5$, the product is $[Rh_2\{MeN(PF_2)_2\}_3(Cl_4)]$ (**151**) in high yields. In the absence of oxidants or reductants, the unsymmetrical mixed-valence $[Rh_2\{MeN(PF_2)_2\}_3(Cl_2)(PF_3)]$ (**152**) is obtained. The trinuclear complex **149** has also been isolated from the reaction mixtures. The formation of the $Rh_2(II,0)$ complex **152** corresponds to an intramolecular disproportionation of the $Rh_2(I,I)$ starting material but the mechanism of this process is not clear. All the above complexes (**150**–**152**) exhibit luminescence as shown by electronic absorption spectral studies and life-time measurements. Electronic structural considerations suggest that the metal–metal bond results from the overlap of one-electron-occupied d_{z^2} orbitals of rhodium centres. Electronic absorption spectra are dominated by intense bands, which are characteristic of $d\sigma$–$d\sigma^*$ transitions. Crystalline solids of **150**–**152** exhibit red, long-lived emissions ($\tau = 53$, 79 and 287 μs, respectively) upon excitation with frequencies concident with the absorption manifold. Luminescence is consistent with a $d\sigma^*$ excited-state parentage of primarily triplet character [157,158].

Heterobimetallic complexes of the type $[MM'(CO)_4Cl\{MeN[P(OPr^i)_2]_2\}_2]$ ($M = Mo$, $M' = Rh$, Ir; $M = W$, $M' = Ir$) (**40**) have been reported by Mague and Johnson (see Scheme 5) [42]. Reaction of **67** with $[IrCl(CO)(PMe_2Ph)_2]$ and $[RhCl(CO)_2]_2$ afford the heterobimetallic complexes $[CpFeIrCl_2(PMe_2Ph)\{MeN(PF_2)_2\}_2]$ (**153**) and $[CpFeRhCl_2\{MeN(PF_2)_2\}_2]$ (**154**). The latter complex (**154**) reacts rapidly with dimethylphenylphosphine to give $[CpFeRhCl_2(PMe_2Ph)\{MeN(PF_2)_2\}_2]$ (**153**; $M' = Rh$) [159].



M = Fe ; M' = Ir*, Rh

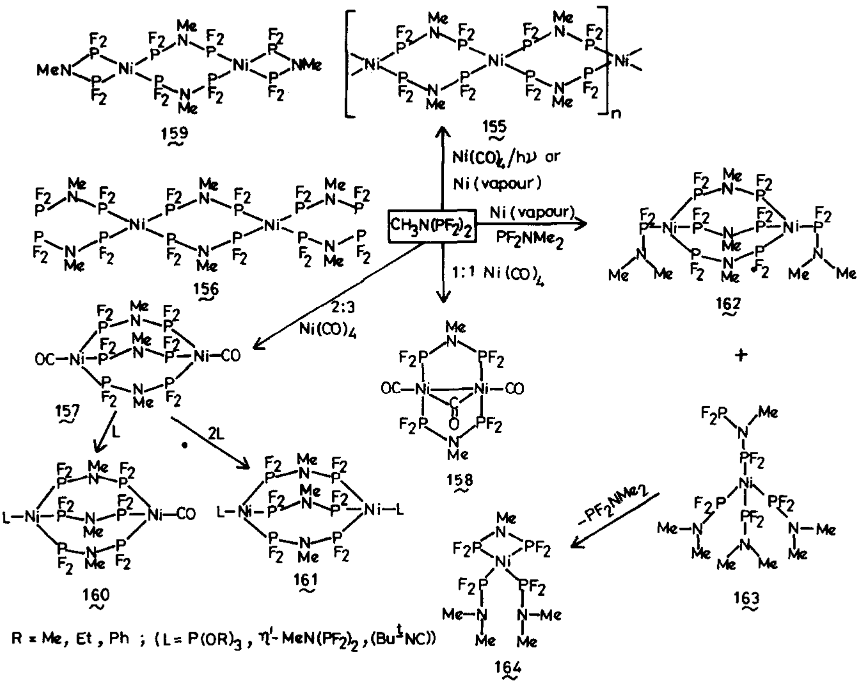
153



154

3.6 Group 10

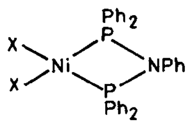
Ultraviolet irradiation of $[Ni(CO)_4]$ in the presence of $MeN(PF_2)_2$ gives the complexes $[Ni\{MeN(PF_2)_2\}_2]_n$ (**155**), $[Ni\{MeN(PF_2)_2\}_3]_2$ (**156**) and $[Ni_2\{MeN(PF_2)_2\}_3(CO)_2]$ (**157**), depending upon the reaction conditions (Scheme 24). On the other hand, the reaction of equimolar quantities of $Ni(CO)_4$ with $MeN(PF_2)_2$ in boiling hexane gives the yellow crystalline complex, $[Ni_2(CO)_3\{MeN(PF_2)_2\}_2]$ (**158**). The mass spectrum of **155** vapour exhibits a high abundance of the binuclear ions $[Ni_2\{MeN(PF_2)_2\}_n]^+$, suggesting that this complex vaporises as the dimer $[Ni_2\{MeN(PF_2)_2\}_4]$ (**159**). A characteristic property of the nickel carbonyl complex **157** is the facile replacement of the carbonyl groups by ligands such as phosphines, phosphites and isonitriles. Both mono- and disubstituted products, $[Ni_2\{MeN(PF_2)_2\}_3(L)(CO)]$ (**160**) and $[Ni_2\{MeN(PF_2)_2\}_3(L)_2]$ (**161**) have been isolated [85]. The co-condensation of nickel vapour with a mixture of $MeN(PF_2)_2$ and Me_2NPF_2 yields $[Ni_2\{PF_2NMe_2\}_2\{MeN(PF_2)_2\}_3]$ (**162**) and $[Ni\{PF_2NMe_2\}_3\{MeN(PF_2)_2\}]$ (**163**); in the latter complex, the lone $MeN(PF_2)_2$ functions as a monodentate ligand. The highest peak in the mass spectrum of **163** corresponds not to the molecular ion but to the ion $[Ni\{PF_2NMe_2\}_2\{MeN(PF_2)_2\}]^+$. This observation suggests that **163** readily loses one of its Me_2NPF_2 ligands to form



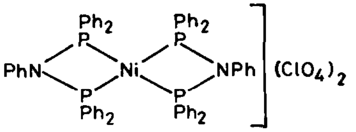
Scheme 24. [83,85].

$[Ni\{PF_2NMe_2\}_2\{MeN(PF_2)_2\}]$ (**164**) in which the $MeN(PF_2)_2$ has changed from a monodentate to a bidentate ligand [83].

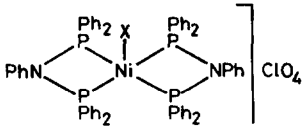
Bis(diphenyl phosphino)aniline reacts with nickel(II) halides and thiocyanate in methanol to yield the diamagnetic planar complexes $[NiX_2\{(Ph_2P)_2NPh\}]$ (X = Cl, Br, I or NCS) (**165**). The perchlorate complex $[Ni\{(Ph_2P)_2NPh\}_2](ClO_4)_2$ (**165a**) containing two chelating diphosphinoamine ligands is obtained by the reaction of nickel perchlorate with the ligand in acetone. Treatment of **165a** with ammonium halides or thiocyanate yields the square pyramidal complexes $[NiX\{(Ph_2P)_2NPh\}_2]ClO_4$ (**165b**) [36]. The reaction of $RN(PPh_2)_2$ with $[NiCp(NBD)]BF_4$ in acetonitrile gives the cationic complexes $[NiCp(PPh_2)_2NR]BF_4$ (**166**) (R = Me, Ph); complex **166** (R = Ph) on treatment with NaCN yields a neutral complex **166a** in which the diphosphinoamine ligand displays a monodentate coordination. (Scheme 25) [160].



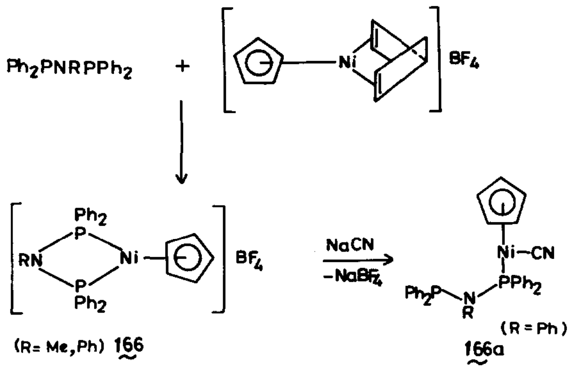
165 (X = Cl, Br, I or NCS)



165a

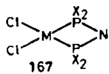


165b(X = Cl, Br, I or NCS)



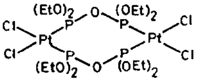
Scheme 25. [160].

Reactions of $RN(PX_2)_2$ with palladium and platinum derivatives such as *trans*-$[PdCl_2(PhCN)_2]$, *cis*-$[PtCl_2(SEt_2)_2]$, *cis*-$[M(COD)Cl_2]$ (M = Pd or Pt) or $[K_2PdCl_4]$ give chelate complexes of the type *cis*-$[MCl_2(PX_2)_2NR]$ (**167**) (R = Et, X = Ph [161]; R = Et, X = OEt or OPh [162]; R = Me or Ph, X = OPh [41]; R = Pr^i, X = Ph [97]). In contrast, tetraethyldiphosphite, $\{P(OEt)_2\}_2O$ affords the dinuclear complex, $[Pt_2Cl_4[P\{(OEt)_2\}O]_2]$ (**168**), in which the diphosphite ligand bridges two metal centres because of the large P—O—P bond angle [162]. Recently, Farrar and co-workers have reported the structures of the complexes, $[PdCl_2\{(Ph_2P)_2NMe\}]$, $[PtCl_2\{(Ph_2P)_2NMe\}]$ and $[Pd(CN)_2\{(Ph_2P)_2NMe\}]$ [163]. Reaction of

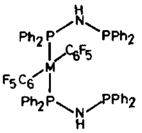


167

[R = Et, X = Ph or OEt ; [161, 162]
R = Me or Ph, X = OPh ; [41]
R = Pr^i, X = Ph ; M = Pd or Pt] [97]
[M = Pd, Pt, X = Ph, R = CHR′CO_2Me
R′ = H or Pr^i [45]]
[M = Pd, Pt, X = Ph, R = Me [163]]

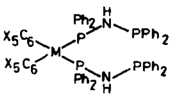


168



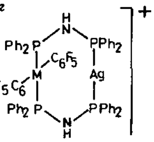
[M = Pd, Pt]

169a



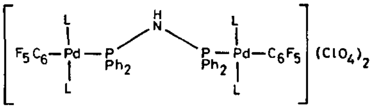
(X = Cl, F)

169b



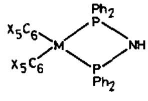
(M = Pd, Pt)

171



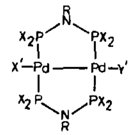
(L = PPh_3, PPh_2Me, PEt_3)

172



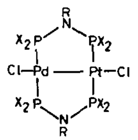
170

(X = Cl, F)



R = Me, X = OPh, X′ = Y′ = Cl
R = Ph*, X = OPh, X′ = Y′ = Cl [41]
R = H*, X = Ph, X′ = Y′ = Cl [165]
R = H, X = Ph, X′ = Y′ = C_6Cl_5
C_6F_5, Br, $SnCl_3$) [164]

173

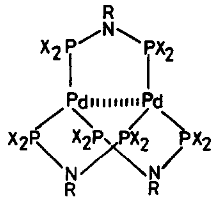


(R = Pr^i, X = Ph)

174

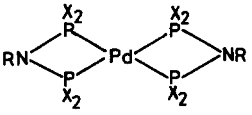
$Ph_2PN(Pr^i)P(Ph)(DMP)$ with $Pd_2(dba)_3{\cdot}CHCl_3$ in the presence of MeI gives $[PdI_2\{Ph_2PN(Pr^i)PPhMe\}]$ as a major product. In this complex the dimethyl pyrazolyl group on the phosphorus is displaced by a methyl group [46]. Complexes such as *trans*-$[M(C_6X_5)_2(dppa)_2]$ (**169a**), *cis*-$[M(C_6X_5)_2(dppa)]$ (**169b**) and the chelate complex $[M(C_6X_5)_2(dppa)]$ (**170**) (M = Pd or Pt; X = Cl or F) can be easily prepared by the appropriate choice of precursors and solvents. Reactions of *trans*-$[M(C_6X_5)_2(dppa)_2]$ (**169a**) with $AgClO_4$ gives heterodinuclear complexes of the type $[M(C_6X_5)_2(\mu\text{-dppa})_2Ag]ClO_4$ (**171**). Cationic homodinuclear singly bridged Pd(II) complexes $[\{Pd(C_6F_5)_2(PR_3)_2\}_2\{\mu\text{-dppa}\}]ClO_4$ (L = PPh_3, PPh_2Me, PEt_3) (**172**) have been prepared by the addition of dppa to $[Pd(OClO_3)_2(C_6F_5)L_2]$ (2 : 1 molar ratio) in benzene [164]. Reactions of $RN(PX_2)_2$ (R = Me or Ph; X = OPh; R = H, X = Ph) with a mixture of a Pd(II) derivative such as $[PdCl_2(PhCN)_2]$ or $[Pd(C_6F_5)_2(dppa)]$ and the Pd(0) derivative $[Pd_2(dba)_3{\cdot}CHCl_3]$ in CH_2Cl_2 give Pd(I) complexes of the type, $[Pd_2\{(PX_2)_2NR\}_2X'Y']$ (**173**) [164–166]. The heterobimetallic complex **174** can be prepared by the treatment of $Pr^iN(PPh_2)_2$ with a mixture of $[PtCl_2(COD)]$ and $[Pd(dba)_2]$ in CH_2Cl_2 solution [97]. The complex $[Pd_2Cl_2(\mu\text{-dppa})_2]$ (**173**) reacts with $SnCl_2$ in CH_2Cl_2 to yield $[Pd_2(SnCl_3)_2(\mu\text{-dppa})_2]$ [165]; evidently, $SnCl_2$ inserts into the Pd–Cl bonds. The reaction of **173** with diazonium salts $[N_2R]BF_4$ (R = $C_6H_4NO_2$-*o*, C_6H_4Me-*p*) yields the "A-frame" homobimetallic complexes $[Pd_2Cl_2(\mu\text{-dppa})_2(\mu\text{-}N_2R)]$, which are structurally similar to **127** [164,165].

A dipalladium(0) complex, $[Pd_2\{(P(OPh)_2)_2NMe\}_3]$ (**175**) with three bridging



(R = Me, X = OPh)

175*



(R = Ph, X = OPh)

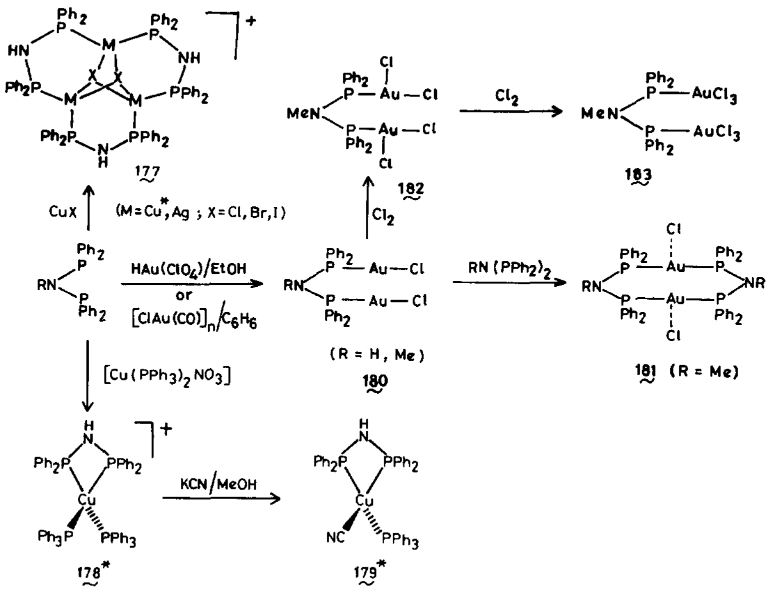
176

diphosphinoamine ligands is obtained by treating [$Pd_2(dba)_3 \cdot CHCl_3$] with an excess of the diphosphinoamine ligand in benzene at 25°C. Under similar experimental conditions, the diphosphinoamine ligand, $PhN(P(OPh)_2)_2$ affords bis-chelated mononuclear palladium(0) complex, [$Pd\{(P(OPh)_2)_2NPh\}_2$] (**176**), which could not be isolated but identified by ^{31}P NMR spectroscopy [166]. The structure of **175** is similar to a manxane-like (bicyclo[3,3,3]undecane-type) molecular frame [167]. The dipalladium(0) complex **175** undergoes oxidative addition reactions with organic halides such as CH_2Br_2 and CH_3I; the structures of the products have not been unambigously established [41].

3.7 Group 11

The coordination chemistry of Group 11 transition metals with diphosphinoamine ligands is yet to be explored in detail. Recently, Ellermann et al. have reported the copper and silver complexes of the diphosphinoamine, dppa. Reactions of copper(I)halides or silver(I)halides with dppa in methanol yields trinuclear complexes [$M_3(\mu_3\text{-}X_2)(\mu\text{-dppa})_3$]X (M = Cu or Ag; X = Cl, Br or I) (**177**); their PF_6^- derivatives have been synthesized by metatheses with NH_4PF_6 [168,169]. Reaction of [$Cu(PPh_3)_2NO_3$] with one molar equivalent of dppa gives [$Cu(dppa)(PPh_3)_2$]$^+$ NO_3^- (**178**), which has also been isolated as its PF_6 salt, by treating it with NH_4PF_6. The complex **178** reacts with the KCN in methanol to give a neutral complex [$Cu(CN)(dppa)(PPh_3)$]·MeOH (**179**). However, substitution of PPh_3 by CO could not be achieved under similar experimental conditions. The geometry around copper in both **178** and **179** is tetrahedral; the dppa ligand is chelated to the metal, thus forming a highly strained four-membered ring [170,171].

Schmidbaur et al. have reported an adduct of AgBr, viz. [$BrAgPh_2PN(Me)PPh_2AgBr$], which exists as a dimer in which the *trans*-[Br_2Ag_4] moiety adopts an octahedral geometry [172]. Reaction of dppa with [$AuCl(CO)$]$_n$ yields a dinuclear gold complex (**180**). The analogous methylamino derivative can be prepared more readily by the treatment of the ligand $MeN(PPh_2)_2$ with $HAuCl_4$ in ethanol. An excess of the ligand in the same solvent yields a cyclic complex (**181**) as shown in Scheme 26. The gold(I) complex **180** reacts with chlorine to form **182** and **183** in which the formal oxidation states of the metal are +2 and +3, respectively



Scheme 26. [168–173].

[173]. Several Group 10 and 11 complexes of the diphenylphosphinoimide anion $[(Ph_2P)_2N]^-$ are known and are discussed in Sect. 4.

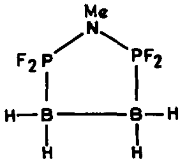
3.8 Group 12

So far no complexes of diphosphinoamine ligands involving the metals Zn, Cd and Hg have been reported. Only mercury–rhodium heterodinuclear and trinuclear complexes which are mentioned in Sect. 3.5 dealing with Group 9 metals, are known.

3.9 Group 13

The reactions of B_2H_6 or $BH_3{\cdot}CO$ with $(F_2P)_2NMe$ produce the stable monoborane and the bis(borane) adducts $F_2PN(Me)PF_2{\cdot}BH_3$ and $F_2PN(Me)PF_2{\cdot}2BH_3$. Under the same conditions, the combination of B_4H_{10} and the above diphosphinoamine produces only the monoligate triborane derivative, $F_2PN(Me)PF_2{\cdot}B_3H_7$. All the three borane adducts are well-characterized by mass spectrometry and IR and NMR spectroscopic techniques [174]. Paine has also reported the preparation of the diphosphino diborane, $B_2H_4{\cdot}(PF_2)_2NMe$ (**184**) by the base-displacement reaction of bis(trifluorophosphino)diborane [175].

Triethylaluminium reacts with $RN(PPh_2)_2$ (R = Me, Et, Pr^n, Bu^n) to form 1 : 1 adducts of the type **185** in which the aluminium is pentacoordinated. Such adducts are not formed with other bis(diphenyl phosphino)amines in which the third substituent on the nitrogen atom is α-methylbenzyl, benzyl or NMe_2. Evidently steric effects



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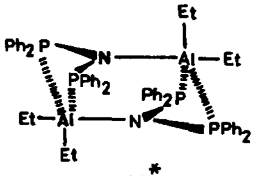

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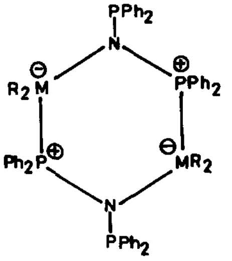
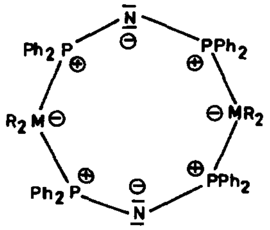


186

(M = Al*, Ga ; R = Me*, Et)



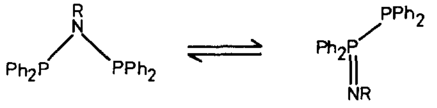
187

(M = Ga ; R = Me or Et)

play a dominant role [176,177]. Clemens et al. have also reported that the reaction of $AlEt_3$ with $HN(PPh_2)_2$ (dppa) leads to ethane elimination accompanied with the formation of a product of composition $Et_2AlN(PPh_2)_2$ for which a dimeric structure involving a six-membered AlNPAlNP ring is assigned on the basis of molecular weight measurements. This finding has been confirmed by the subsequent work of Schmidbaur et al. [178] who investigated the reactions of dppa with aluminium as well as gallium alkyls MR_3 (M = Al, Ga; R = Me, Et) and carried out the X-ray crystal structure analysis of $[Me_2AlN(PPh_2)_2]_2$ (**186**); M = Al; R = Me). The six-membered ring is present in a twist-conformation. The gallium derivative appears to exist in solution as a mixture of **187** in equilibrium with the six-membered ring isomer (**186**).

4. REACTIONS OF COORDINATED DIPHOSPHINOAMINE LIGANDS

It has long been known that strong bases such as MeLi can deprotonate either free or coordinated dppm. The crystal structure of $(Ph_2PCH_2PPh_2)Li{:}TMEDA$ has been determined [179]; lithium is only coordinated to the phosphorus atoms. Lithiation of $(PPh_2)_2NH$ with Bu^nLi gives $(PPh_2)_2NLi$ [180], which reacts readily with MeOD to give $(PPh_2)_2ND$; reaction with MeI gives $[\{Ph_2(Me)P\}_2N]I$ from which the iodide ion can be substituted by PF_6^- or BPh_4^- to form the respective iminium salts [181]. Lithium derivatives also react with $SiClRR'_2$ (R = R' = Me, Et, Pr^i or Ph; R = Me, R' = Ph; R = Ph, R' = Me, R = Cl, R' = Pr^i; R = Cl, R' = Me) to



188a (R = SiRR$'_2$) **188b**

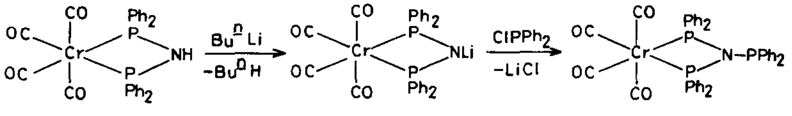
give *N*-silylated diphosphazanes, $(Ph_2P)_2NSiRR'_2$ (**188a**) or the isomeric P-diphenylphosphino diphenylphosphine (silylimides), $Ph_2PPPh_2({=}NSiRR'_2)$ (**188b**), depending on the substituents on silicon. In three cases, both the isomers could be detected in solution by NMR spectroscopy. It is not yet clear whether these compounds exist in the solid state in the two isomeric forms. Reaction of $(Ph_2P)_2NLi$ with Me_2PCl yields the phosphinoimine $Me_2P{-}PPh_2({=}NPPh_2)$ instead of the expected triphosphino amine species [182]. The complex $[Cr(CO)_4(PPh_2)_2NH]$ reacts with Bu^{n}Li to give $[Cr(CO)_4(PPh_2)_2NLi]$ (**189a**), which on subsequent treatment with $ClPPh_2$ yields $[Cr(CO)_4(PPh_2)_2NPPh_2]$ (**189b**) [183] (see Scheme 27).

Reaction of $(PPh_2)_2NLi$ with K_2PtCl_4 or $PdCl_2$ in the presence of PMe_3 yields the homoleptic complexes **190a** and **190b**, respectively; with $NiCl_2/PMe_3$ the chlorobridged complex **191** is obtained. A symmetrical bonding of the $[Ph_2P{-}N{-}PPh_2]$ anion to the metal through the phosphorus atoms is indicated for these diamagnetic complexes by ^{31}P NMR spectroscopy. Complexes **190a** and **190b** dissolve in CF_3COOH with protonation at the nitrogen atoms to give bis(diphenyl phosphino)-amine complexes **192a** and **192b**. Methylation of the complexes **190a,b** and **191** with CH_3OSO_2F leads to the formation of **193a,b** and **194**; the structure of the palladium complex **193a** has been confirmed by X-ray crystallography. The PdPNP skeletons and the geometry around nitrogen atoms are planar [184]. The reaction of $(PPh_2)_2NLi$ with Ph_3PAuCl gives **195** in 75% yield [185]. The above reactions are illustrated in Scheme 28.

Uson et al. [186] have studied the reactions of bis(diphenyl phosphino)amine and -amide ligands with gold(I) and silver(I) complexes and have isolated di- and tetranuclear complexes **196–199** in which the bis(diphenyl phosphino)amide ligand acts as a six-electron donor. A few reactions are illustrated in Scheme 29.

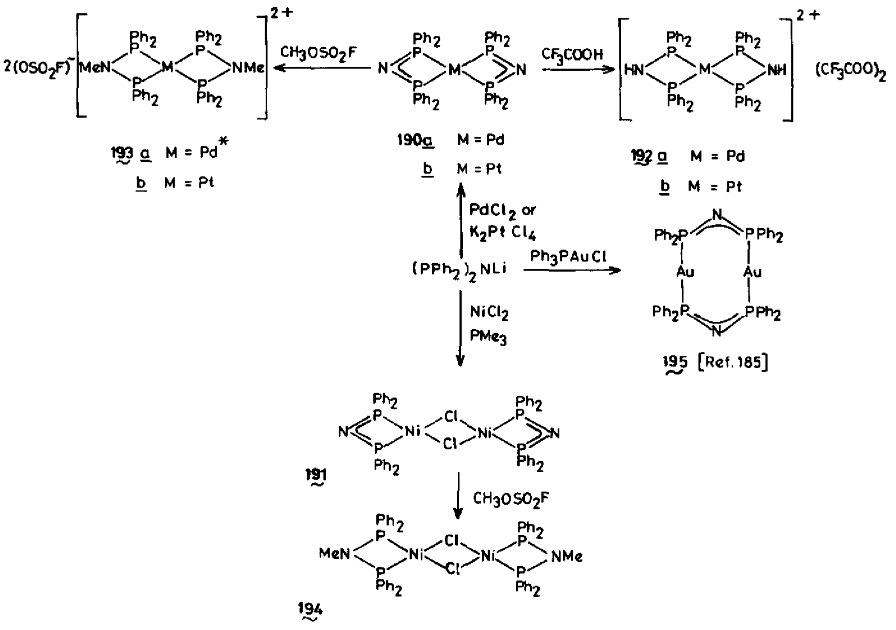
5. TRANSITION METAL CHEMISTRY OF CYCLODIPHOSPHAZANES

The coordination chemistry of cyclodiphosphazanes (1,3,2λ^3,4λ^3-diazadiphosphetidines) has been studied to a limited extent compared with analogous studies



189a **189b**

Scheme 27. [183].

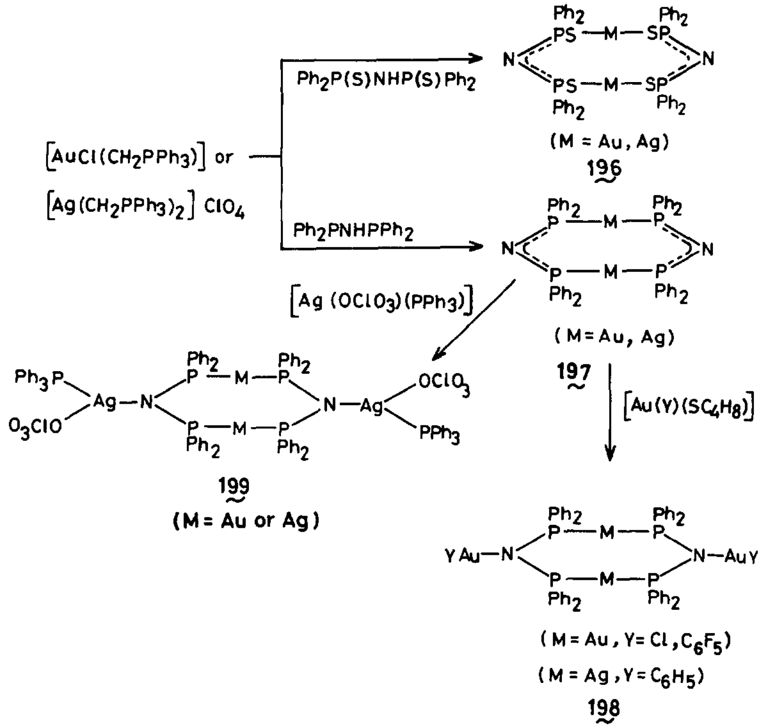


Scheme 28. [184].

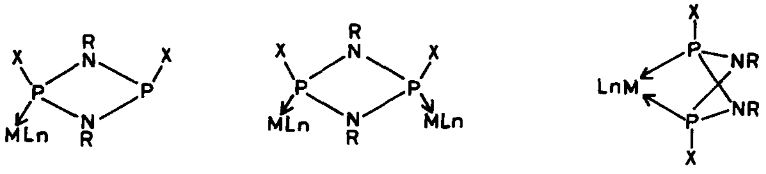
with acyclic diphosphazanes outlined in the previous sections. Cyclodiphosphazanes possess four potential donor sites [187]. To date no transition metal complexes of cyclodiphosphazanes wherein a nitrogen atom is involved in coordination have been reported. Transition metal complexes of cyclodiphosphazanes can have the structures I–III shown in Fig. 2, assuming that nitrogens are not the donor sites.

The first metal complex of a cyclodiphosphazane (**200**) was reported in 1977 by Zeiss and Feldt [188]. Later, Maisch [189] reported analogous complexes. In both the cases, the cyclodiphosphazane functions as a bridging ligand between two metal pentacarbonyl moieties. Maisch [190] has also reported the synthesis of the complex, $[Mo(CO)_5\{P(NHBu^t)NBu^t\}_2]$ (**201**) by the reaction between $[Mo(CO)_5PCl_3]$ and an excess of Bu^tNH_2 or by UV irradiation of a THF solution of $[Mo(CO)_6]$ and the free ligand. In complex **201**, the ligand is coordinated in an η^1 fashion. The stereochemistry of the P_2N_2 ligand in these complexes is not known. Such an η^1 coordination is also observed in the complex $[M(CO)_5(PFNBu^t)_2]$, which is identified as the major product (by ^{19}F and ^{31}P NMR studies) in the reaction of $[M(CO)_4(NBD)]$ or $[M(CO)_5(NCMe)]$ with $(PFNBu^t)_2$ [187].

The reactions of the cyclodiphosphazanes, $[RNPX]_2$ (R = Ph, Bu^t; X = alkoxy or aryloxy), with $[M(CO)_4(pip)_2]$ (M = Mo or W), $[M(CO)_4(NBD)]$ (M = Cr or W) or $[M(CO)_6]$, (M = Cr, Mo or W) in the presence of TMNO lead to the formation of a variety of products as shown in Scheme 30. The stereochemistry of the ligand appears to play a significant role in determining its coordination behaviour. The



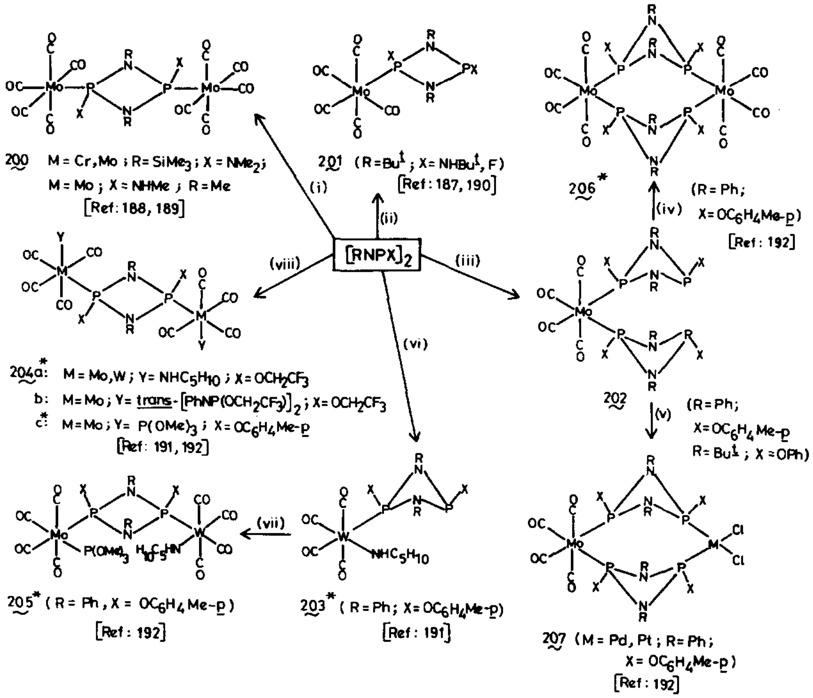
Scheme 29. [186].



I II III

Fig. 2. Possible coordinating modes of cyclodiphosphazanes.

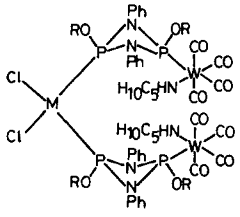
reactions of $[RNPX]_2$ ($R = Ph$, $X = OC_6H_4Me$-*p*) (a 3:1 mixture of cis and trans isomers) with $[M(CO)_4(pip)_2]$ ($M = Cr$, Mo and W) or with $[Mo(CO)_4(NBD)]$ afford complexes of the type **202** and **203**, in which the cyclodiphosphazane ligand in its cis form exhibits a monodentate mode of coordination [191,192]. The X-ray structure of **203** confirms the retention of a piperidine ligand in the product. Complexes of the type **202** are also obtained from the reaction of *cis*-$[Bu^tNP(OPh)]_2$ with $[M(CO)_4(NHC_5H_{10})_2]$ ($M = Mo$, W) or $[Cr(CO)_4(NBD)]$ [193]. The *trans*-cyclodiphosphazane ligand, $[PhNP(OCH_2CF_3)]_2$ reacts with $[Mo(CO)_4(pip)_2]$ ($M = Mo$ or W) or with $[Mo(CO)_4(NHC_5H_{10})(P(OMe)_3)]$ to give dinuclear complexes of the type **204**, in which the cyclodiphosphazane functions as a bridging ligand between two



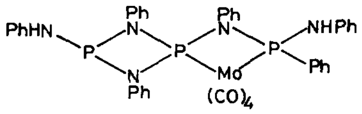
Scheme 30. (i) $2[M(CO)_5(NCMe)](M{=}Cr$, Mo or W); (ii) $Mo(CO)_6$; (iii) $[M(CO)_4(NHC_5H_{10})_2]$ (Mo or W) or $[M(CO)_4NBD](M{=}Cr$, Mo or W); (iv) $[Mo(CO)_4(NHC_5H_{10})_2]$; (v) $[MCl_2(COD)]$ (M=Pd or Pt); (vi) $[W(CO)_4(NHC_5H_{10})_2]$; (vii) $[Mo(CO)_4(NHC_5H_{10})P(OMe)_3]$; (viii) (a) $[M(CO)_4(NHC_5H_{10})_2]$ (M=Mo or W), (b) $[Mo(CO)_4NBD]$, (c) $2[Mo(CO)_4(NHC_5H_{10})P(OMe)_3]$.

metal carbonyl moieties. The trans ligand reacts with $[Mo(CO)_4(NBD)]$ to afford $[Mo_2(CO)_8\{\mu\text{-}[PhNP(OCH_2CF_3)]_2\}\{[PhNP(OCH_2CF_3)]_2\}_2]$ (**204b**) in which one of the ligands is coordinated in the bridged-bidentate fashion whilst other two ligands are coordinated in monodentate fashion. It is interesting to note that the cyclodiphosphazane, $[PhNP(OC_6H_4Me\text{-}p)]_2$ adopts the trans configuration in the homobimetallic complex **204c**, whereas it adopts the cis configuration in heterobimetallic complex **205**. Evidently, the nature of the product formed depends on the metal moieties involved in bonding and the geometrical arrangement of the cyclodiphosphazane that leads to the more stable complex. The two uncoordinated phosphorus centres of complex **202** can be used for further coordination: thus reaction of **202** with $[Mo(CO)_4(pip)_2]$ or $[Pt(COD)Cl_2]$ give the complexes **206** and **207**, respectively. Similarly, reaction of **203** with $[MCl_2COD]$ gives trinuclear complexes of the type **208** [192].

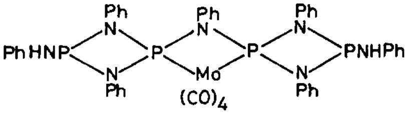
Norman and co-workers [94], have reported that the reactions of $[PhNPX]_2$ (X = Cl or NHPh) with *cis*-$[Mo(CO)_4(NBD)]$ give a mixture of products. The ^{31}P NMR spectra of the reaction mixtures were complex and authors could not assign the observed resonances to any particular compound. However, the authors have



208 R = C_6H_4Me-p
(M = Pd, Pt)



209a

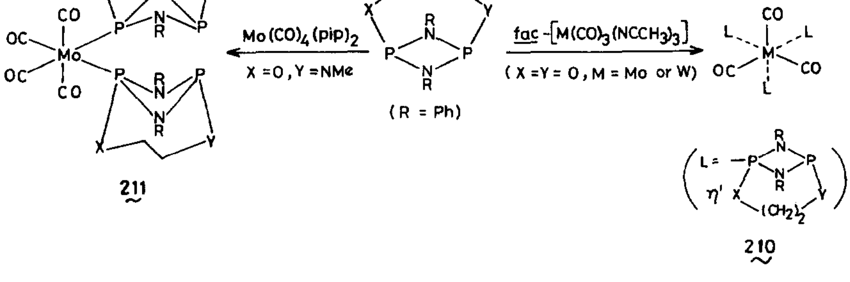


209b

isolated the complexes **209a** and **209b** by the treatment of $[Mo(CO)_4NBD]$ with the appropriate cyclodiphosphazanes.

Bicyclodiphosphazanes of the type $[(RNP)_2\{X(CH_2)_nY\}]$ react with Group 6 metal carbonyl derivatives to give complexes of the type $[M(CO)_3\{(RNP)_2(O(CH_2)_2O)\}_3]$ (**210**) and $[M(CO)_4\{(RNP)_2(O(CH_2)_2NMe)\}_2]$ (**211**) as shown in Scheme 31 [97].

Willey and co-workers have reported that the reactions of $[Bu^tNPCl]_2$ with transition metal derivatives such as $[Fe_2(CO)_9]$, $[RhCl(CO)_2]_2$, $[Mn_2(CO)_{10}]$ and $TiCl_4$ lead to various products [194,195]. Although the authors claim that both chelating as well as bridged bidentate modes of coordination of the ligands are observed, the assignments of the structures are doubtful because of the later results obtained by Nixon and others [196–199] (see below). Willey and co-workers do not report any Rh–P coupling for their rhodium complexes and their phosphorus-31 chemical shifts do not fall in the range observed for a variety of complexes containing

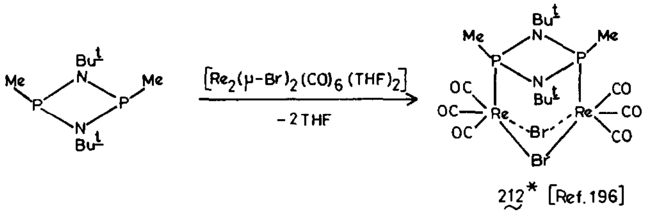


Scheme 31. [205].

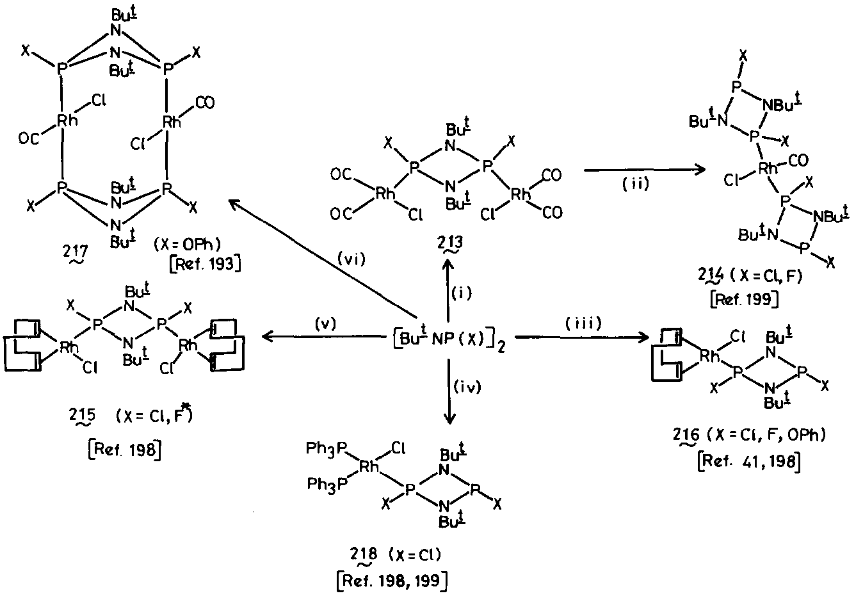
trivalent phosphorus. The shifts are more suggestive of ring oxidation products containing pentavalent phosphorus.

Interaction of *cis*-$[Bu^tNPMe]_2$ with $[Re_2(\mu\text{-}Br)_2(CO)_6(THF)]_2$ affords the dinuclear complex **212** in which the cyclodiphosphazane acts as a bridging bidentate ligand (Scheme 32) [196,197].

Nixon and co-workers have carried out the reactions of $(Bu^tNPX)_2$ (X = Cl, F) with $[RhCl(COD)]_2$ [198] and $[RhCl(CO)_2]_2$ [199]. The various products isolated are shown in Scheme 33. When a toluene solution of $[RhCl(CO)_2]_2$ is treated with a single equivalent of $[Bu^tNPF]_2$ in toluene under CO atmosphere, the orange-yellow complex **213** is obtained, which on treatment with three equivalents of $[Bu^tNPF]_2$ gives a stable complex **214**. The formation of complexes **213** and **214** contrasts markedly with the interaction between $[RhCl(CO)_2]_2$ or **213** with



Scheme 32.

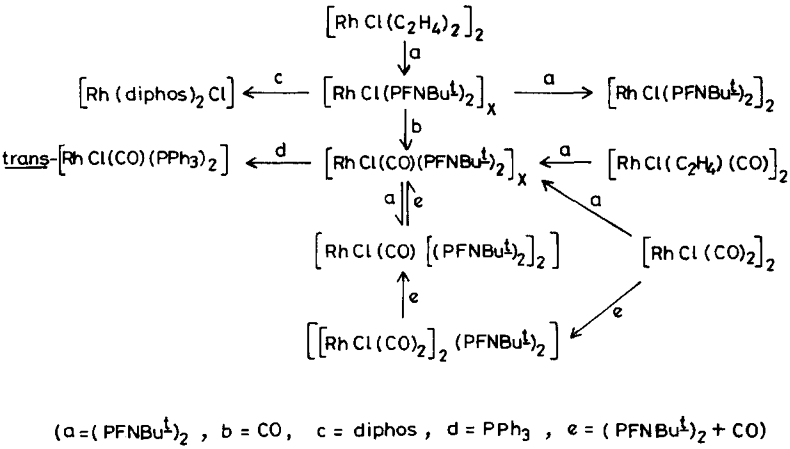


Scheme 33. (i) $[RhCl(CO)_2]$ (1 : 1 M/L ratio); (ii) $3[Bu^tNPX]_2$; (iii) 1/2 $[RhCl(COD)]_2$; (iv) $[Rh(PPh_3)_3Cl]$; (v) $[RhCl(COD)]_2$; (vi) $[RhCl(CO)_2]_2$.

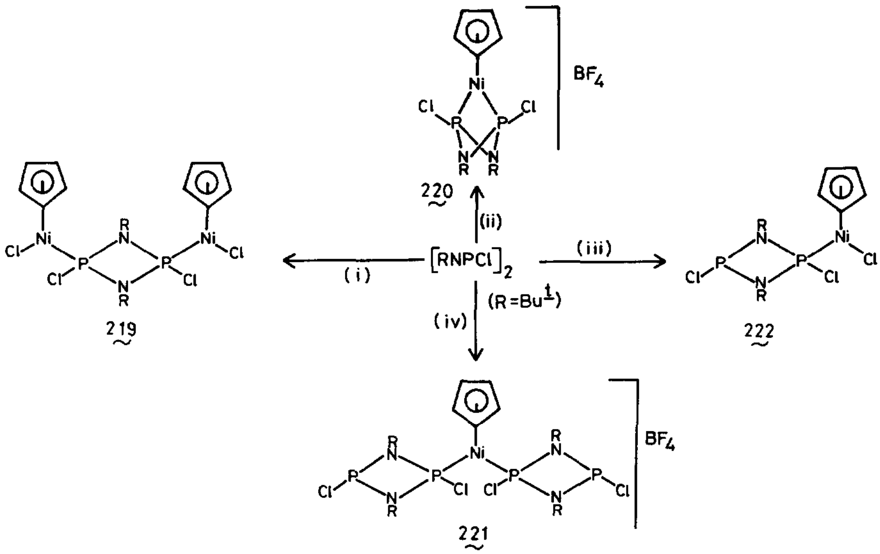
$[\mathrm{Bu^tNPF}]_2$ in the absence of CO, when the reaction product is a highly insoluble derivative formulated as $[\mathrm{RhCl(CO)[Bu^tNPF)_2}]$, which can also be obtained by the displacement of ethylene from $[\mathrm{RhCl(C_2H_4)(CO)}]_2$. A polymeric structure having chloro bridges has been proposed for this insoluble complex. The various reactivity patterns and the products obtained are shown in Scheme 34 [199]. It has also been possible to synthesize the dinuclear complexes **215** by slow addition of $(\mathrm{PXNBu^t})_2$ (X = F, Cl) to $[\mathrm{RhCl(COD)}]_2$ in 1 : 1 molar ratio. The dinuclear complexes **215** could be converted quantitatively (^{31}P NMR evidence) into the mononuclear analogues **216** by treatment with further $(\mathrm{PFNBu^t})_2$ [198]. The cyclodiphosphazane *cis*-$[\mathrm{Bu^tNP(X)}]_2$ (X = F, Cl or OPh) reacts with $[\mathrm{RhCl(COD)}]_2$ in benzene to give the mononuclear complex, $[\mathrm{RhCl(COD)}\eta^1\text{-}\{\mathrm{Bu^tNP(X)}\}_2]$ (**216**) [193,198]. Interestingly, the reaction of $[\mathrm{Bu^tNP(OPh)}]_2$ with $[\mathrm{RhCl(CO)_2}]_2$ yields the dinuclear complex, $[\mathrm{RhCl(CO)}\{\mathrm{Bu^tNP(OPh)}\}_2]_2$ (**217**); here, the cyclodiphosphazanes exhibit bridged bidentate mode of coordination [41,193].

The reactions of $[\mathrm{Bu^tNPCl}]_2$ with nickel cyclopentadienyl compounds have been studied by Kuhn and Winter [200]. The various products obtained (**219**–**222**) are shown in Scheme 35. It is proposed that the cyclodiphosphazane ligand exhibits monodentate, bridged bidentate or chelating modes of coordination. However, the authors did not report ^{31}P NMR data in support of the structure of the chelated complex **220**.

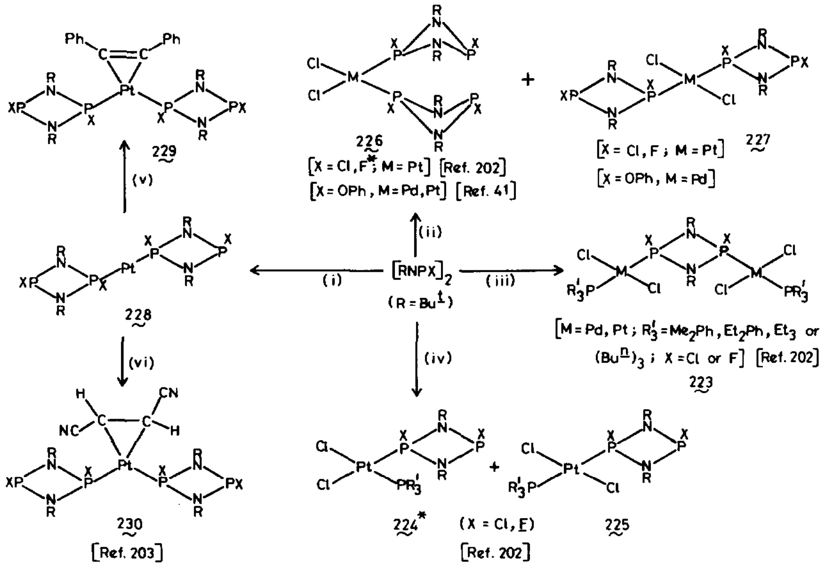
Nixon and co-workers have investigated the reactions of $[\mathrm{RNPX}]_2$ with palladium and platinum derivatives such as $[\mathrm{M_2Cl_4(PR'_3)_2}]$ ($\mathrm{PR'_3 = PPr^n_3}$, $\mathrm{PBu^n_3}$, $\mathrm{PPh_3}$, $\mathrm{PMe_2Ph}$ or $\mathrm{PEt_2Ph}$) and with $[\mathrm{MCl_2(COD)}]$ (M = Pd, Pt). The products obtained (**223**–**227**) are shown in Scheme 36 [187,193,201,202]. Monomeric complexes of the type $[\mathrm{PtCl_2(PR'_3)(RNPX)_2}]$ (**224**–**227**) in which the $\mathrm{P_2N_2}$ ring exhibits monodentate type of coordination are readily formed by the treatment of $[\mathrm{Pt_2Cl_4(PR_3)_2}]$ with



Scheme 34. [199].



Scheme 35. [200]. (i) 2[NiCp$_2$] in CCl$_4$. (ii) [CpNiC$_5$H$_6$]BF$_4$. (iii) [NiCp$_2$] in CCl$_4$. (iv) ½[CpNiC$_5$H$_6$]BF$_4$.

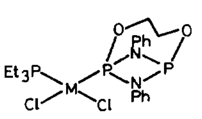


Scheme 36. (i) Pt(COD)$_2$. (ii) M(COD)Cl$_2$. (iii) [M$_2$Cl$_4$(PR'$_3$)$_2$]. (iv) ½[Pt$_2$Cl$_4$(PR'$_3$)$_2$]. (v) PhC≡CPh. (vi) H(NC)C≡C(CN)H.

two equivalents of [RNPX]$_2$. Both cis and trans isomers of the types **224** and **225** are formed, depending, to some extent, on the solvent used but more so on the nature of the ligand. The stereochemistry of each complex has been unambiguously determined by ^{31}P and ^{19}F NMR spectroscopy and subsequently confirmed by a single-crystal X-ray structural determination of *cis*-$[\mathrm{PtCl_2(PEt_3)(PFNBu^t)_2}]$ [201,202]. The reaction of $[\mathrm{RNPX}]_2$ ($\mathrm{R=Bu^t}$ $\mathrm{X=OPh}$) with $[\mathrm{Pd(COD)Cl_2}]$ also gives both cis and trans isomers (**226** and **227**); however, reaction with $[\mathrm{Pt(COD)Cl_2}]$ gives the cis isomers (**226**) exclusively [193]. Scherer and Krieger have reported the preparation of the two-coordinate platinum(0) complex $\mathrm{PtL_2}$ (**228**) by the reaction between $\mathrm{Pt(COD)_2}$ and $[\mathrm{Bu^tNPMe}]_2$ (L). In benzene solution, $\mathrm{PtL_2}$, $\mathrm{Pt_2L_3}$ and L are in equilibrium. The complex $\mathrm{PtL_2}$ (**228**) reacts with diphenylacetylene or fumaric acid dinitrile to give the platinum diazadiphosphetidine complexes $[\mathrm{L_2Pt(PhC{\equiv}CPh)}]$ (**229**) and $[\mathrm{L_2Pt(H(NC)C{=}C(CN)H)}]$ (**230**), respectively [203]. In the above complexes, cyclodiphosphazanes exhibit both bridged bidentate and monodentate modes of coordination. Formation of chelate complexes is not observed.

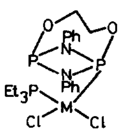
The combination of cyclodiphosphazane and diborane in 1 : 0.5 and 1 : 1, results in the formation of monoborane (**231**) and bisborane (**232**) complexes. The bisborane derivative has been characterized by single-crystal X-ray diffraction [204] (Scheme 37).

The bicyclodiphosphazane, $[\mathrm{(PhNP)_2\{O(CH_2)_2O\}}]$ reacts with platinum and palladium derivatives, $[\mathrm{M_2Cl_4(PEt_3)_2}]$ to give complexes of the type $[\mathrm{MCl_2(PEt_3)\{(PhNP)_2(O(CH_2)_2O\}}]$ which exist in two isomeric forms (**233a,b**) of which **233a** is the major product. Binuclear complexes can also be isolated from the same reaction. An interesting aspect of these studies is that the dinuclear palladium

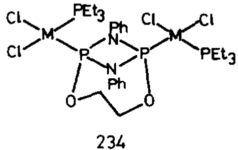


(M = Pd, Pt)

233a



233b



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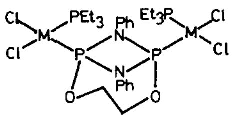

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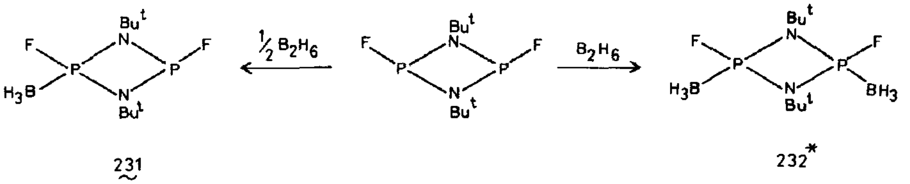


Scheme 37. [204].

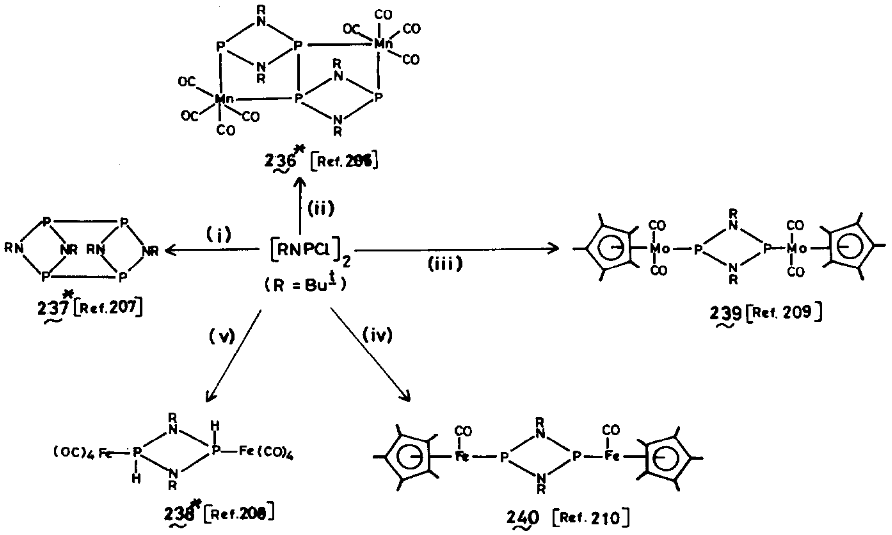
derivative (**234**) has a cis–trans disposition of the PEt_3 groups whereas the platinum derivative (**235**) shows the cis–cis arrangement [205].

Heterocyclic P—Cl bond cleavage has been demonstrated when $[\mathrm{Bu}^t\mathrm{NPCl}]_2$ reacts with $[\mathrm{Mo(Me_5C_5)(CO)_3}]^-$, $[\mathrm{Fe(Me_5C_5)(CO)_2}]^-$ or $[\mathrm{Mn(CO)_5}]^-$ moieties as shown in Scheme 38. The reaction of $\mathrm{Na[Mn(CO)_5]}$ with $[\mathrm{Bu}^t\mathrm{NPCl}]_2$ gives **236**, which is the first characterized example of coupling of cyclodiphosphazane units with the incorporation of metal fragments into a cage structure [206]. The $[\mathrm{Mn(CO)_4X_2}]$ units adopt a distorted octahedral geometry. The structural framework of the compound **236** suggests that it represents an early intermediate in the formation of the cage compound $[\mathrm{P_4(Bu}^t\mathrm{N)_4}]$ (**237**) from $[\mathrm{Bu}^t\mathrm{NPCl}]_2$, which has been trapped by two $[\mathrm{Mn(CO)_4}]$ fragments before P—N bond breaking and making process has occurred [207].

The reaction of $\mathrm{Na_2Fe(CO)_4}$ with $[\mathrm{Bu}^t\mathrm{NPCl}]_2$ gives the di-iron complex **238**, whose structure has been established by single-crystal X-ray diffraction. Apparently the source of hydrogen is the traces of water present in the reaction medium. Each phosphorus atom of the ligand ring is tetrahedral and occupies an equatorial position of the $[\mathrm{Fe(CO)_4L}]$ trigonal bipyramid [208]. The reaction between $[\mathrm{Bu}^t\mathrm{NPCl}]_2$ and $\mathrm{Na[Mo(C_5Me_5)(CO)_3]}$ or $\mathrm{Na[Fe(C_5Me_5)(CO)_2]}$ give the complexes **239** and **240**, respectively in which the cyclodiphospazane bridges two metal carbonyl moieties [209,210] (see Scheme 38).

6. PHYSICAL TECHNIQUES

A variety of physical and analytical techniques have been used to study transition metal complexes of diphosphazanes. The application of spectroscopic and X-ray



Scheme 38. (i) Mg/THF; (ii) $\mathrm{Na[Mn(CO)_5]}$; (iii) $\mathrm{Na[Mo(C_5Me_5)\ (CO)_2]}$; (iv) $\mathrm{Na[Fe(C_5Me_5)\ (CO)]}$; (v) $\mathrm{Na_2[Fe(CO)_4]}$.

crystallographic techniques to characterize these complexes are discussed below with typical examples.

6.1 Vibrational spectroscopy

The infrared spectroscopy can be used to distinguish the terminal and bridging carbonyl groups in transition metal complexes of diphosphinoamines; terminal carbonyls show ν(CO) absorption in the region 2100–1850 cm^{-1} and the bridging carbonyls in the region 1825–1650 cm^{-1}. The IR spectra of the tetracarbonyl complexes, *cis*-$[M(CO)_4(PX_2)_2NR]$ exhibit four strong ν(CO) absorptions, which are assigned to $2A_1$, B_1 and B_2 modes of the $M(CO)_4$ moiety having local C_{2v} symmetry [211–213]. The relative π acid strengths of diphosphinoamines with varying substituents on nitrogen and phosphorus atoms of the P—N—P skeleton could be discerned by comparing the pairs of the ν(CO)(A_1) absorptions for $X_2PN(alkyl)PX_2$ complexes. A similar spectral pattern is observed for the tetracarbonyl complexes of the cyclodiphosphazanes, *cis*-$[M(CO)_4\{[RNPX]_2\}_2]$ [192].

The carbonyl frequencies for diphosphinoamine, $Ph_2PN(R)PPh_2$ complexes $[M(CO)_4(L{-}L)]$ are very near to those for closely related complexes of dppm in which the phosphorus is bonded to carbon only. The absence of any marked effect on ν(CO) frequencies shows that the replacement of CH_2 or CHR by NR does not greatly change the ability of phosphorus to accept electrons from the metal. Whilst N—P π bonding is expected to lower the carbonyl frequency, the higher electronegativity of nitrogen should have the opposite effect. However, for the tetracarbonyl complexes of $RN(PX_2)_2$ (R = alkyl, aryl; X = F, OMe, OCH_2CF_3 or OPh) the ν(CO) absorptions are shifted to higher wavenumbers, reflecting the higher π acceptor capability of these ligands [81,96]. The IR spectra have been effectively used to distinguish the fac and mer isomers of the tricarbonyl complexes, $[M(CO)_3LL]$ and also to differentiate the cis and trans isomers of $[M(CO)_4LL]$ where L is $(PF_2)_2NMe$ [81].

The asymmetrical and symmetrical P—N vibrations of the P—N—P group in diphosphinoamine ligands are observed around 880 and between 800 and 900 cm^{-1}, respectively [80]. The spectra of the cyclodiphosphazanes contain characteristic absorptions in the range 830–900 cm^{-1}, which can be attributed to the ν(asym)P—N—P associated with the P_2N_2 ring. Although this technique does not provide any easy distinction between the geometrical isomers (cis and trans) of cyclodiphosphazanes, the spectrum of the cis isomer displays a more complex pattern [64,69]. A shift in the P—N frequencies to lower values is observed for the complexes of cyclodiphosphazanes. This could be the result of a competition between metal–phosphorus and nitrogen–phosphorus back-bonding [80]. The IR spectra of diphosphinoamines also show a strong band in the region 1150–1200 cm^{-1}, assigned to the C—N(P—N—P) stretching mode [20].

IR and Raman spectroscopic data for dppa complexes together with detailed vibrational assignments have been reported by Ellermann et al. The data clearly indicate that the dppa ligand in the complexes is involved in hydrogen bonding with anions (halides, PF_6^-) or neutral molecules such as methanol or diethyl either in the crystal lattice [149–152,168–171].

6.2 *Nuclear magnetic resonance spectroscopy*

^1H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopic measurements have been used extensively to elucidate the structures of transition metal complexes of diphosphinoamines and cyclodiphosphazanes. The principal parameters derived from NMR studies are chemical shifts (δ) and spin–spin couplings (J) [e.g. J(MP), J(PP), J(PF) and J(FF)]. These parameters are frequently diagnostic of the molecular structures of compounds [212,214–216].

6.2.1 *^1H NMR*

While ^1H NMR data have been routinely reported for a large number of complexes of diphosphinoamines and cyclodiphosphazanes, in only a few instances, has any correlation between the NMR parameters and the structures been established.

The ^1H resonances for the methyl protons of the diphosphinoamine ligand, $MeN(PF_2)_2$ are sensitive to the structure of the complexes. The coupling between phosphorus and the protons in diphosphines may also change upon coordination to the metal. The ^1H NMR data for complexes of $MeN(PF_2)_2$ are listed in Table 4. In the proton NMR spectra of complexes containing a single $MeN(PF_2)_2$ ligand, which is biligate monometallic [Fig. 3(a)], the *N*-methyl resonance appears as a sharp triplet ($J = 11$–12 Hz) apparently owing to coupling of the methyl protons with two equivalent phosphorus atoms. However, in the proton NMR spectra of complexes containing a single $MeN(PF_2)_2$, which is monoligate monometallic [Fig. 3(b)], the *N*-methyl resonances appears as a broad doublet ($J = 7$–8 Hz). The coupling of the methyl protons to the complexed phosphorus atom is appreciable but their coupling to the uncomplexed phosphorus atom is only sufficient to broaden the resonances but not to permit their resolution. In the case of biligate bimetallic complexes of $MeN(PF_2)_2$, [Fig. 3(c)], the *N*-methyl protons exhibit a triplet ($J = 6$–7 Hz) owing to coupling of the methyl protons with two equivalent phosphorus nuclei.

The ^1H resonances for the *N*-methyl protons of $MeN\{P(OPh)_2\}_2$ are also structure-sensitive. For Pd(II), Pd(I) and Pd(0) complexes, these resonances appear at 3.05 ppm, 2.85 ppm and 2.80 ppm, respectively. The spin–spin splitting due to ^3J(PH) differs in these complexes [41]. For the chelated Pd(II) complexes, the coupling constant is ca. 11.0 Hz. For the bridged dinuclear Pd(I) and Pd(0) complexes, a smaller coupling (ca. 4.5 Hz) is observed. A similar trend is observed for palladium complexes of the dppm ligand [217] (Table 5).

A hydride ligand bonded to a transition metal exhibits a chemical shift in the region 7–35 ppm upfield to tetramethyl silane. In the proton NMR spectrum of the

TABLE 4

^{1}H-NMR data for selected $(PF_2)_2NMe$ complexes[a]

No.	Compound	δ_{NMe}[b]	$^3J(PH)$ (Hz)
(η^2-PP')			
1	$[Cr(CO)_4(PF_2)_2NMe]$	2.75 t	10.0
2	$[Mo(CO)_4(PF_2)_2NMe]$	2.75 t	10.0
3	$[W(CO)_4(PF_2)_2NMe]$	2.73 t	10.0
(η^1-PP')			
4	*trans*-$[Cr(CO)_4\{(PF_2)_2NMe\}_2]$	2.97 dd	8.0, 1.0
5	*cis*-$[Mo(CO)_4\{(PF_2)_2NMe\}_2]$	2.89 br.d	6.0
6	*cis*-$[W(CO)_4\{(PF_2)_2NMe\}_2]$	2.92 ddd	5.6, 3.0, 0.9
7	mer-$[Cr(CO)_4\{(PF_2)_2NMe\}_2]$	2.89 d 2.75 t	7.0, 11.0
8	mer-$[Mo(CO)_4\{(PF_2)_2NMe\}_2]$	2.96 d 2.78 t	6.0, 10.0
9	mer-$[W(CO)_4\{(PF_2)_2NMe\}_2]$	2.91 d 2.73 t	6.0, 10.0
(μ-PP')			
10	$\{Cr_2(CO)_5\{(PF_2)_2NMe)_3]$	3.17 t 2.85 t	6.0
11	$[Mo_2(CO)_5\{(PF_2)_2NMe\}_3]$	3.11 t 2.87	6.0
12	$[W_2(CO)_5\{(PF_2)_2NMe\}_3]$	3.02 t 2.87	6.0

[a] Ref. 81.

[b] t = triplet, d = doublet, br = broad.

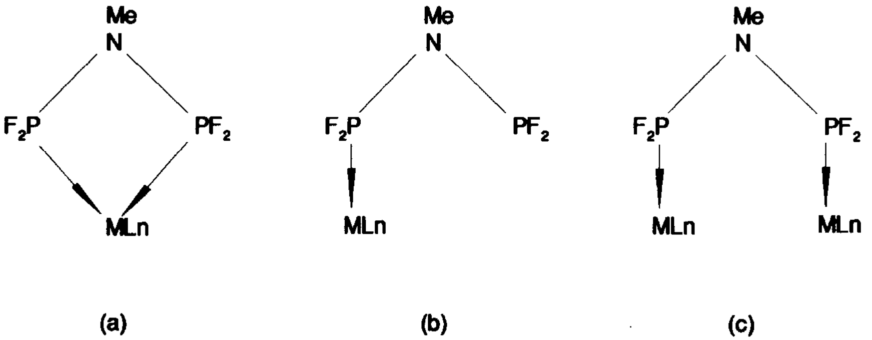


Fig. 3. (a) Chelating, (b) monodentate and (c) bridging modes of coordination of $MeN(PF_2)_2$ ligand.

TABLE 5

The ^{1}H and ^{31}P NMR parameters for palladium complexes of diphosphine ligands in +2, +1 and 0 oxidation states

Complex	^{1}H		^{31}P (ppm)	$\Delta\delta$[b]
	ppm[a]	J(PH) (Hz)		
L = MeN(P(OPh)$_2$)$_2$[c]			135.1	
$PdCl_2L$	3.05 (t)	11.0	65.5	−69.6
$Pd_2Cl_2L_2$	2.85 (t)	4.5	112.1	−23.0
Pd_2L_3	2.80 (t)	4.5	124.5	−10.6
L′ = dppm[d]			−23.6	
$PdCl_2L'$	4.28 (t)	10.8	−53.7	−30.1
$Pd_2Cl_2L'_2$	4.17 (q)	4.0	−2.5	21.1
$Pd_2L'_3$	3.00 (br)	—	14.6	48.2

[a] t = triplet; q = quintet; br = broad.

[b] $\Delta\delta = \delta_{(complex)} - \delta_{(ligand)}$.

[c] Ref. 41.

[d] Ref. 217.

rhodium complex, $[RhHgCl(\mu\text{-}H)(CO)_2\{\mu\text{-}(P(OPh)_2)_2NEt\}_2]$ (**129**), the resonance due to the bridging hydride ligand is observed at −12.03 ppm [148]. In the case of iron complexes of the type $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PX_2)_2NR\}_2]BF_4$ (**87**) (R = Et, X = OEt), the resonance due to metal hydride (Fe—H—Fe) is observed in the region −11 to −13 ppm [123].

6.2.2 ^{31}P NMR

Of all the nuclei that have been probed for NMR measurements, ^{31}P NMR data have proved the most informative in the study of metal–phosphazane complexes. Complex formation invariably causes a change in the ^{31}P chemical shifts. This coordination shift, $[\Delta\delta = \delta P_{(complex)} - \delta P_{(free\ ligand)}]$ is either positive or negative depending on the metal derivatives.

The ^{31}P chemical shifts of the chelated complexes of Group 6 metal carbonyls, $[M(CO)_4\{(PX_2)_2NR\text{-}PP'\}]$ undergo a downfield shift compared with the value for the free ligands. Such a deshielding of the phosphorus nuclei upon complexation has also been observed for analogous dppm complexes and the observed shift is presumed to arise from a combination of deshielding caused by coordination and a shielding effect on account of the formation of a four-membered ring [216].

The coordination shift for various diphosphinoamine complexes, $[Mo(CO)_4\{(PX_2)_2NR\text{-}PP'\}]$ are listed in Table 6. Assuming that the ring contribution remains the same for the complexes shown in Table 6, it is evident that $\Delta\delta$ for various X_2PNRPX_2 complexes increases with the substituent X in the order: X =

TABLE 6

Comparison of ^{31}P coordination shifts for *cis*-$[Mo(CO)_4(PX_2)_2NR]$

$RN(PX_2)_2$	$\delta_{P(complex)}$	$\delta_{P(ligand)}$	$\Delta\delta$	Ref.
$PhN(PCl_2)_2$	122.4	155.5	−33.1	94,12
$MeN(PF_2)_2$	144.5	141.3	3.2	81
$EtN(PF_2)_2$	144.8	145.3	−0.5	73
$PhN(PF_2)_2$	141.3	132.3	9.1	81
$MeN(P(OCH_2CF_3)_2)_2$	152.3	149.9	2.4	96
$PhN(P(OCH_2CF_3)_2)_2$	148.7	140.3	8.4	96
$MeN(P(OPh)_2)_2$	143.3	135.1	8.2	96
$PhN(P(OPh)_2)_2$	151.6	127.7	23.9	96
$PhN(P(NHPh)_2)_2$	95.6	67.8	27.8	84
$Pr^iN(PPh_2)_2$	89.4	48.8	40.6	96
$Pr^iN[P(O_2C_6H_4)]_2$	157.8	149.9	7.9	46
$Ph_2PN(Pr^i)P(O_2C_6H_4)$	75.1(d)[a]	28.9	46.2	46
	163.5(d)[b]	155.8	7.7	
$Ph_2PN(Pr^i)P(O_2C_{12}H_8)$[c]	74.8(d)[a]	27.9	46.9	46
	154.0(d)[b]	148.6	5.4	

[a] *P*Ph_2.

[b] Other phosphorus.

[c] 2,2′-Biphenylene dioxy.

$Cl \ll F \approx CF_3CH_2O < PhO < PhNH < Ph$. This order is the same as the decreasing order of the π acidity of the ligands [218] except for the anomalous shift when $X = Cl$. The magnitude of $\Delta\delta$ is also higher when the substituent on the nitrogen is changed from an alkyl to an aryl group. The anomalous value for $X = Cl$ probably indicates that steric effects also contribute to ^{31}P chemical shifts. In all other complexes, the atoms attached to the phosphorus atoms are the small first-row elements (C, N, O and F). The X-ray crystal structure of the chelated complexes, $[Mo(CO)_4(Ph_2P)_2NEt]$ [79], $[Mo(CO)_4(P(NHPh)_2)_2NPh]$ [94], $[Mo(CO)_4(P(OPh)_2)_2NPh]$ [96], and $[W(CO)_4(PPh_2)_2NPr^i]$ [96] show a planar MPNP ring; in the $Cl_2PNPhPCl_2$ complex, the ring may deviate from planarity causing the observed large upfield shift upon complexation. For the $M(CO)_4$ complexes of unsymmetrical diphosphinoamines, $Ph_2PN(Pr^i)P(O_2C_6H_4)$ and $Ph_2PN(Pr^i)P(O_2C_{12}H_8)$ (see Table 6), the P—P coupling constants for the complexes (32 and 33 Hz) increase markedly from those observed for the ligands (14 and 25 Hz, respectively).

^{31}P chemical shifts of Pd(II), Pd(I) and Pd(0) complexes of the diphosphazane ligand, $MeN(P(OPh)_2)_2$ show an interesting trend. For the palladium(0) and Pd(I) dinuclear complexes, the ^{31}P resonance appears at 124.5 ppm and 112.1 ppm, respectively, while for the corresponding Pd(II) complex, this resonance appears at 65.5 ppm [41] (see Table 5). The ^{31}P chemical shifts of Pd(II) and Pt(II) diphosphazane complexes are unusual as they are very much upfield to those of the free ligands.

Coordination of phosphines generally results in a shift of the ^{31}P resonance to the downfield region [216]. However, upfield shifts are observed for dppm complexes such as [Pt(dppm)Cl_2] [219], [Pd(dppm)Cl_2] [217], and [Pd(dppm)Me_2] [219]. The unusual shifts for these Pd(II) and Pt(II) complexes of diphosphine ligands cannot be simply related to the presence of a four-membered ring since the chelated complexes of [$M(CO)_4(PX_2)_2NR$] (M = Cr, Mo) show downfield shifts as noted above.

The ^{31}P NMR chemical shifts of the cyclodiphosphazane complexes are listed in Table 7. It is now possible to generalize the trends observed for both mono(η^1)-coordinated and bridging cyclodiphosphazanes involving Group 6 metal carbonyl moieties. The chemical shifts of the monocoordinated cis and trans cyclodiphosphazanes move downfield for chromium and molybdenum complexes and upfield for tungsten complexes compared with the values for the free ligands. For bridging *cis*-cyclodiphosphazanes, the ^{31}P chemical shifts move downfield upon complexation for molybdenum and upfield for tungsten but, for *trans*-cyclodiphosphazanes, the shift is towards upfield region for both molybdenum and tungsten complexes. In contrast, for palladium and platinum complexes of cyclodiphosphazanes, the ^{31}P resonances move upfield upon complexation (see Table 7).

6.2.3 *M—P coupling constants*

Metal—phosphorus coupling constants are very useful in the structural elucidation of diphosphine complexes and also in assessing the relative magnitude of trans influence experienced by various ligands [212,215,220]. The same trends are observed in the M—P coupling constants for diphosphinoamine complexes. For platinum complexes of diphosphinoamines, the ^{1}J(PtP) values are in the range 3000–5000 Hz. A large ^{1}J(PtP) coupling (> 5000 Hz) is observed for complexes of cyclodiphosphazanes (see Table 7). Rhodium—phosphorus coupling constants have also been widely used in characterizing metal—phosphine complexes [41,198,199]. The ^{1}J(Rh—P) values for chelated complexes are in the range 250–300 Hz (see Table 8), whereas for dinuclear complexes with bridging diphosphinoamine ligands, the ^{1}J(Rh—P) values are in the range 180–220 Hz. The ^{1}J(W—P) values observed for diphosphinoamine complexes (e.g. **31**, Scheme 4) are in the range of 180–400 Hz [96].

6.2.4 *^{13}C NMR*

^{13}C NMR data available for transition metal complexes of diphosphinoamines and cyclodiphosphazanes are much more limited than ^{1}H or ^{31}P NMR data.

The ^{13}C methyl resonances in the proton decoupled ^{13}C NMR spectra of $MeN(PF_2)_2$ complexes are singlets (Table 9). These chemical shifts provide a basis for differentiating a monodentate from a bidentate $MeN(PF_2)_2$ ligand [81]. Thus the $^{13}CH_3$ resonances of monoligated monometallic $MeN(PF_2)_2$ ligand fall in the range 25–27 ppm, whereas ^{13}C methyl resonances of biligate monometallic $MeN(PF_2)_2$ ligands fall in the range 29–31 ppm. In the case of biligate bimetallic $MeN(PF_2)_2$ ligands, the $^{13}CH_3$ resonances fall over a wide range (28–33 ppm) but

TABLE 7

^{31}P NMR data for some selected metal complexes of cyclodiphosphazanes

Compound	$\delta_{P(coor)}$ (ppm)	$\delta_{P(uncoor)}$ (ppm)	$\Delta\delta$[a] (ppm)	^1J(MP) (Hz)	Ref.
cis-$[PhNP(OC_6H_4Me$-*p*$)]_2(L_1)$	—	137.0	—	—	191
$[Cr(CO)_4\{[PhNP(OC_6H_4Me$-*p*$)]_2\}_2]$	186.4(s)	119.6(s)	49.4	—	191
$[Mo(CO)_4\{[PhNP(OC_6H_4Me$-*p*$)]_2\}_2]$	154.4(s)	126.7(s)	17.4	—	191
$[W(CO)_4\{[PhNP(OC_6H_4Me$-*p*$)]_2\}_2]$	125.3(s)	127.6(s)	−11.7	—	191
$[W(CO)_4(pip)\{[PhNP(OC_6H_4Me$-*p*$)]_2\}]$	132.3(s)	122.0(s)	−5.7	372.0	191
cis-$[Bu^tNP(OPh)]_2(L_2)$	—	143.3	—	—	193
$[Cr(CO)_4\{[Bu^tNP(OPh)\}_2]_2]$	181.8(d)	128.4(d)	38.5	—	193
$[Mo(CO)_4\{[Bu^tNP(OPh)\}_2]_2]$	152.0(s)	129.9(s)	8.9	—	193
$[W(CO)_4\{[Bu^tNP(OPh)\}_2]_2]$	114.8(s)	127.1(s)	−28.5	—	193
trans-$[PhNP(OCH_2CF_3)]_2(L_3)$	—	189.8	—	—	66
$[Mo_2(CO)_8(pip)_2\{\mu$-*trans*-$L_3\}]$	176.4(s)	—	−13.4	—	191
$[Mo_2(CO)_8\{P(OMe)_3\}_2\{\mu$-*trans*-$L_3\}]$	179.8(d)	—	−10.0	—	191
$[W_2(CO)_8(pip)_2\{\mu$-*trans*-$L_3\}]$	150.1(s)	—	−39.7	—	191
$[\{Mo(CO)_4P(OMe)_3\}_2\{\mu$-*cis*-$L_1\}]$	158.8(d)	—	21.8	—	192
$[\{Mo(CO)_4P(OMe)_3\}_2\{\mu$-*trans*-$L_1\}]$	178.0(d)	—	−11.8	—	192
$[\{W(CO)_4(NHC_5H_{10})\}_2\{\mu$-*cis*-$L_1\}]$	132.6(s)	—	−4.4	376.0	192
$[\{MoW(CO)_8(NHC_5H_{10})P(OMe)_3\}\{\mu$-*cis*-$L_1\}]$	137.3(d)[b]	—	0.3	379.0	192
	150.3(dd)[c]	—	13.3		
trans-$[(Me_3Si)NP(NMe_2)]_2(L_4)$	—	107.6	—	—	188
$[Cr_2(CO)_{10}\{\mu$-$L_4\}]$	155.0	—	47.4	—	188
$[Mo_2(CO)_{10}\{\mu$-$L_4)\}]$	131.0	—	23.4	—	188
cis-$[PdCl_2\{[Bu^tNP(OPh)]_2\}_2]$	78.8(t)	127.7(t)	−64.5	—	193
trans-$[PdCl_2\{[Bu^tNP(OPh)]_2\}_2]$	84.5(t)	128.6(t)	−58.8	—	193
cis-$[PtCl_2\{[Bu^tNP(OPh)]_2\}_2]$	44.5(d)	125.8(d)	−98.9	4835	193
cis-$[PtCl_2\{[PhNP(OC_6H_4Me$-*p*$)]_2\}_2]$	64.0(s)	120.1(s)	−73.0	5214	192
cis-$[PtCl_2\{$*cis*$[W(CO)_4(NHC_5H_{10})(L_1)]\}_2]$	62.9(d)	—	−74.1	5344	192
cis-$[Bu^tNP(Me)]_2(L_5)$	—	171.4	—	—	203
$Pt(L_5)_2$	165.0(s)	162.1(s)	−6.4	4250	203
$[Pt(L_5)_2C_2Ph_2]$	147.2(s)	178.2(s)	−24.2	3908	203
$[Pt(L_5)_2C_2H_2(CN)_2]$	143.5(s)	187.4(s)	−27.9	4215	203
$[Pt_2(\mu$-$L_5)(\eta^1$-$L_5)_2]$ $(\eta^1$-$L_5)$	165.4	162.5	−6.0	4306	203
$(\mu$-$L_5)$	157.5	—	−13.9	4373	

TABLE 8

^{31}P NMR[a] data for dirhodium complexes[b]

Compound	δ_P	^1J(Rh–P) (Hz)
$[Rh_2Cl_2(COD)(P(OPh)_2)_2NPh]$	88.8 (d)	282.5
$[\{RhCl(P(OPh)_2)_2NPh\}_2]$	86.1 (d)	284.0
$[\{RhCl(CO)(P(OPh)_2)_2NPh\}_2]$	112.9 (d)	214.0
$[\{RhCl(CO)(P(OPh)_2)_2NMe\}_2]$	114.0 (d)	187.5
$[\{RhCl(P(OC_6H_4Br\text{-}p)_2)_2NPh\}_2]$	90.2 (d)	281.2

[a] in ppm relative to 85% H_3PO_4; d = doublet.
[b] Ref. 41.

TABLE 9

^{13}C NMR data[a] for Group 6 metal carbonyl derivatives of $(PF_2)_2NMe$ ligand (L) [81]

Compound	$\delta_{(CO)}$	$\delta_{(CH_3)}$
$[Cr(CO)_4L]$	220.1 d (23), 215.0 (18)	29.6
$[Mo(CO)_4L]$	209.0 br, 203.9 t (13)	29.0
$[W(CO)_4L]$	200 m, 194.8 t (9)	30.3
trans-$[Cr(CO)_4L_2]$	213.9 br	25.8
cis-$[Mo(CO)_4L_2]$	206.1 d (47), 203.4 t (12)	25.1
cis-$[W(CO)_4L_2]$	195 m	25.3
mer-$[Cr(CO)_3L_2]$	223.3 br, 216.0 q (19)	30.2, 25.8
mer-$[Mo(CO)_3L_2]$	212.0 br, 205 m	29.1, 25.3
mer-$[W(CO)_3L_2]$	202 m, 195 m	30.1, 25.5
$[Cr_2(CO)_5L_3]$	221	32.0, 29.3
$[Mo_2(CO)_5L_3]$	—	31.6, 28.4
$[W_2(CO)_5L_3]$	199.6	33.0, 29.0

[a] Chemical shifts in ppm; ^1J(P–C) in Hz are given in parentheses.

still do not overlap with the range (25–27 ppm) observed for the monoligate monometallic $MeN(PF_2)_2$ ligand. The chemical shifts of the ^{13}C carbonyl resonances increase in the sequence $Cr < Mo < W$ for the Group 6 metal carbonyl complexes of $MeN(PF_2)_2$ ligand as shown in Table 9 and also for the complexes of $Pr^iN(PPh_2)_2$ [96]. The ^{13}C resonances of the carbonyl groups cis to the diphosphazane lie upfield to the resonances of the carbonyl groups trans to the ligand. Also for the tetracarbonyl chelate complexes, $M(CO)_4(L\text{–}L)$ (L–L = diphosphinoamine) $\delta_{(CO)}(\text{trans}) > \delta_{(CO)}(\text{cis})$; this trend is the same as that observed for complexes of the $M(CO)_4L_2$ (L = a monophosphine or a phosphite). The high field (100 MHz) spectrum of the complex *cis*-$[Mo(CO)_4(Ph_2PNPr^iP(Ph)(DMP))]$ shows four different ^{13}CO resonances at δ

219.1, 218.1 (assigned to trans CO groups) and 214.4 and 207.2 (assigned to cis CO groups) [46].

The ^{13}C NMR spectra of $[Re_2(\mu\text{-}Br)_2(CO)_6\{\mu\text{-}[Bu^tNPMe]_2\}]$ containing a bridging cyclodiphosphazane ligand shows two carbonyl resonances in 1:2 ratio; δ CO (axial) 191.2 (d, $^2J(PC)=92.5$ Hz) and δ CO (equitorial) 190.8 (s). A large $^2J(PC)$ coupling of 92.5 Hz signifies the trans coupling between the phosphorus and carbon nuclei [197].

6.2.5 ^{19}F NMR

King et al. have made use of ^{19}F NMR in the study of metal carbonyl complexes of $(PF_2)_2NR$ (R = Me, Ph) ligands [81,87].

The ^{19}F NMR chemical shifts (δ_F) appear to be diagnostic of the type of phosphorus atoms to which the fluorines are bonded as follows: (a) PF_2 groups of uncomplexed phosphorus atoms (δ 75); (b) PF_2 groups of chelating $RN(PF_2)_2$ ligands (δ 40–55); (c) PF_2 groups of complexed phosphorus atoms in monodentate $(PF_2)_2NR$ ligands (δ 20–35). The $^1J(PF)$ and $^3J(PF)$ values for Group 6 metal carbonyl complexes of $RN(PF_2)_2$ ligands are in the range 1100–1350 Hz and 15–60 Hz, respectively.

The ^{19}F NMR studies of cyclodiphosphazane complexes have been carried out by Nixon and co-workers [187]. The ^{19}F NMR spectrum of *cis*-$[PtCl_2(PEt_2Ph)\{\eta^1\text{-}[PFNBu^t]_2\}]$ exhibits two distinct resonances at δ −0.5 and +35.2 for the fluorines attached to the coordinated and uncoordinated phosphorus nuclei, respectively. In addition to the large directly bonded $^1J(PF)$ coupling (ca. 1150 Hz), further fine structure arises from coupling due to ^{195}Pt ($^2J(PtF)=835$ Hz; $^4J(PtF)=39$ Hz) and the cross-ring coupling ($^4J(FF)=53$ Hz). The large magnitude of $^4J(FF)$ suggests that the two fluorines are on the same side of the ring.

The ^{19}F NMR spectrum for the cyclodiphosphazane, $[PhNP(OCH_2CF_3)]_2$ shows a triplet with a $^3J(HF)$ of 8.2 Hz. The magnitude of the coupling remains unchanged even after complexation (e.g. **204a**). However, for the complex **204b**, three sets of multiplets are observed because of the presence of three chemically different fluorine nuclei [191].

6.3 Mass spectrometry

Mass spectral data for diphosphinoamine and cyclodiphosphazane complexes are sparse. Particular mention must be made of the use of this technique by King et al. to characterize a number of $MeN(PF_2)_2$-substituted carbonyl complexes of Cr, Mo, W, Fe, Mn, Co and Ni [85,107,133].

6.4 X-ray crystallography

X-ray crystallographic studies of a few diphosphinoamine ligands and a large number of their transition metal complexes have been carried out. The data are listed in Tables 10–12. X-ray structures of a few cyclodiphosphazanes and their transition metal complexes are also available and these data are listed in Table 13. A few general trends in the structural parameters and some of the unusual structural features observed are discussed.

In general, diphosphinoamine ligands adopt a C_{2v} conformation in the solid state (an exception is $Pr^iN(PPh_2)_2$, which exhibits C_s conformation in the solid state [11]), in which the phosphorus lone-pairs of electrons are eclipsed and are trans to the R group. The P—N—P angles lie in the range 110–123°; the P—N skeletal bond lengths lie in the range 1.61–1.70 Å. The geometry around the phosphorus atoms is pyramidal [33] as in $PhN(P(NHPh)_2)_2$ or in between pyramidal and tetrahedral [12] as in $PhN(PCl_2)_2$; the nitrogen atom always exhibits a planar geometry. The molecular structure of $MeN(PF_2)_2$ has been established by electron diffraction at a nozzle-tip temperature of −35 and 25°C [77].

The hetero functional ligand $Ph_2PN(Pr^i)P(O_2C_6H_4)$ adopts a conformation in the solid state in which the lone pair on the PPh_2 centre is cis to the N—C bond. It also shows two different P—N bond distances; the P—N bond from the PPh_2 is longer than that connecting the $P(O_2C_6H_4)$ centre [44].

The first report of an X-ray study of a diphosphinoamine pertains to the complex, $[Mo(CO)_4(PPh_2)_2NEt]$ and confirms that this complex has the expected cis configuration of the carbonyl groups [79]. In the complexes of the type $[M(CO)_4L]$ (L = chelating diphosphinoamine), a contraction of the P—N—P bond angle is observed as a result of decrease in the P···P separation due to chelate formation. The MPNP skeleton exhibits planarity except in the case of $[Mo(CO)_4(meso\text{-}Pr^iN\{P(Ph)(Pr^iNH)\}_2)]$ [95]. Even though the P—N—P angle shows

TABLE 10

X-ray structural data for diphosphinoamine ligands

No.	Compound	Symmetry	Average P—N bond length (Å)	Average P—N—P bond angle (°)	P··P separation (Å)	Ref.
1	$(PPh_2)_2NPr^i$	C_s	1.71	122.8	3.00	11
2	$(PF_2)_2NMe$[a]	C_{2v}	1.68	116.1	2.85	77
3	$(PCl_2)_2NPh$	C_{2v}	1.69	110.8	—	12
4	$(P(NHPh)_2)_2NPh$	C_{2v}	1.69	117.7	2.90	33
5	$(PF_2)_2NH$ (at −110°C)	C_{2v}	1.67	120.7	2.89	31a
6	$(Ph_2PN(Pr^i)P(O_2C_6H_4)$	C_s	1.65[b] 1.74	120.7	2.95	44

[a] Structure has been investigated by electron diffraction studies at nozzle-tip temperatures of −35°C and 25°C.

[b] $N-P(O_2C_6H_4)$ bond distance.

TABLE 11

X-ray structural data for mononuclear diphosphinoamine complexes

No.	Compound	Mean P–N bond length (Å)	Mean P–N–P bond angle (°)	Mean M–P bond length (Å)	Mean M–CO bond length (Å)	Ref.
1	$[Mo(CO)_4(PPh_2)_2NEt]$	1.72	103.8	2.50	1.90	80
2	$[Mo(CO)_4(P(NHPh)_2)_2NPh]$	1.71	104.0	2.48	2.03	94
3	$[W(CO)_4(PPh_2)_2NPr^i]$	1.70	103.3	2.48	2.01	96
4	$[Mo(CO)_3(PF_2PhN)_3P]$	1.67	124.8	2.34	2.05	86
5	$[MoCp\{(PF_2)_2NMe\}_2Cl]$	—	120.3 93.5	—	—	91
6	$[Mo(CO)_4(P(OPh)_2)_2NPh]$	1.69	101.3	2.43	2.03	96
7	$[WI_2(CO)_3(P(OPh)_2)_2NPh]$	1.68	97.6	2.43	2.04	100
8	$[Mo(CO)_4\{meso\text{-}Pr^iN(P(Ph)(NHPr^i))_2\}]$	1.70	—	2.49	2.00	95
9	$[Mo(CO)_4\{P(O)Ph_2NPr^iPPh_2]$	1.70	113.2	2.51	1.99	97a
10	$[Fe(CO)\{(PF_2)_2NMe\}\{PhCH{=}CH$ $CCH_3{=}C(POF_2)NMePF_2\}]$	1.66	119.4	2.13	1.77	115
11	$[Ir(CO)\{(P(OMe)_2)_2NMe\}(PPh_3)_2]^+$	1.67	100.4	2.28	1.90	153
12	$[PdCl_2(PPh_2)_2NEt]$	1.72	97.7	2.22	—	161
13	$[Ru(\eta^5\text{-}Cp)Cl(P(OMe)_2)_2NMe]$	1.68	96.7	2.23	—	42
14	$[Co(CO)_2\{P(OMe)_3\}_2\{(MeO)_2PN(Et)P(OMe)_2\text{-}\eta^1\}^+]$	1.68	116.0	2.21	1.71	138

a wide variation in chelate complexes, the planar geometry around nitrogen is retained in all cases [96].

The structure of the seven-coordinated complex, $[WI_2(CO)_3)(P(OPh)_2)_2NPh]$ (**42**) shows that the geometry around the tungsten atom is distorted pentagonal bipyramidal; two phosphorus atoms, two iodine atoms and a carbonyl group are in the equatorial plane whilst the other two carbonyl groups occupy apical positions. The MP_1P_2N ring atoms are crystallographically coplanar and the geometry around the nitrogen is strictly planar [100].

The structure of the unusual complex, $[Mo(CO)_3(PF_2PhN)_3P]$ (**14**) is quite interesting and is similar to the bicyclo(2,2,2)octane cage-like structure. It is the first example of a tridentate chelating strong π acceptor ligand containing three PF_2 groups bonded to Mo which exhibits an octahedral geometry [86]. The metal–metal triple bond observed in the novel dimolybdenum complex, $[Mo_2Cl_2\{(PF_2)_2NMe\}_4]$ (**25**) is the longest (2.457 Å), ever found for a triple bond between two metal atoms [74]. This may be due to the presence of strongly π-accepting PF_2 groups, which allow considerable electron density to be removed from Mo–Mo δ-bonding orbitals, thus weakening the Mo–Mo bond to the extent that it lengthens by 0.24 Å. The structures of the above two complexes (**14** and **25**) are shown in Fig. 4.

The X-ray structure of the cobalt complex, $[Co_2(CO)_4\{(P(OMe)_2)_2NMe\}_2]$

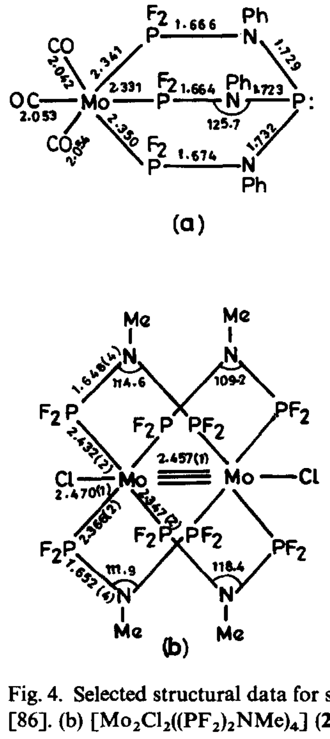


Fig. 4. Selected structural data for some diphosphinoamine complexes. (a) $[Mo(CO)_3[PF_2N(Ph)]_3P]$ (**14**) [86]. (b) $[Mo_2Cl_2((PF_2)_2NMe)_4]$ (**25**) [74].

TABLE 12

X-ray structural data for di- and polynuclear diphosphinoamine complexes

No.	Compound	Mean P—N bond length (Å)	Mean P—N—P bond angle (°)	Mean M—P bond length (Å)	M··M separation (Å)	Ref.
1	$[Mo_2(CO)_5\{(PF_2)_2NPh\}_3]$	—	—	—	3.14	82
2	$[Mo_2((CO)_3\{(PF_2)_2NMe\}_4]$	—	—	—	3.14	82
3	$[Mo_2(CO)_3\{(PF_2)_2NMe\}_2(\mu\text{-}PF_2)(\mu\text{-}Cl)(PF_2NHMe)]$	1.66	120.0	2.35	2.97	88
4	$[Mo_2Cl_2\{(PF_2)_2NMe\}_4$	1.66	113.5	2.40	2.46	74
5	$[W_2Br_2(\mu\text{-}Br)\{\mu\text{-}C(C_6H_4Me)\}\{(PF_2)_2NMe\}_2]$	—	—	2.41	2.62	92
6	mer-$[W_2(CO)_6\{(P(OMe)_2)_2NMe\}_2\{\mu\text{-}(P(OMe)_2)_2NMe\}]$	1.67	107.4	2.44	—	42
7	$[Fe_2(CO)_6\{(PF_2)_2NMe\}_2]$	—	—	—	3.90	110
8	$[Fe_2(CO)_5\{(PF_2)_2NMe\}_2]$	—	—	—	2.66	110
9	$[Fe_2(CO)\{(PF_2)_2NMe\}_4]$	1.59, 1.65–1.68	—	—	2.73	109
10	$[\{FeCp\}_2\{(PF_2)_2NMe\}(\mu\text{-}PF_2)(\mu\text{-}PF_2NMe)]$	1.52, 1.67	—	2.12	3.65	113
11	$[Fe_2(\mu\text{-}Br)(CO)_4\{(P(OPh)_2)_2NEt\}_2]PF_6$	1.66	119.4	2.22	2.72	13
12	$[Fe_2I(CO)_5\{(P(OMe)_2)_2NEt\}_2]PF_6$	1.66	119.8	2.21	2.79	13
13	$[Ru_2(\mu\text{-}CO)(CO)_4\{(P(OMe)_2)_2NEt\}_2]$	1.67	120.5	2.29	2.80	117
14	$[Ru_2I(\mu\text{-}I)(CO)_3\{(P(OPr^i)_2)_2NEt\}_2]$	—	—	2.33	2.79	120
15	$[Ru_3(CO)_{10}(PPh_2)_2NEt)]$	1.72	118.0	2.31	2.82	118
16	$[Ru_2(SC_4H_8)(CO)_5\{\mu\text{-}[(Pr^iO)_2)P]_2NEt)]^{2+}$	—	—	2.35	2.93	127
17	$[Ru_2(\mu\text{-}SPh)(CO)_4\{\mu\text{-}[(MeO)_2)P]_2NEt)]^+$	1.67	118.2	2.33	2.80	128a
18	$[Ru_2(H_2O)(CO)_5\{\mu\text{-}[(Pr^iO)_2)P]_2NEt)]^{2+}$	—	—	2.34	2.87	128

19	$[Ru_2\{\mu\text{-}OC(OEt)\}(CO)_4\{\mu\text{-}[(MeO)_2)P]_2NEt)]^+$	—	—	2.32	2.78	128
20	$[Ru_2\{\mu\text{-}\eta^1\text{-}N(CHPh)\}(CO)_4\{(P(OPr^i)_2)_2NEt\}_2]^+$	—	—	2.33	2.71	125
21	$[Ru_4(\mu_3,\eta^2\text{-}CO)(CO)_9\{\mu\text{-}((MeO)_2P)_2NEt\}_2]$	—	—	2.25	2.85	119
22	$[Co_2(CO)_2\{(PF_2)_2NMe\}_3]$	—	—	—	2.72	131
23	$[Co_2Br_4\{(PF_2)_2NMe\}_3]$	—	—	—	2.72	133
24	$[Co_2(CO)_4\{(P(OMe)_2)_2NMe\}_2]$	1.68	112.6	2.15	2.70	43
25	$[Co_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2\{\mu\text{-}[(MeO)_2P]_2NEt\}]^+$	—	—	2.17	2.50	138
26	$[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}[(MeO)_2P]_2NEt\}_2]^+$	—	—	2.14	2.74	137
27	$[Rh_2Cl_2(CO)_2\{(P(OMe)_2)2NEt\}_2]$	1.67	—	2.29	2.69	144
28	$[Rh_2Cl_2(CO)\{(P(OPh)_2)_2NEt\}_2]$	1.68	—	2.19	2.66	146
29	$[Rh_2(CO)_3\{(P(OPh)_2)_2NEt\}_2]$	—	—	2.26	2.72	147
30	$[Rh_2HgCl(\mu\text{-}H)(CO)_2\{(P(OPh)_2)_2NEt\}_2]$	—	118.4	2.45	2.76 2.71[*] 2.78[*]	148
31	$[Rh_2\{(P(OMe)_2)_2NMe\}_4]^{2+}$	1.68	101[b] 115[c]	2.27	3.27	153
32	$[Rh_2\{(PF_2)_2NMe\}_3(PF_3)_2]$	—	—	2.21	2.84	158
33	$[Rh_2\{(PF_2)_2NMe\}_3(PF_3)Cl_2]$	—	—	2.25	2.78	158
34	$[Rh_2\{(PF_2)_2NMe\}_3(Cl)_4]$	—	—	2.29	2.71	158
35	$[IrMo(CO)_4Cl\{(P(OPr^i)_2)_2NMe\}_2]$	1.69	121.1	2.36	2.89	42
36	$[RhMo(CO)_4Cl\{(P(OPr^i)_2)_2NMe\}_2]$	1.67	123.5	2.36	2.86	42
37	$[Rh_3(\mu\text{-}Cl)_3\{\mu\text{-}MeN(PF_2)_2\}_3]$	1.66	122.5	2.13	3.09	156
38	$[\{PdCl(P(OPh)_2)_2NPh\}_2]$	1.68	113.4	2.26	2.62	166
39	$[\{PdCl(PPh_2)_2NH\}_2]$	1.69	114.4	2.27	2.63	165
40	$[Pd_2\{(P(OPh)_2)_2NMe\}_3]$	1.68	118.1	2.27	2.85	166

[*] Rh—Hg bond lengths.

[b] η^2-ligand.

[c] μ-ligand).

TABLE 13

X-ray structural data for selected cyclodiphosphazanes and metal complexes of cyclodiphosphazanes

No.	Compound	Mean P–N bond length (Å)	Mean M–P bond length (Å)	Mean P–N–P bond angle (°)	Mean N–P–N bond angle (°)	Ref.
1	$[\mathrm{PhNPCl}]_2$	1.69	—	99.7	80.3	70
2	$[\mathrm{Bu^tNPCl}]_2$	1.69	—	97.3	82.4	224
3	$[\mathrm{PhNP(OC_6H_4Me}\text{-}p)]_2$	1.72	—	100.1	79.9	192
4	$[\mathrm{PhNP(OCH_2CF_3)}]_2$	1.72	—	100.2	79.8	66
5	$[\mathrm{P_4(NBu^t)_4}]$	1.73	—	109.5	—	207
6	$[\mathrm{Re_2(CO)_6Br_2\{Bu^tNP(Me)\}_2}]$	1.68	2.43	93.0	81.8	203
7	$[\mathrm{Mn_2(CO)_8\{P_4(NBu^t)_4\}}]$	1.78	2.29	91.0	—	206
8	$[\mathrm{Rh_2Cl_2(COD)(Bu^tNPF)_2}]$	1.66	2.20	—	—	198
9	$[\mathrm{PtCl_2(PEt_3)(Bu^tNPF)_2}]$	1.67	—	95.0	—	202
10	$[\mathrm{PtCl_2\{(Bu^tNPF)_2\}_2}]$	1.65	—	95.0	—	202
11	$[\mathrm{PtCl_2(PPhMe_2)(PClNBu^t)_2}]$	1.69		96.5	—	202
12	$[\mathrm{W(CO)_4(NHC_5H_{10})\{PhNP(OC_6H_4Me}\text{-}p)\}_2]$	1.70^a				
		1.72^b	2.43	99.8	80.0	191
13	$[\{\mathrm{Mo(CO)_4(NHC_5H_{10})}\}_2\{\mathrm{PhNP(OCH_2CF_3)}\}_2]$	1.71	2.43	99.1	80.9	191
14	$[\{\mathrm{Mo(CO)_4P(OMe)_3}\}_2\{\mu\text{-}trans\text{-}[\mathrm{PhNP(OC_6H_4Me}\text{-}p]_2\}]$	1.71	2.46	99.9	80.1	192
15	$[\mathrm{Mo(CO)_4P(OMe)_3}\{\mu\text{-}cis\text{-}[\mathrm{PhNP(OC_6H_4Me}\text{-}p)]_2\}\{\mathrm{W(CO)_4(NHC_5H_{10})}\}]$	1.71	2.46	99.4	80.6	192
16	$[\mathrm{Mo_2(CO)_8}\{[\mathrm{PhNP(OC_6H_4Me}\text{-}p)]_2\}_2]$	1.71	2.48	98.8	81.2	192

[a] N–P(coordinated).

[b] N–P(uncoordinated).

(**111**) shows an unusual structure in which one cobalt atom has approximately square pyramidal geometry, whereas the other cobalt displays a distorted trigonal bipyramidal geometry [43]. This type of structural distortion may be attributed to the packing of the chelate rings. A similar feature is observed in the X-ray structure of the complex, $[Rh_2(CO)_3\{(P(OPh)_2)_2NEt\}_2]$ (**128**), shown in Fig. 5(b). One of the rhodium atoms with a C.N. of 4 has a square planar geometry whereas the other, with a C.N. of 5, adopts an approximately trigonal bipyramidal configuration. Both rhodium atoms have the same formal oxidation number of zero but because of different

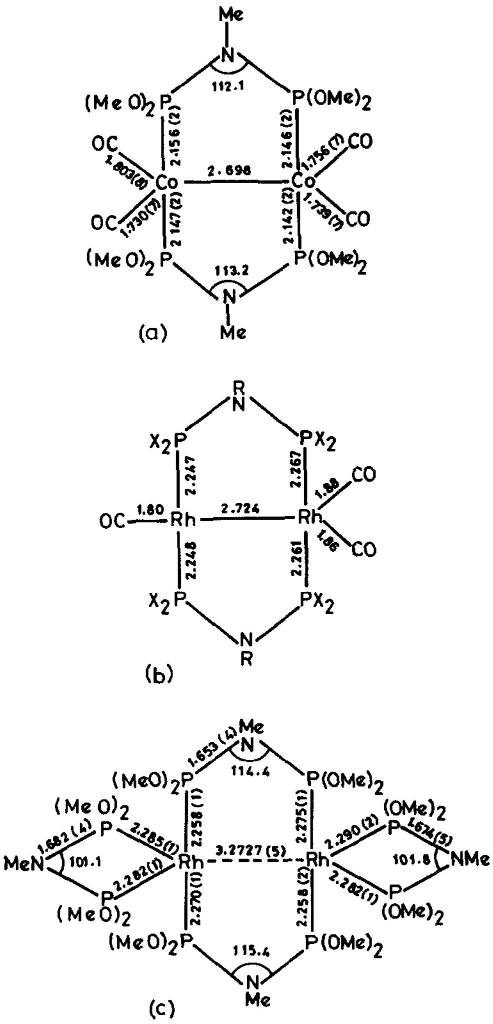


Fig. 5. Selected structural data for some dinuclear diphosphinoamine complexes. (a) $[Co_2(CO)_4[P(OMe)_2)_2NMe]_2]$ (**111**) [43]. (b) $[Rh_2(CO)_3[P(OPh)_2)_2NEt]_2]$ (**128**) [147]. (c) $[Rh_2[P(OMe)_2)_2NMe]_4]^{2+}$ (**143**) [154].

coordination numbers, Rh(1) (C.N. 5) is an 18-electron while Rh(2) (C.N. 4) is a 16-electron system [147]. The structure of the rhodium complex $[Rh_2\{(P(OMe)_2)_2NMe\}_4]$ $(OTF)_2$ (**143**) shows diphosphinoamine ligands exhibiting both chelating and bridged bidentate modes of coordination in the same molecule [154]. The P—N—P bond angle for chelating ligand is 101°, whereas for the bridging ligand it is 115°. The structures of the above three complexes (**111**, **128** and **143**) are shown in Fig. 5.

Haines and co-workers [135] have used two parameters to define the conformations of five-membered rings in dinuclear cobalt complexes of diphosphinoamines as shown in Table 14. These parameters are ϕ, which is the Co—P—P—Co torsion angle and δ, which is the angle between the least-squares plane through the atoms of the Co_2P_2 unit and the plane through the atoms of the P_2N unit. These angles indicate the extent of twisting of the ligands ($\phi \neq 0$) and buckling ($\delta \neq 0$) of the M_2P_2N rings. If, in addition to the diphosphinoamine ligands, another group or atom bridges the two metal atoms, the twisting of diphosphinoamine ligands becomes very small; in these cases ϕ is close to zero. Presumably the additional bridging group sterically hinders any twisting of the diphosphinoamine ligand. A plot of increasing the M—P—P—N torsional angle (ϕ) vs. the M—P—N valence angle shows that even quite large changes in ϕ result in only small changes in the angle at the phosphorus atom,

TABLE 14

ϕ and δ values for M—P—N—P—M rings (M = metal) in bridging diphosphazane ligands

Compound	ϕ (°)	δ (°)	Ref.
$[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$	29	16	135
	40	13	
$[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Me)P(OMe)_2\}_2]$	35	21	43
	41	16	
$[Rh_2(CO)_3\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$	21	14	150
	26	13	
$[Rh_2Cl_2(CO)\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$	25	13	145
	43	20	
$[Fe_2I(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(Me)_2\}_2]^+$	28	13	13
	30	12	
$[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]^+$	4	13	13
$[Rh_2Cl_2(\mu\text{-}CO)(CO)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$	2	7	144
	1	1	
$[Pd_2Cl_2\{\mu\text{-}(PhO)_2PN(Ph)P(OPh)_2\}_2]$	37	29	166
$[Pd_2Cl_2\{\mu\text{-}Ph_2PN(H)PPh_2\}_2$	37	—	165
$[RhMo(CO)_3(\mu\text{-}CO)(\mu\text{-}Cl)\{\mu\text{-}MeN(P(OMe)_2)_2\}_2]$	0.1	3.0	42
	0.3	3.4	
$[IrMo(CO)_3(\mu\text{-}CO)(\mu\text{-}Cl)\{\mu\text{-}MeN(P(OMe)_2)_2\}_2]$	0.6	1.4	42
	0.6	4.4	

e.g. increasing ϕ from 0 to 45° results in a decrease in the M—P—N angle of only about 8° [135]. This suggests that angle strain caused by twisting of the diphosphinoamine ligand is minimal. In fact the P—N—P angle in the coordinated bridging diphosphinoamine ligand is often less than 120°, which has the effect of opening up of the M—P—N angle, thus allowing even greater twisting before angle strain at the phosphorus atoms becomes severe.

The molecular structure (Fig. 6) of the dinuclear palladium(0) complex, $[Pd_2\{(P(OPh)_2)_2NMe\}_3]$ (**175**) [166] is similar to that of the analogous Pt and Pd complexes of dppm [221,222]. It comprises two palladium(0) atoms linked by three bridging diphosphinoamine ligands as shown in Fig. 6. The metal—metal distance of 2.855 Å is much shorter than that observed for the analogous complexes, $[Pd_2(dba)_3]$ [223], $[Pd_2(dppm)_3]$ [222] and $[Pt_2(dppm)_3]$ [221] and is more than the bonding distances observed in dinuclear palladium(I) complexes, $[PdCl(P(OPh)_2)_2NPh]_2$ (2.620 Å) [166] (Fig. 7) and $[PdCl(PPh_2)_2NH]_2$ (2.638 Å) [165]. The P—N—P angles are in the range 117.0–120.3°. The angles around each of the nitrogen atoms add up to 360°.

Single-crystal X-ray studies of $[PhNPCl]_2$ [70] and $[Bu^tNPCl]_2$ [224] estab-

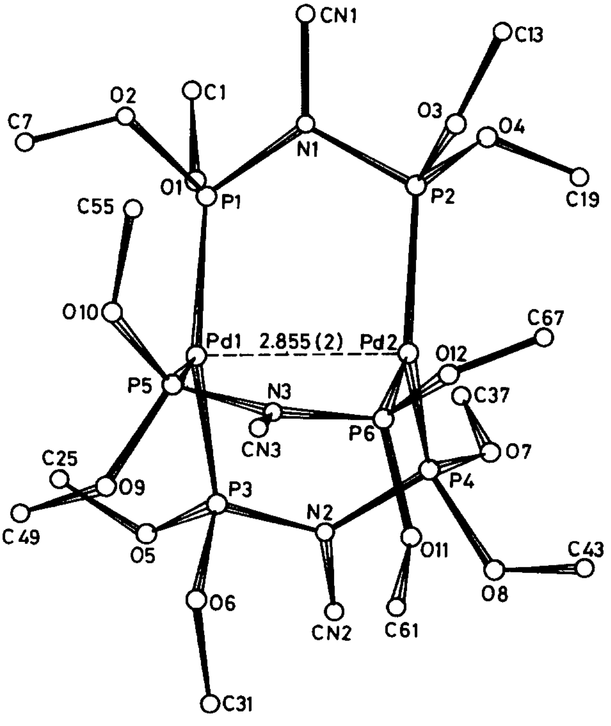


Fig. 6. The molecular structure of $[Pd_2\{\mu\text{-}MeN(P(OPh)_2)_2\}_3]$. For clarity, only ipsocarbon atoms of the phenyl groups are retained.

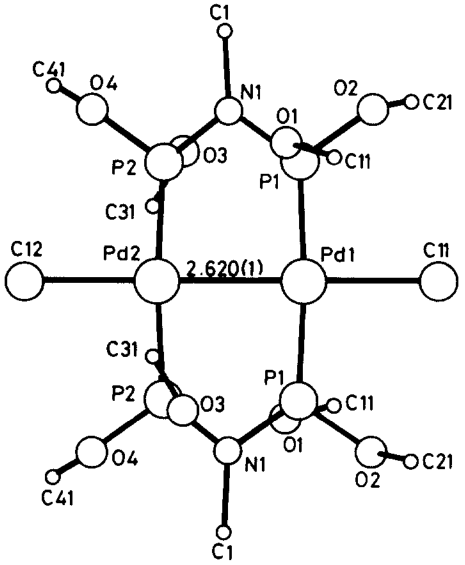


Fig. 7. The molecular structure of $[Pd_2Cl_2\{\mu\text{-}MeN(P(OPh)_2)_2\}_2]$. For clarity, only ipsocarbon atoms of the phenyl groups are retained.

lish that the N_2P_2 ring is planar in the *N*-phenyl derivative and slightly puckered in the *N-tert*-butyl derivative. The chlorine atoms are mutually cis and located on the same side of the ring as the nitrogen atoms. The X-ray structure of $[PhNP(OCH_2CF_3)]_2$ [66] shows that it has the trans structure. The four-membered P_2N_2 ring is virtually planar. Available structural data reveal that the cis structures are puckered whereas trans structures are nearly planar. Recently, it has been shown that, in the bicyclic derivatives of cyclodiphosphazanes, the puckering of the P_2N_2 ring occurs in a manner opposite to that observed for the cis structures [72]. The structures of three cyclodiphosphazanes are shown in Fig. 8.

The single-crystal X-ray structures of the complexes $[\{Mo(CO)_4P(OMe)_3\}_2\{\mu\text{-}$*trans*-$[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ (**204c**) and $[Mo(CO)_4\{P(OMe)_3\}\{\mu\text{-}$*cis*-$[PhNP(OC_6H_4Me\text{-}p)]_2\}W(CO)_4(NHC_5H_{10})]$ (**205**) are shown in Figs. 9 and 10, respectively. It is interesting to compare the framework of the cyclodiphosphazane in both the complexes with that of the free ligand, $[PhNP(OC_6H_4Me\text{-}p)]_2$ (which exists in the crystal as the trans isomer) as well as that in the mononuclear complex *cis*-$[W(CO)_4(NHC_5H_{10})\{$*cis*-$[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ (**203**) (in which the cyclodiphosphazane adopts the cis configuration). The bond distances and angles within the P_2N_2 ring in the dinuclear complexes do not show much variation from those observed for the free ligand. In the η^1-cyclodiphosphazane complex (**203**), the P—N distances at the coordinated end is slightly shorter than those at the uncoordinated end. The puckering of the P_2N_2 ring in the cis configuration is different for different types of coordination. The puckering is more in the dibridged dinuclear complex

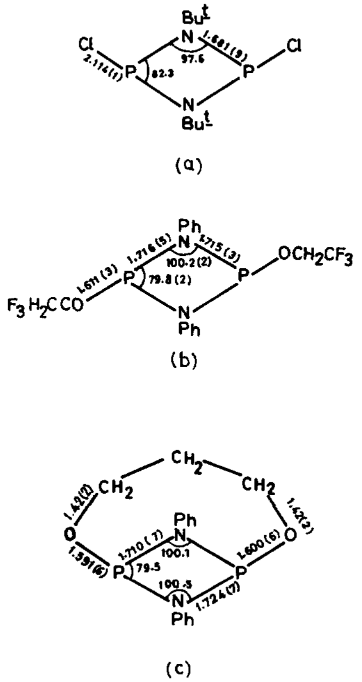


Fig. 8. Selected structural data for some cyclodiphosphazanes. (a) $[\mathrm{Bu^tNP(Cl)}]_2$ [224]. (b) $[\mathrm{PhNP(OCH_2CF_3)}]_2$ [66]. (c) $[\{\mathrm{(PhN)P}\}_2\{\mathrm{-O(CH_2)_3O-}\}]$ [72].

206 than in the η^1-type coordinated complex **203**, which in turn is more than that in the mono-bridged bimetallic complex **205**. However, in its trans configuration, the P_2N_2 ring maintains its planarity.

The M–P distances in the Group 6 carbonyl complexes fall in the range 2.43–2.48 Å; the M–P bond distance of 2.43 Å in **203** as well as **204** is the shortest of all (see Table 13), indicating the strong metal–phosphorus π-bonding interaction. The W–N bond distance of 2.308 Å in **203** is very short compared with other M–N distances, indicating the strong metal–nitrogen interaction, which is reflected in the difficulty of replacing the piperidine ligand by P donor ligands [191]. The M–C distances are sensitive to the groups which are located trans to them; those that are trans to CO are longer compared with those that are trans to phosphorus, which in turn, are still longer than the M–C distances trans to nitrogen.

The X-ray structure of the dinuclear complex, $[\mathrm{Re_2Br_2(CO)_6\{Bu^tNP(Me)\}_2}]$ (**212**) shows that the cyclodiphosphazane ligand exhibits a bridged bidentate mode of coordination (Fig. 11) [196]. The non-bonded metal–metal distance is 3.952 Å. Nixon and co-workers [198] have reported the crystal structure of the rhodium complex, $[\mathrm{Rh_2Cl_2(COD)_2(Bu^tNPF)_2}]$ (**215**) in which the cyclodiphosphazane, $(\mathrm{Bu^tNPF})_2$ bridges two [RhCl(COD)] moieties as shown in Fig. 11.

The X-ray crystallographic studies on platinum complexes of $(\mathrm{Bu^tNPF})_2$ such

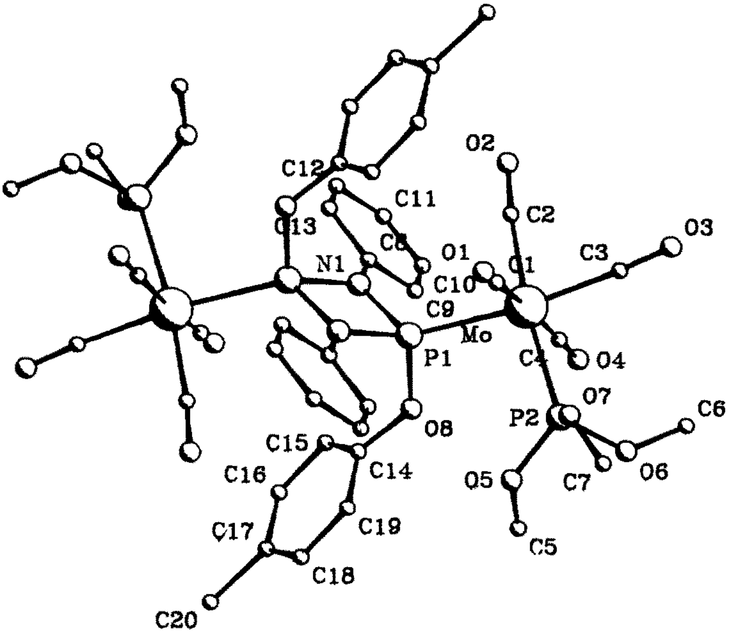


Fig. 9. Molecular structure of [{Mo(CO)$_4$P(OMe)$_3$}$_2$-{μ-*trans*-[PhNP(OC$_6$H$_4$Me-*p*)]$_2$}].

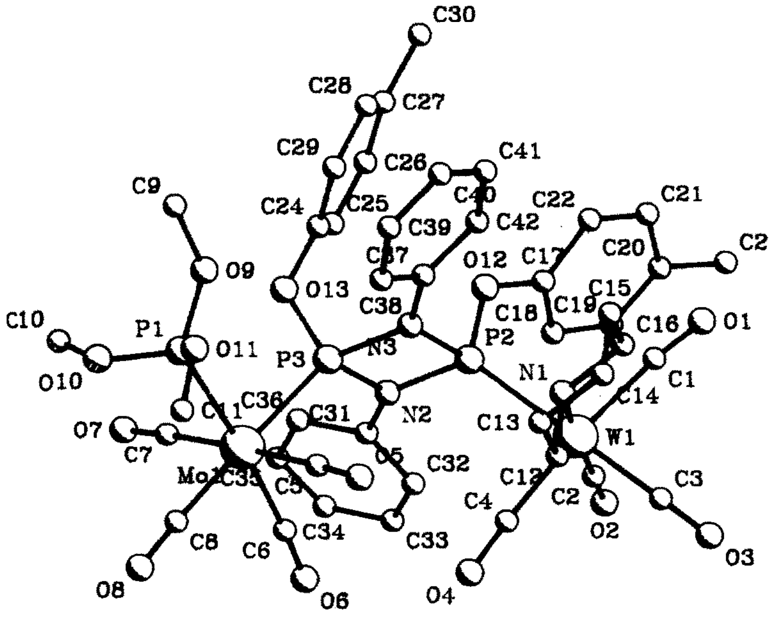


Fig. 10. Molecular structure of [W(CO)$_4$(NHC$_5$H$_{10}$){μ-*cis*-[PhNP(OC$_6$H$_4$Me-*p*)]$_2$}Mo(CO)$_4$P(OMe)$_3$].

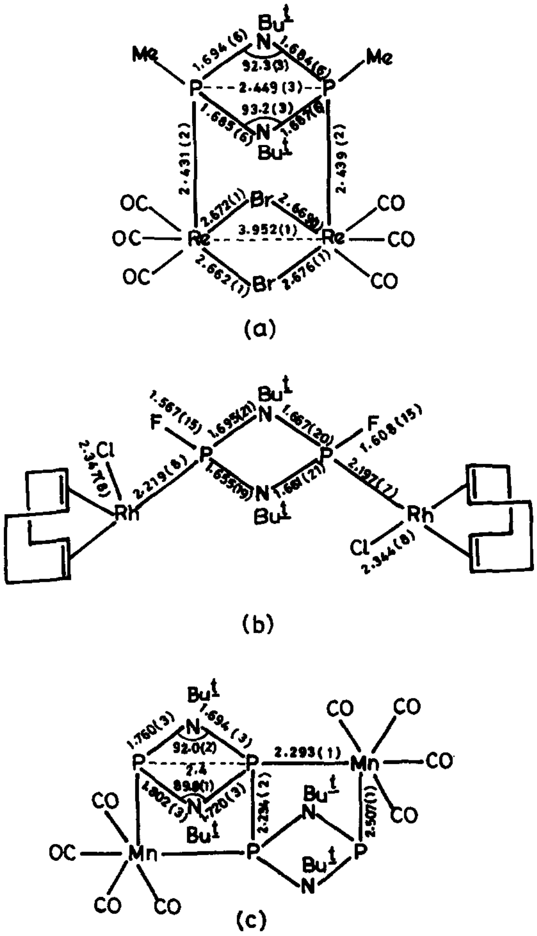


Fig. 11. Selected structural data for some cyclodiphosphazane complexes. (a) $[Re_2(CO)_6(Br)_2\{Bu^tNP(Me)\}_2]$ (**212**) [197]. (b) $[Rh_2(COD)_2Cl_2\{Bu^tNP(F)\}_2]$ (**215**) [198]. (c) $[Mn_2(CO)_8\{P_4(NBu^t)_4\}]$ (**236**) [206].

as $[PtCl_2\{(Bu^tNPF)_2\}_2]$ (**226**) and $[PtCl_2(PEt_3)(Bu^tNPF)_2]$ (**224**) and the dichlorodiphosphazane complex, *cis*-$[PtCl_2(PPhMe_2)(PClNBu^t)_2]$ (**224**) show that the cyclodiphosphazane ligand exhibits monodentate mode of coordination [202]. The structures of the above three complexes are shown in Figs. 12, 13 and 14, respectively.

The X-ray structure [207] of the cage compound $[P_4(NBu^t)_4]$ (**238**) is similar to that of S_4N_4 ring [225]. The structure of the complex, $[Mn_2(CO)_8\{P_4(Bu^tN)_4\}]$ (**236**) (Fig. 11) provides the first example of coupling of two cyclodiphosphazane units and their incorporation into a cage structure [206]. The P–P bond distance is 2.234(2) Å.

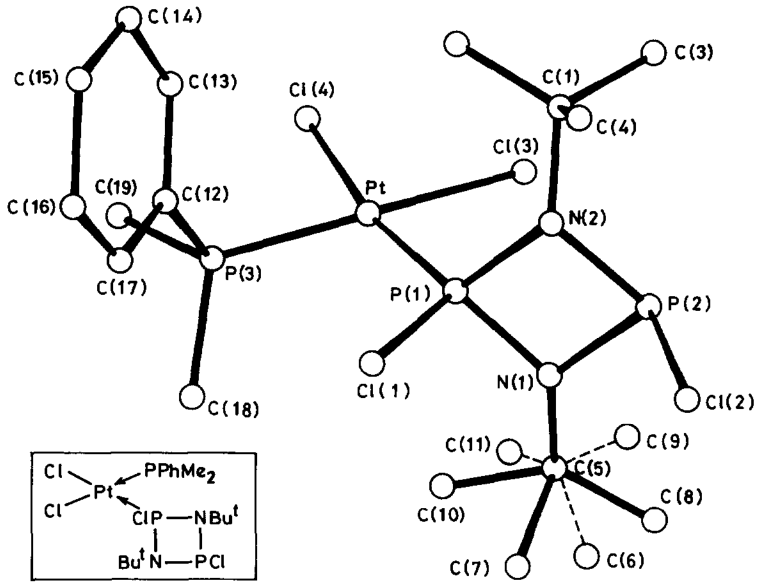


Fig. 12. Molecular structure of *cis*-[PtCl$_2$(PPhMe$_2$){[Bu^{t}NPF]$_2$}] (**224**) [202].

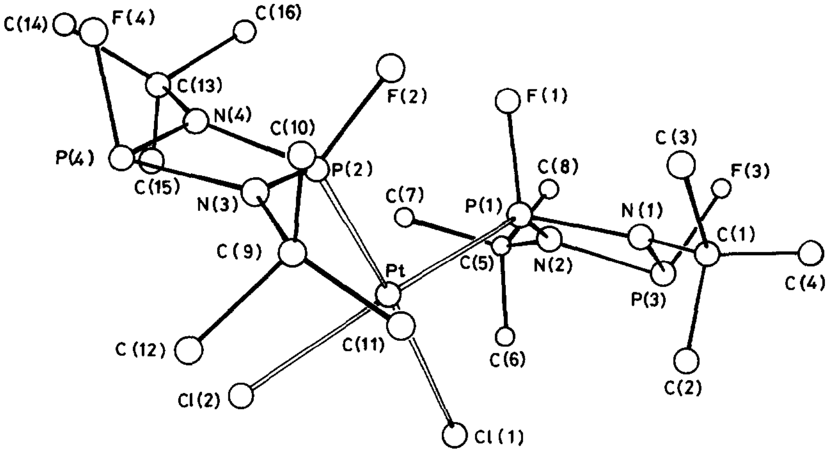


Fig. 13. Molecular structure of *cis*-[PtCl$_2${[Bu^{t}NPF]$_2$}$_2$] (**226**) [202].

7. OUTLOOK

Catalytic studies involving transition metal complexes of diphosphinoamines (e.g. C–H activation and hydrogenation reaction using Rh or Pd complexes or hydroformylation reactions using cobalt complexes) is an area which has not been investigated at all and could prove rewarding. In view of the current upsurge of interest in chiral catalysts for enantioselective transformations, it would also be

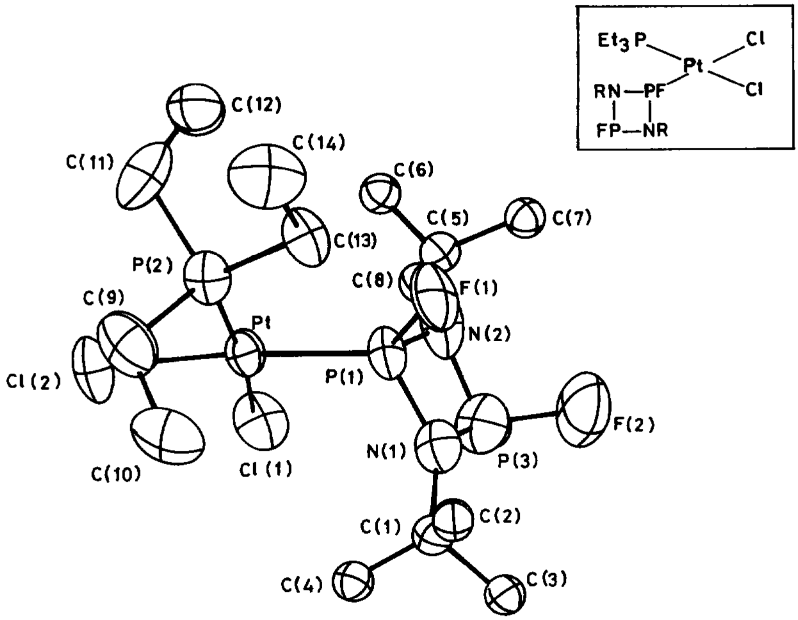


Fig. 14. Molecular structure of *cis*-[PtCl$_2$(PEt$_3$){[Bu^{t}NPF]$_2$}] (**224**) [202].

interesting to incorporate chiral entities into acyclic diphosphazane ligands and use such chiral diphosphinoamines to synthesize transition metal complexes that may function as homogeneous catalysts. The chirality of diphosphinoamines may be centred at the substituents on nitrogen or phosphorus; alternatively, either or both phosphorus centres may themselves be made chiral by introducing different substituents at these phosphorus centres.

Diphosphazanes in which the two phosphorus centres are differently substituted, and their transition metal complexes have been sparsely investigated [44,46]. These are particularly interesting in that the P—P coupling constant can be measured directly from the NMR spectra of the ligands as well as the complexes. The synthetic methodology for diphosphinoamines lends itself to facile incorporation of other types of donor atoms such as O, N or S into the skeleton, e.g. Ph$_2$PNPr^{i}P(Ph)(DMP) [46]. Such hybrid ligands could generate interesting coordination chemistry, particularly for the synthesis of heterobimetallic and high-nuclearity complexes. There is another way in which hybrid ligands with different donor sites can be prepared from diphosphinoamines. This involves the selective oxidation of one of the λ^3-phosphorus centres to λ^5-P(O), P(S) or P(NR) functionalities. These hybrid ligands can form novel transition metal complexes, which may prove to be useful catalysts in industrial processes (e.g. recent work on Ph$_2$PCH$_2$PPh$_2$(=NSiMe$_3$)) [226,227].

Another area of study that merits attention is the reactions of coordinated diphosphinoamines and their complexes such as electrochemical redox reactions, protonation–deprotonation reactions, reactions of the low-valent dinuclear species with small molecules and nucleophilic substitution reactions. Some work has been carried out by King, Uson, Haines and their co-workers [87,120–123,184–186] in this connection, but the scope of such reactions has not been fully explored.

Condensation reactions of chlorophosphines with amines or silylated amines yield cyclotri, cyclotetra, bicyclic or tricyclic phosphazanes besides acyclic and cyclic diphosphazanes and monophospha*zenes* [14,15,228]. Coordination chemistry of cyclotetraphosphazanes has been explored to a limited extent; coordination chemistry of other systems remains virtually unexplored and offers a virgin field for investigation. In this context, reactions of chlorophosphanes coordinated to transition metal moieties, e.g. $M(CO)_n$, with primary amines or silylamines can lead to novel structures. A beginning was made by Noeth and Thorn [229] in this direction several years ago but the difficulties encountered in isolating and characterizing the products presumably acted as a damper on the continuation of these studies. A more detailed study using high-field ^{31}P NMR measurements (in particular, multiple-pulse 2D techniques) should help us to understand the nature of the products formed and also to unravel some of the intimate details of the course of the condensation reactions.

With such a vast and unlimited scope, the future augers well for the coordination chemistry of diphosphazane ligands and other related higher-membered ring systems containing λ^3-phosphorus centres.

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NOTE ADDED IN PROOF

The reaction of $[W(CO)_4(PPh_3)(MeCN)]$ with $MeN(PF_2)_2$ gives *cis*-$[W(CO)_4(Ph_3P)\{MeN(PF_2)_2\}]$ in which the diphosphazane is coordinated to the metal in monodentate fashion. Similarly, the reaction of $[W(CO)_5(MeCN)]$ with $MeN(PF_2)_2$ gives $[W(CO)_5\{MeN(PF_2)_2\}]$ and $[\{W(CO)_5\}_2\{\mu\text{-}MeN(PF_2)_2\}]$ containing a monodentate and bridged bidentate diphosphazane ligand, respectively. Treatment of *cis*-$[W(CO)_4(Ph_3P)\{MeN(PF_2)_2\}]$ with Me_3NO in acetonitrile results in the replacement of the fluorophosphazane ligand rather than CO [230].

The utility of $[CpFeCl(\eta^1\text{-}L)_2]$ (**67**) and $[Mo(CO)_3(\eta^1\text{-}L)\ (\eta^2\text{-}L)]$ (**16**) $[L{=}Me_2N(PF_2)_2]$ as synthons for the directed synthesis of heterobimetallic complexes of the type $[CpFe(\mu\text{-}L)_2Co(CO)_2]$ or $[PtCl(PPh_3)\ (\mu\text{-}PF_2)\ (\mu\text{-}PF_2NMe)Fe(PF_2NHMe)Cp]$ as well as $[Mo(CO)_3(\mu\text{-}L)_2M(PPh_3)]$ (M=Ni,Pt),

[$Mo(CO)_3(\mu\text{-}L)_2IrCl(CO)(PPh_3)$] and [$Mo(CO)_3(\mu\text{-}L)_2RhCl(PPh_3)$] has been demonstrated. The reaction of $MeN(PF_2)_2$ with [$Cp_2Mo_2(CO)_4$] or [$Pt(C_2H_4)(PPh_3)_2$] gives the complexes [$Cp_2Mo_2(CO)_4(\mu\text{-}L)$] and [$Pt_2(\mu\text{-}L)_3(PPh_3)$], respectively [231]. In the latter complex, three diphosphazane units bridge the two platinum centres, one of which is also bonded to a PPh_3 ligand; the Pt–Pt distance is 2.8911(4) Å compared with the M–M distance of 2.855 Å in [$Pd_2(\mu\text{-}L')_3$] (L′= $(PhO)_2PN(Me)P(OPh)_2$) (**175**) (see Sect. 3.6).

Haines and co-workers [232] have reported further details of the reactions of diphosphazane bridged diruthenium derivatives, [$Ru_2(\mu\text{-}CO)$ $(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}$] (R=Me,$Pr^i$) with electron acceptors, tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and the characterization of the products by a combined EPR/ENDOR, UV–Visible/near-IR and IR spectroscopic and electrochemical investigations. They have also reported details of the synthesis and reactivity of the unsaturated diruthenium diphosphazane bridged species [$Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2$] (R = Me or Pr^i) [233]. Mixed diphosphorus ligand-bridged dinuclear iron carbonyl complexes, [$Fe_2(\mu\text{-}(CO)(CO)_4(\mu\text{-}Me_2PCH_2PMe_2)$ (μ-L–L)] [(L–L = $(MeO)_2PN(Et)P(OMe)_2$ or $(EtO)_2PN(Me)P(OEt)_2$] and [$Fe_2(\mu\text{-}Co)$ $(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)$ (μ-L–L) [L–L = $Ph_2PN(Et)PPh_2$, $(MeO)_2PN(Et)P(OMe)_2$, or $(EtO)_2PN(Me)P(OEt)_2$] have been synthesized by the reaction of [$Fe_2(\mu\text{-}CO)$ $(CO)_6(\mu\text{-}R_2PCH_2PR_2)$] (R = Me or Ph) with the appropriate diphosphazane ligand under photochemical conditions [234].

Recently, there has been an enhanced interest in rhenium complexes of diphosphazanes. The reaction of pentacarbonyl tetrafluoroboratorhenium with dppa gives the monomeric and the dimeric complexes [$Re(CO)_5(\eta^1\text{-}dppa)$]$^+BF_4^-$ and [$Re(CO)_5(\mu\text{-}dppa)Re(CO)_5$]$^{2+}\cdot 2BF_4^-$. The former complex reacts with azide ion to give [$Re(CO)_4(NCO)(dppa)$] which loses CO to give the chelate complex [$Re(CO)_3(NCO)(dppa)$]. The structures of these complexes have been confirmed by X-ray crystallography [235].

Treatment of [$ReOCl_4$]$^-$[$AsPh_4$]$^+$ with dppa in boiling $CHCl_3$ affords the complexes [$ReCl_3(OH_2)\{OPPh_2N(H)PPh_2\}$] and [$ReCl_4\{OPPh_2NHPPh_2\}$]$^-$-[$AsPh_4$]$^+$ in which the bidentate ligand forms a five-membered ring through the two P atoms, one of which is directly attached to the metal whilst the other to the oxygen atom of the fragment [Re=O]$^{3+}$. Reaction of [$ReOCl_3(PPh_3)_2$] with dppa gives a similar complex [$ReCl_3(PPh_3)\{OPPh_2NHPPh_2\}$]. However, the ethoxy compound, [$ReOCl_2(OEt)(PPh_3)_2$] forms with dppa the bischelate complex, [$ReO_2(dppa)_2$]$^+Cl^-$ containing two four-membered rings [236]. Six-coordinated rhenium complexes, *fac*-[$Re(NMe)Cl_3(dppa)$] and [$Re(N)Cl(dppa)_2$]$^+X^-$ (X = Cl or BPh_4), are obtained from the reaction of [$Re(NMe)Cl_3(PPh_3)_2$] and [$Re(N)Cl_2$-$(PPh_3)_2$] with dppa in boiling chloroform. In both the complexes, the dppa acts as a bidentate chelate ligand. In the former complex, the chlorine atoms assume facial disposition; in the latter, the chlorine is trans to the nitrogen [237].

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