

Coordination Chemistry of Phosphorus(III) and Phosphorus(V) Hydrazides

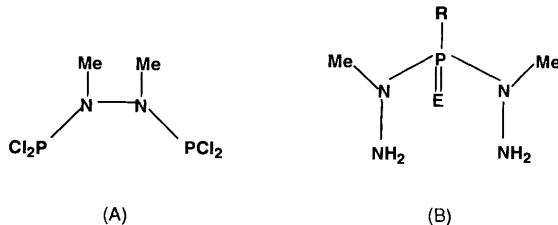
Kattesh V. Katti,* V. Sreenivasa Reddy, and Prahlad R. Singh

Centre for Radiological Research and MU Research Reactor, Allton Building Laboratories, University of Missouri, 301 Business Loop 70 West, Columbia, MO 65203, U.S.A.

1 Introduction

Hydrazine and its derivatives have been used extensively as versatile ligands in transition metal chemistry.¹ In addition to substitution reactions at nitrogen centres, hydrazines exhibit certain reactions at the N–N bond making them unique among nitrogen-based donor systems. The multi-electron donating ability of hydrazines make them versatile 'hard' donor systems. Incorporation of other electron donor centres such as oxygen, sulfur, or phosphorus on hydrazine backbones should provide unique opportunities in their use as multifunctional ligands in transition metal chemistry. In particular, the introduction of phosphorus(III) and phosphorus(V) centres within the hydrazine backbone has provided a diverse range of phosphorus hydrazides, formulae (A)^{2,3} and (B).^{4,5}

The main group chemistry of linear, cyclic, and polymeric phosphorus–nitrogen compounds has been known for more than a century.⁶ In contrast, the chemistry of phosphorus–nitrogen compounds containing the phosphorus hydrazide backbones [in particular, the chemistry relating to phospho-



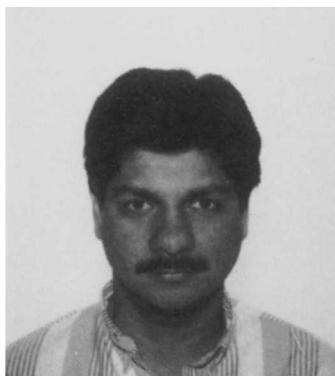
rus(III) hydrazides] is a relatively recent development. This approach of constructing hydrazine compounds functionalized with P^{III} or P^V centres not only enhances the scope of phosphorus–nitrogen chemistry, but also presents potential for the utility of phosphorus hydrazides as ligands [e.g. (A) and (B)] for use in transition metal and organometallic chemistry. This article summarizes the latest developments in the main group and coordination chemistry of phosphorus(III) and phosphorus(V) hydrazides.

Prahlad R. Singh was born in 1964 in Bombay, India. He obtained his Ph.D. from the University of Missouri-Columbia under the supervision of Professors David E. Troutner, Kattesh V. Katti, and Wynn A. Volkert. He continued his postdoctoral work with Professors Katti and Volkert before joining the faculty in the Radiological Sciences at the University of Missouri-Columbia in 1994. His research interests include radiopharmaceutical chemistry with special emphasis on *in vitro* and *in vivo* pharmacokinetic studies; development of new MRI contrast agents for clinical applications, and chemistry and radiochemistry as they relate to nuclear waste treatment.

V. Sreenivasa Reddy was born in Kolar, India in 1964. He received his M.Sc. in chemistry from Bangalore University and Ph.D. from the Indian Institute of Science, Bangalore under the supervision of Professor S. S. Krishnamurthy in 1992. He then joined Professors Kattesh V. Katti and Wynn A. Volkert at the University of Missouri-Columbia, U.S.A. as a Postdoctoral Research Associate in the Department of Radiology. His research interests have been in the areas of main-group chemistry of phosphorus–nitrogen and

also organophosphorus and transition-metal chemistry. He is also actively researching in the design of new ligand systems for transition-metal-based catalysts and also for use in nuclear medicine.

Kattesh V. Katti was born in Dharwad, India in 1956. He obtained his M.S.Ed. degree from the Regional College of Education, Mysore and Ph.D. from the Indian Institute of Science in 1984 under the supervision of Professor S. S. Krishnamurthy. He was awarded the Alexander von Humboldt fellowship for his research at the University of Göttingen in Professor Herbert W. Roesky's research group. Following that he worked with Ronald G. Cavell as a Research Associate and later as a Research Scientist at the University of Alberta, Canada before joining the faculty at the University of Missouri-Columbia, U.S.A. in 1990. He currently holds the position of Assistant Professor in Radiological Sciences with a joint appointment as a Research Scientist at the University of Missouri Research Reactor and also as adjunct Professor of Chemistry. His research interests have been in main-group chemistry of phosphorus, nitrogen, and silicon compounds, transition-metal chemistry, and inorganic polymer chemistry with special emphasis in three areas: development of new ligands and bioconjugates for use in the design of site-specific radiopharmaceuticals for diagnosis and therapy of cancer; design of ligand frameworks for the transition-metal-based novel catalysts; and application of new monomers and polymers for the development of new precursors for use in the remediation of nuclear waste.



Prahlad R. Singh



V. Sreenivasa Reddy

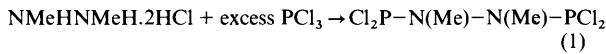


Kattesh V. Katti

2 Synthesis of Phosphorus(III) Hydrazides

2.1 Acyclic Phosphorus(III) Hydrazides

Gilje *et al.*² and Nöth *et al.*³ have pioneered the synthesis of bis(dichlorophosphino)dimethylhydrazine (1) through: (i) the condensation of PCl_3 with 1,2-dimethylhydrazine² at -196°C and (ii) the reaction of the cage-compound $\text{P}[\text{N}(\text{Me})\text{N}(\text{Me})_3]\text{P}$ with PCl_3 .³ Both these methods produced (1) in 15–20% yields. A recent discovery from our laboratory gave (1) in near quantitative yields from the reaction of 1,2-dimethylhydrazine hydrochloride with PCl_3 (equation 1).⁷



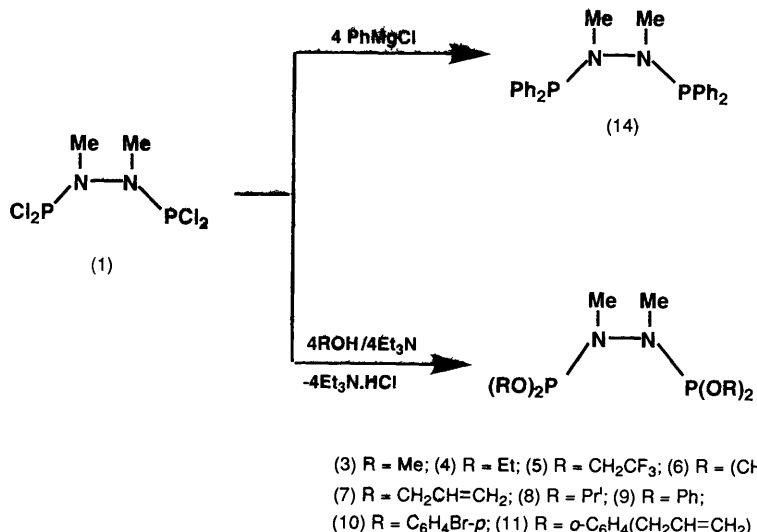
As shown in Scheme 1, the chloro precursor undergoes facile nucleophilic substitution reactions and also reactions with Grignard reagents to produce a broad-spectrum of alkoxy-, aryloxy-, and aryl-substituted phosphanyl hydrazides.^{8,9} The ^{31}P NMR chemical shifts of (1)–(11) indicate a gradual change to upfield resonances on going from chlorine to alkoxide or aryloxide substituents on the P^{III} centres (Table 1). (All the ^{31}P chemical shifts reported in Tables 1–3, 5–7 were referenced to 85% H_3PO_4 .) Since the discovery of bis(dichlorophosphino)amine, $[\text{Cl}_2\text{P}=\text{N}(\text{R}^1)-\text{PCl}_2]$, numerous derivatives of this compound have been reported in the last three decades.¹⁰ The phosphanyl hydrazide compounds described in Scheme 1 may be considered

as the next homologues to the $>\text{P}=\text{N}(\text{R})-\text{P}<$ -based phosphinoamines.¹⁰ Table 1 lists examples of various combinations of $>\text{P}=\text{N}(\text{R}^1)-\text{N}(\text{R}^1)-\text{P}<$ -frameworks developed by our group^{7–9} and by others.¹¹

2.2 Cyclic Phosphorus(III) Hydrazides

As outlined in Scheme 2, cyclic phosphorus hydrazides $\text{RP}[\text{N}(\text{Me})\text{N}(\text{H})_2]\text{PR}$ [$\text{R} = \text{Et}$, (16); Ph , (17); Bu^t , (18)] were prepared by the reaction of RPCl_2 with four equivalents of methylhydrazine.¹² It is interesting to note that these reactions did not produce the acyclic phosphorus(III) bis hydrazides $[\text{RP}(\text{NMeNH}_2)_2]$ (Scheme 2) although similar reactions with $\text{RP}(\text{E})\text{Cl}_2$ ($\text{E} = \text{O}$, S ; $\text{R} = \text{Ph}$) produced the acyclic phosphorus(v) bis hydrazides $[\text{RP}(\text{E})(\text{NMeNH}_2)_2]$ exclusively.^{4,5}

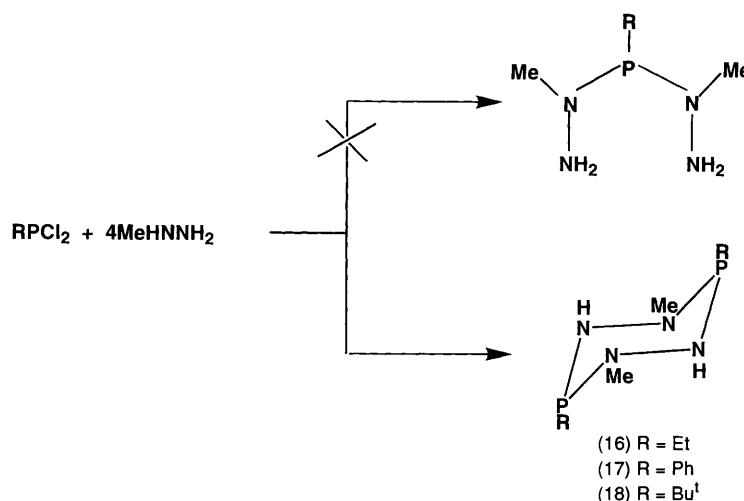
^{31}P NMR spectroscopic data indicated that the ethyl-substituted phosphorus hydrazide (16), exists in chair and boat conformations in solution, whereas, the phenyl and *t*-butyl analogues, (17) and (18) respectively, showed only one conformer in solution. The solid state X-ray structures confirmed chair conformations for (16)–(18).¹² The $-\text{NH}$ nitrogens showed trigonal planar geometries whereas the $-\text{N}(\text{CH}_3)$ nitrogens were trigonal pyramidal. These observations complement strong multiple $\text{P}=\text{N}$ bonds for the $\text{P}=\text{N}(\text{H})$ (mean $\text{P}=\text{N} 1.68\text{\AA}$) linkages in (16) and (17). Nöth *et al.* have also reported a number of functionalized cyclic phosphanyl hydrazides, as listed in Table 2.³



Scheme 1

Table 1 ^{31}P NMR data for bis phosphanyl hydrazides and their derivatives

No.	Compound	δ (p.p.m.)	Ref.
1	$\text{Cl}_2\text{P}=\text{N}(\text{Me})\text{PCl}_2$ (1)	160.2	7
2	$\text{Br}_2\text{P}=\text{N}(\text{Me})\text{PBr}_2$ (2)	157.1	11
3	$(\text{MeO})_2\text{P}=\text{N}(\text{Me})\text{P}(\text{OMe})_2$ (3)	148.5	8
4	$(\text{EtO})_2\text{P}=\text{N}(\text{Me})\text{P}(\text{OEt})_2$ (4)	139.9	8
5	$(\text{CF}_3\text{CH}_2\text{O})_2\text{P}=\text{N}(\text{Me})\text{P}(\text{OCH}_2\text{CF}_3)_2$ (5)	147.3	8
6	$[\text{CH}_3(\text{CH}_2)_7\text{O}]_2\text{P}=\text{N}(\text{Me})\text{P}[\text{O}(\text{CH}_2)_7\text{CH}_3]_2$ (6)	143.1	8
7	$(\text{CH}_2=\text{CHCH}_2\text{O})_2\text{P}=\text{N}(\text{Me})\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$ (7)	142.3	8
8	$(\text{PrO})_2\text{P}=\text{N}(\text{Me})\text{P}(\text{OPr})_2$ (8)	143.0	9
9	$(\text{PhO})_2\text{P}=\text{N}(\text{Me})\text{P}(\text{OPh})_2$ (9)	137.0	8
10	$(p\text{-BrC}_6\text{H}_4\text{O})_2\text{P}=\text{N}(\text{Me})\text{P}(\text{OC}_6\text{H}_4\text{Br-}p)_2$ (10)	138.0	9
11	$(\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{O-}o)_2\text{P}=\text{N}(\text{Me})\text{P}(\text{o-OC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2)_2$ (11)	137.1	11
12	$(\text{Me}_2\text{N})_2\text{P}=\text{N}(\text{Me})\text{P}(\text{NMe}_2)_2$ (12)	123.1	11
13	$\text{Me}_2\text{P}=\text{N}(\text{Me})\text{PMe}_2$ (13)	41.2	11
14	$\text{Ph}_2\text{P}=\text{N}(\text{Me})\text{PPh}_2$ (14)	62.5	18
15	$\text{MeClP}=\text{N}(\text{Me})\text{PClMe}$ (15)	145.1	11

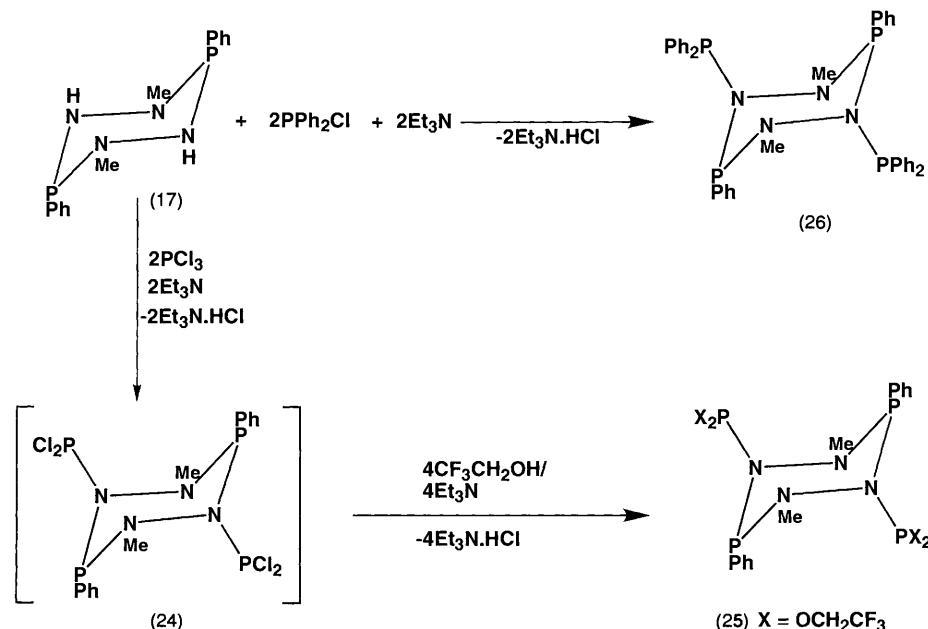


Scheme 2

Table 2 ^{31}P NMR data for Tetraazadiphosphorinananes, $[\text{XPN}(\text{R})\text{N}(\text{R}')_2]$

No	X	R	R'	Compound No	δ (ppm)	Ref
1	Et	Me	H	(16)	89.2	12
2	Ph	Me	H	(17)	90.0	12
3	Bu ^t	Me	H	(18)	95.3	12
5	Me	Me	Me	(19)	91.1	3
4	Cl	Me	Me	(20)	120.1	3
6	OMe	Me	Me	(21)	127.7	3
7	SMe	Me	Me	(22)	117.5	3
8	CN	Me	Me	(23)	50.4	3

The heterocyclic 1,2,4,5,3,6-tetraazadiphosphorinananes (16)–(18) can be used as synthons for the synthesis of novel tetraphosphaphanes via the reactions with the phosphorus(III) halides as shown in Scheme 3. The new tetraphosphaphanes (24)–(26) represent first examples of compounds that combine the phosphinoamine, $[\text{R}_2\text{P}(\text{R}^1)-\text{N}(\text{R}^1)-\text{RP}_2]$, and phosphorus(III) hydrazide, $[\text{R}_2\text{P}(\text{R}^1)-\text{N}(\text{R}^1)-\text{N}(\text{R}^1)-\text{PR}_2]$, functionalities in a single molecular framework.¹³



Scheme 3

3 Coordination Chemistry of Acyclic and Cyclic Phosphorus(III) Hydrazides

3.1 Acyclic Phosphorus(III) Hydrazides

The bisphosphanyl hydrazides described in Scheme 1 react cleanly with Group 6 metal carbonyls to produce the mono-nuclear Mo^0 and W^0 complexes (27)–(30) as outlined in Scheme 4.⁸ A significant difference in the ^{31}P NMR chemical shifts of the parent ligands (5) and (9) and their corresponding Mo^0 or W^0 complexes (Table 3) indicates that these phosphine centres are efficient π -acceptors. Typically, a difference of ~ 48 and 28 ppm were found between the chemical shifts of (5) and its Mo^0 (27) and W^0 (29) complexes respectively (Table 3). IR spectroscopic data for (27)–(30) and the representative X-ray crystallographic data (*vide infra*) for (30) confirmed the *cis*-disposition of the carbonyls around the Mo^0 and W^0 centres.⁸

The reactions of $\text{X}_2\text{P}(\text{R}^1)-\text{N}(\text{R}^1)-\text{PX}_2$ with Pd^{II} and Pt^{II} precursors produce a diverse range of metallacyclic phosphane hydrazides (31)–(43) as described in Scheme 4.¹⁴ The magnitude of $^{1}\text{J}_{\text{P}_1\text{P}}$ for (37)–(43) indicate *cis* disposition of the phosphane units around the metal centres (Table 3). In fact, X-ray crystallographic investigations (*vide infra*) of (35), (41), and (43) have confirmed that the Pd^{II} and Pt^{II} metal centres are bound in *cis* fashions with the P^{III} centres.^{9,14} The reactions of

Table 3 ^{31}P NMR data^a for the metal complexes of phosphanyl hydrazides

No.	Compound	δ (p.p.m.)	$^1\text{J}(\text{MP})$
1	<i>cis</i> -[Mo(CO) ₄ {(CF ₃ CH ₂ O) ₂ PN(Me)N(Me)P(OCH ₂ CF ₃) ₂ }](27)	194.0	—
2	<i>cis</i> -[Mo(CO) ₄ {(PhO) ₂ PN(Me)N(Me)P(OPh) ₂ }](28)	172.6	—
3	<i>cis</i> -[W(CO) ₄ {(CF ₃ CH ₂ O) ₂ PN(Me)N(Me)P(OCH ₂ CF ₃) ₂ }](29)	173.9	366
4	<i>cis</i> -[W(CO) ₄ {(PhO) ₂ PN(Me)N(Me)P(OPh) ₂ }](30)	169.3	373
5	<i>cis</i> -[PdCl ₂ {Cl ₂ PN(Me)N(Me)PCl ₂ }](31)	151.9	—
6	<i>cis</i> -[PdCl ₂ {(CF ₃ CH ₂ O) ₂ PN(Me)N(Me)P(OCH ₂ CF ₃) ₂ }](32)	126.4	—
7	<i>cis</i> -[PdCl ₂ {(PrO) ₂ PN(Me)N(Me)P(OPr) ₂ }](33)	120.7	—
8	<i>cis</i> -[PdCl ₂ {(PhO) ₂ PN(Me)N(Me)P(OPh) ₂ }](34)	119.3	—
9	<i>cis</i> -[PdCl ₂ {(p-BrC ₆ H ₄ O) ₂ PN(Me)N(Me)P(OC ₆ H ₄ Br- <i>p</i>) ₂ }](35)	118.4	—
10	<i>cis</i> -[PdCl ₂ {(CH ₂ =CHCH ₂ C ₆ H ₄ O- <i>o</i>) ₂ PN(Me)N(Me)P(o-OC ₆ H ₄ CH ₂ CH=CH ₂) ₂ }](36)	104.1	—
11	<i>cis</i> -[PtCl ₂ {Cl ₂ PN(Me)N(Me)PCl ₂ }](37)	121.4	5196
12	<i>cis</i> -[PtCl ₂ {(CF ₃ CH ₂ O) ₂ PN(Me)N(Me)P(OCH ₂ CF ₃) ₂ }](38)	103.6	5362
13	<i>cis</i> -[PtCl ₂ {(CH ₃ (CH ₂) ₇ O) ₂ PN(Me)N(Me)P(OCH ₂) ₇ CH ₃) ₂ }](39)	99.7	5384
14	<i>cis</i> -[PtCl ₂ {(PrO) ₂ PN(Me)N(Me)P(OPr) ₂ }](40)	94.8	5412
15	<i>cis</i> -[PtCl ₂ {(PhO) ₂ PN(Me)N(Me)P(OPh) ₂ }](41)	95.7	5497
16	<i>cis</i> -[PtCl ₂ {(p-BrC ₆ H ₄ O) ₂ PN(Me)N(Me)P(OC ₆ H ₄ Br- <i>p</i>) ₂ }](42)	95.4	5408
17	<i>cis</i> -[PtCl ₂ {(o-CH ₂ =CHCH ₂ C ₆ H ₄ O) ₂ PN(Me)N(Me)P(OC ₆ H ₄ CH ₂ CH=CH ₂ - <i>o</i>) ₂ }](43)	80.4	5536

^a From refs. 7, 8, and 10

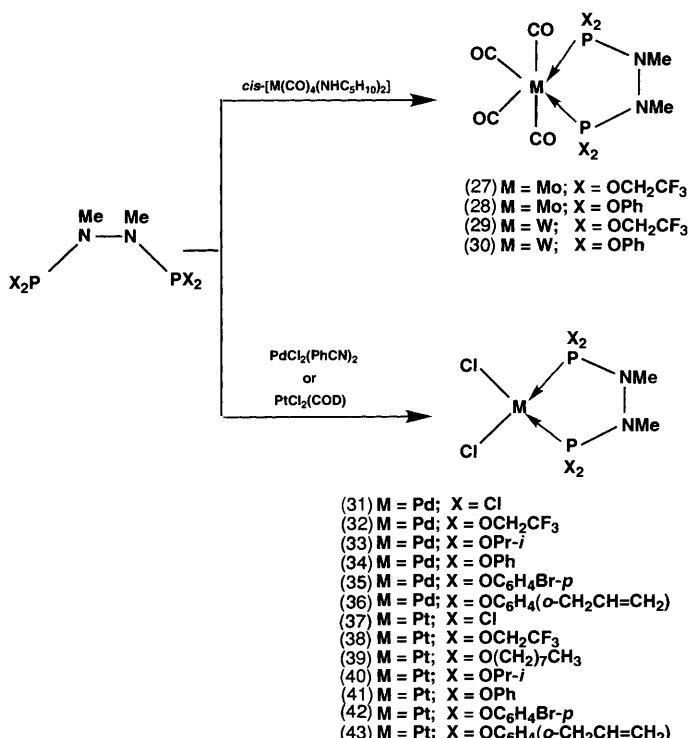
(OR)₂P—N(Me)—N(Me)—P(OR)₂ [R = CH₂CF₃ (5); Ph, (9)] with [RhCl(CO)₂]₂ to produce the chloride-bridged dimers (44) and (45) in near quantitative yields are described in Scheme 5. The absence of bands due to νCO in the IR spectra of (44) and (45) confirmed complete decarbonylation in these reactions. Observation of single resonances in the ^{31}P NMR spectra of (44) and (45) [$^1\text{J}_{\text{RhP}}$ of 287.0 Hz for (44) and 296.5 Hz for (45)] indicated chelate structures with *cis* dispositions of the P^{III} centres around Rh¹ as shown in Scheme 5.¹⁴ The chloride bridge in (44) and (45) can be readily cleaved upon reactions with triaryl phosphines or arsines (Scheme 5). It is important to note that the integrity of the five-membered P—N—N—P—Rh rings in (46) and (47) were retained even when 4–10 fold excess of ER₃ (E = As or P) were used in these reactions. Compounds (46) and (47) can be considered as ‘hybrids’ to the Wilkinson catalyst [RhCl(PPh₃)₃]. However, judicious variations of substituents in

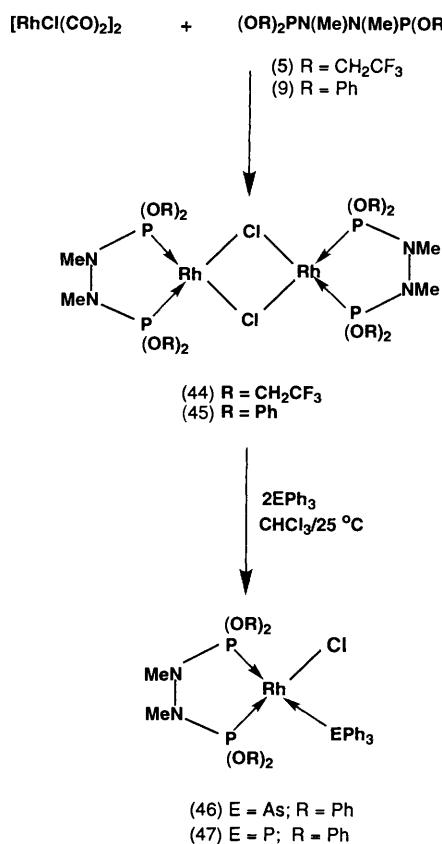
(OR)₂P—N(R¹)—N(R¹)—P(OR)₂ may afford complexes of the type (46) and (47) for potential catalytic applications.

The coordination chemistry of phosphinoamines, R₂P—N(R¹)—PR₂, has been the subject of extensive studies over the past three decades.¹⁰ In fact more than 300 papers have been published describing the rich chemistry of this class of bisphosphines.¹⁰ In sharp contrast, the transition metal chemistry of the next homologue, R₂P—N(R¹)—N(R¹)—PR₂, was largely unexplored until our work, as summarized in Schemes 3–5.^{7–9}

3.2 Cyclic Phosphorus(III) Hydrazides

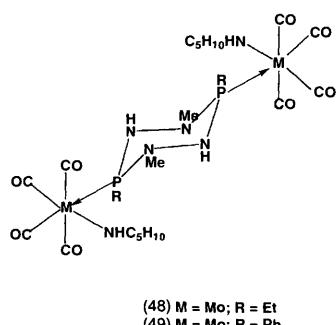
The cyclic phosphorus hydrazides (16)–(18) can be used as functionalized phosphanes for reactions with transition metal precursors. The bimetallic Mo⁰ complexes (48) and (49) have been characterized.¹² The coordination chemistry of cyclic

**Scheme 4**



Scheme 5

tetraphosphphanes (24)–(26) present unique opportunities to study the preferred modes of coordination ($>\text{P}-\text{N}-\text{P}<$ versus $>\text{P}-\text{N}-\text{N}-\text{P}<$) with the transition metals. For example W^0 , Mo^0 , and Pt^{II} react exclusively *via* the $>\text{P}-\text{N}-\text{P}<$ functionality to produce the bimetallic compounds (50)–(52) (Scheme 6). The *X*-ray crystal structure of a representative W^0 complex (51), confirms the four-membered metallacyclic structure as formulated in Scheme 6.¹³

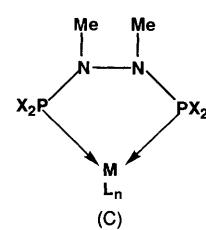


Scheme 6

favoured four-membered $\text{M}-\text{P}-\text{N}-\text{P}$ metallacycle as (50)–(52) depicted in Scheme 6.

4 X-Ray Crystallographic and Bonding Aspects of Phosphorus(III) Hydrazide Metal Complexes

The neutral mononuclear structures for (30), (35), (41), and (43) were confirmed by *X*-ray crystallographic analysis (Table 4). The dimeric chloride-bridged rhodium structure of (45) and the monomeric rhodium structure of (46) were also confirmed by *X*-ray crystallography.¹⁴ The geometries around the metal centres and the salient bonding features of these complexes are summarized in Table 4. The most striking feature in the structures of these complexes is the differences noted for the geometries of the hydrazide nitrogens. For the W^0 (30), Pt^{II} (41), and Rh^1 (45) complexes, one of the nitrogens is trigonal planar whereas the other one is trigonal pyramidal. However, trigonal planarity for both the hydrazide nitrogens has also been observed for the Pd^{II} (42) and Pt^{II} (43) complexes. Significant shortening of the $\text{P}-\text{N}$ bonds were noted in compounds where phosphorus interacted with the trigonal planar nitrogens (Table 4). The coordination chemistry of diphosphanes based on $>\text{P}-\text{N}(\text{R})-\text{P}<$ and $>\text{P}(\text{CH}_2)_n\text{P}<$ ($n = 1,2$) has revealed a wide variety of bonding modes with the transition metals. In sharp contrast, the coordination chemistry of bisphosphanyl hydrazides (3)–(11), outlined in Schemes 4 and 5, is clearly unique, demonstrating strong propensity to form well-defined mononuclear chelates of the general structure (C). The bite angles across the $>\text{P}-\text{N}-\text{N}-\text{P}<$ and also the cone angle at P^{II} in (3)–(11) appear to be ideal for the ‘strictly’ mononuclear bidentate (chelate) coordination chemistry of this class of ligands.



The preference for the four-membered $\text{M}-\text{P}-\text{N}-\text{P}$ over the five-membered $\text{M}-\text{P}-\text{N}-\text{N}-\text{P}$ coordination may be rationalized in terms of electronic effects. The disposition of the lone pairs on P_A and P_B in an axial fashion is essential for them to coordinate with the metal across the $>\text{P}_A-\text{N}(\text{R})-\text{N}(\text{R})-\text{P}_B<$ frameworks (Scheme 6). However, recent *X*-ray structural investigations of cyclic phosphorus(III) hydrazides has suggested equatorial dispositions of the lone pairs on the ring- P^{III} centres.¹² Therefore, the metal is forced to interact with the equatorial lone pairs of P_A and P_C to yield the four-membered structures as outlined in Scheme 6.¹³ It may be reasoned that the energy involved for the equatorial-to-axial flip of the lone pair of P_A , to produce a five-membered $\text{M}-\text{P}-\text{N}-\text{N}-\text{P}$ metallacycle, is presumably much more than the strain involved in a less-

Table 4 X-ray crystallographic data for *cis*-[ML_n{(RO)₂PN(Me)N(Me)P(OR)₂}]

ML _n	R	M-P(1)	M-P(2)	Bond distances (Å)	P(2)-N(2)	Geometry
				P(1)=N(1)	N(1)	N(2)
W(CO) ₄	OPh (30)	2.433	2.409	1.681	1.715	tpy tpy
PdCl ₂	OC ₆ H ₄ Br- <i>p</i> (35)	2.178	2.187	1.649	1.652	tp tp
PtCl ₂	OPh (41)	2.182	2.180	1.639	1.669	tp tpy
PtCl ₂	OC ₆ H ₄ (CH ₂ -CH=CH ₂ - <i>o</i>) (43)	2.174	2.181	1.651	1.665	tp tp
RhCl ₂ ^a	OPh (45)	2.121	2.128	1.705	1.661	tpy tp
RhCl(AsPh ₃)	OPh (46)	2.130 ^b	2.193 ^c	1.705	1.662	tpy tp

^a Dimeric structure; ^b *trans* to Cl; ^c *trans* to AsPh₃; tp = trigonal planar; tpy = trigonal pyramidal.

5 Main Group Chemistry of Phosphorus(v) Hydrazides

5.1 Synthesis

Reactions of methyl hydrazine with functionalized phosphorus(v) halides [e.g. P(E)Cl₃, or RP(E)Cl₂, or R₂P(E)Cl; R = Me, Et, Ph, OMe, OEt, or OPh; E = S or O] afford the corresponding substituted phosphorus hydrazides.^{4,5,15,16,17} Synthetic approaches for the mono, bis, and the tris phosphorus hydrazides are summarized in Scheme 7. In all these reactions, the excess hydrazine acts as a hydrogen halide abstractor. These reactions, in general, produce products in near quantitative yields. All the phosphorus hydrazides are soluble in common organic solvents including alcohols and some of the alkoxy-substituted derivatives, such as (MeO)₂P(E)(NM₂NH₂) (E = O or S), show moderate solubility in aqueous media. The ³¹P NMR spectroscopic data for the functionalized phosphorus hydrazides are summarized in Table 5.

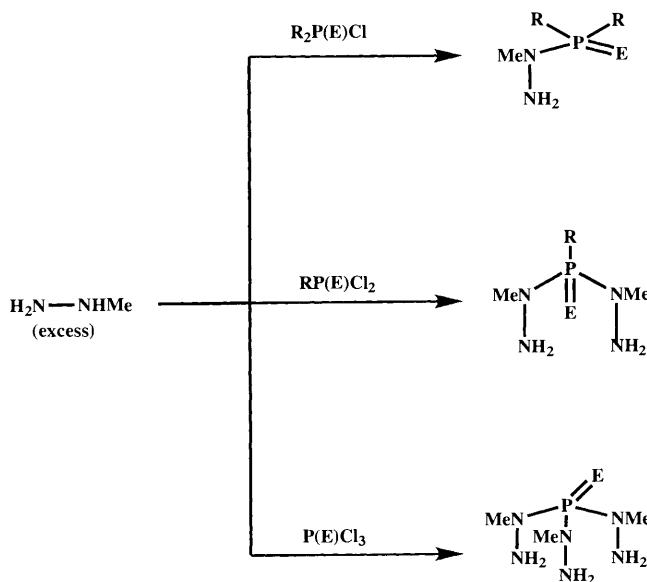
5.2 Stability Features of Phosphorus(v) Hydrazides *versus* the Parent Hydrazines

Methyl hydrazine which is a precursor in all the reactions described in Scheme 7 is hydrolytically unstable. In sharp contrast, the phosphorus hydrazides (53)–(56) and (61)–(68) (Table 5) exhibit remarkable hydrolytic stability. Even the simplest of the phosphorus hydrazides where the hydrogen from methyl hydrazine is replaced with a P^V centre [e.g. (MeO)₂P(E)(NM₂NH₂) (E = O or S)] can be exposed to atmos-

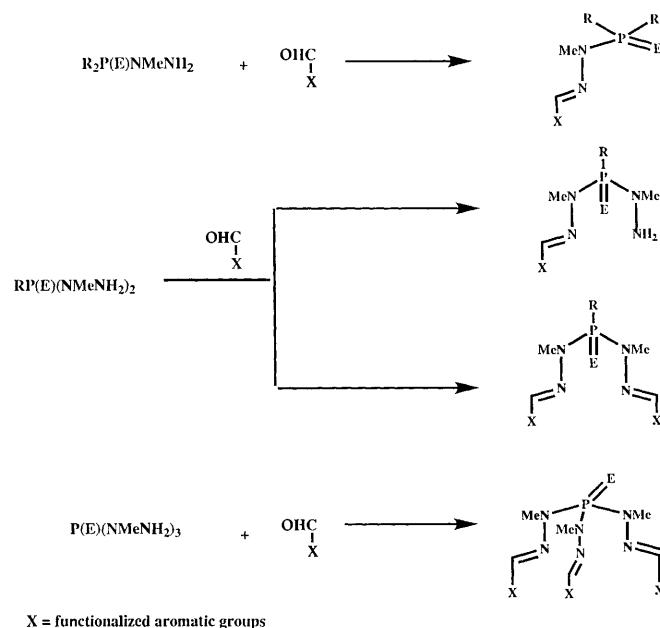
pheric moisture or dissolved in wet ethanol without any detectable decomposition. It appears that the linkage of the hydrazine >N–N< bond to the P^V centre(s) brings about hydrolytic (and thermal) stabilities to both the N–N and P–N bonds. Therefore, phosphorus hydrazides can be referred to as ‘hybrid’ hydrazines. The presence of strong *p*π–*d*π type of bonding between P^V and N and also the operation of π–π type of bonding in the N–N bond(s) in the phosphorus hydrazides may, presumably, be responsible for the unusual hydrolytic and thermal stabilities observed for this class of compounds. Other bonding models which minimize inter electronic repulsions and confer resonance of electronic charge across the P^V–N(R)–N< skeleton may also account for the significant stability of phosphorus hydrazides as compared to the parent hydrazine precursors.¹⁸

5.3 Reactions of Phosphorus Hydrazides

The reactivities of the terminal –NH₂ groups of all the phosphorus hydrazides (53)–(56), (61)–(68) are comparable to those of primary amines. For example, Schiff base coupling reactions, as outlined in Scheme 8, can be carried out to afford functionalized phosphorus hydrazides (59)–(60) and (69)–(80) (Table 5).^{15–17,19–20,22–25,28} The stability of P–N and N–N bonds in phosphorus hydrazides is again manifested because these compounds are generated in near quantitative yields despite the fact that water is a leaving group in all the reactions (Scheme 8). The mono- and the tris-phosphorus hydrazides undergo similar Schiff base coupling reactions with various functionalized aldehydes (Scheme 8). Representative



Scheme 7

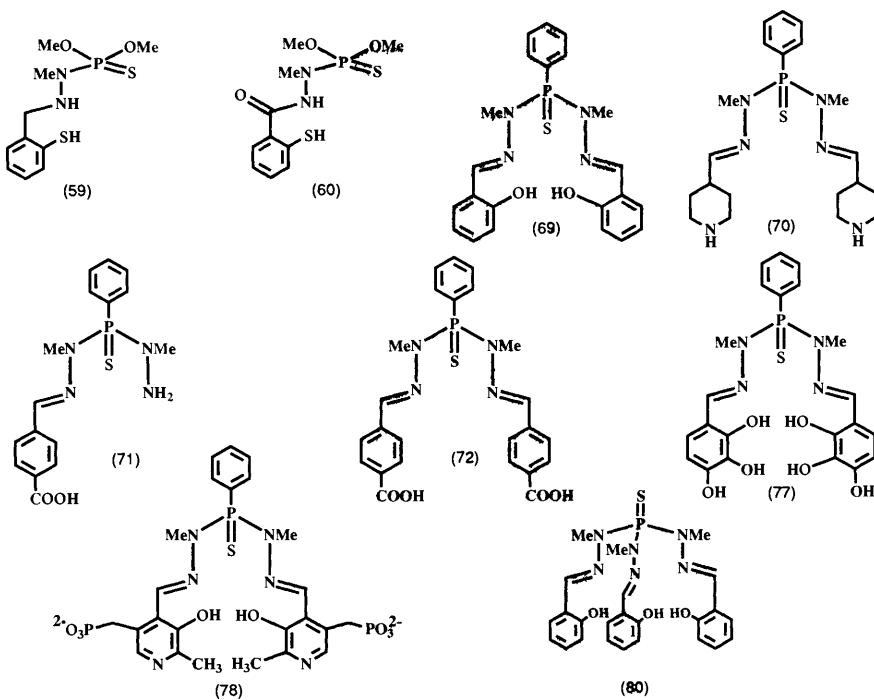


Scheme 8

Table 5 ^{31}P NMR chemical shifts of mono- and bis-phosphorus hydrazides.

No.	Formula	δ (p.p.m.)	Ref.
1	$(\text{MeO})_2\text{P}(\text{S})(\text{NMeNH}_2)$ (53)	81.5	17
2	$(\text{EtO})_2\text{P}(\text{S})(\text{NMeNH}_2)$ (54)	77.9	17
3	$\text{Ph}_2\text{P}(\text{O})(\text{NMeNH}_2)$ (55)	29.2	17
4	$(\text{PhO})_2\text{P}(\text{O})(\text{NMeNH}_2)$ (56)	0.3	17
5	$(\text{MeO})_2\text{P}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_4\text{COOH})$ (57)	74.5	24
6	$(\text{MeO})_2\text{P}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_4\text{OH})$ (58)	75.2	24
7	$(\text{MeO})_2\text{P}(\text{S})(\text{NMeNHCH}_2\text{C}_6\text{H}_4\text{SH})$ (59)	80.1	20
8	$(\text{MeO})_2\text{P}(\text{S})(\text{NMeNHCOCH}_2\text{C}_6\text{H}_4\text{SH})$ (60)	78.9	20
9	$\text{MeP}(\text{S})(\text{NMeNH}_2)_2$ (61)	90.1	24
10	$\text{EtP}(\text{S})(\text{NMeNH}_2)_2$ (62)	96.6	24
11	$\text{PhP}(\text{S})(\text{NMeNH}_2)_2$ (63)	86.5	23
12	$\text{EtOP}(\text{S})(\text{NMeNH}_2)_2$ (64)	82.5	25
13	$\text{PhP}(\text{O})(\text{NMeNH}_2)_2$ (65)	82.5	25
14	$\text{EtP}(\text{O})(\text{NMeNH}_2)_2$ (66)	82.5	25
15	$\text{MeP}(\text{O})(\text{NMeNH}_2)_2$ (67)	82.5	25
16	$(\text{MeOOCC}_6\text{H}_4\text{O})\text{P}(\text{S})(\text{NMeNH}_2)_2$ (68)	81.9	25
17	$\text{PhP}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_4\text{OH})_2$ (69)	80.6	15
18	$\text{PhP}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_5\text{NH})_2$ (70)	78.1	15
19	$\text{PhP}(\text{S})(\text{NMeNH}_2)(\text{NMeN}=\text{CHC}_6\text{H}_4\text{COOH})$ (71)	82.3	19
20	$\text{PhP}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_4\text{COOH})_2$ (72)	80.0	19
21	$\text{PhP}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_4\text{F})_2$ (73)	78.9	25
22	$\text{PhP}(\text{S})(\text{NMeNH}_2)(\text{NMeN}=\text{CHC}_6\text{H}_5)$ (74)	81.8	25
23	$\text{PhP}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_5)_2$ (75)	79.0	25
24	$\text{PhP}(\text{S})(\text{NMeNH}_2)(\text{NMeN}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHCOOH})$ (76)	81.4	19
25	$\text{PhP}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_2(\text{OH})_3)_2$ (77)	81.2	25
26	$\text{PhP}(\text{S})\text{NMeN}=\text{CHpyp}_2$ (78)*	80.6	25
27	$\text{P}(\text{S})(\text{NMeNH}_2)_3$ (79)	85.3	25
28	$\text{P}(\text{S})(\text{NMeN}=\text{CHC}_6\text{H}_4\text{OH})_3$ (80)	79.4	25

* pyp = Pyridoxal phosphate.

**Figure 1** Examples of Schiff base adducts derived from multifunctional phosphorus hydrazides.

examples of Schiff base adducts derived from the mono (59), (60),²⁰ bis [(69), (70)–(72), (77), (78)],^{15,19,22} and the tris (80) phosphorus hydrazides are given in Figure 1. The ^{31}P NMR spectroscopic data for all the Schiff base adducts, summarized in Table 5, indicate a modest upfield shift compared to their corresponding precursor phosphorus hydrazides.

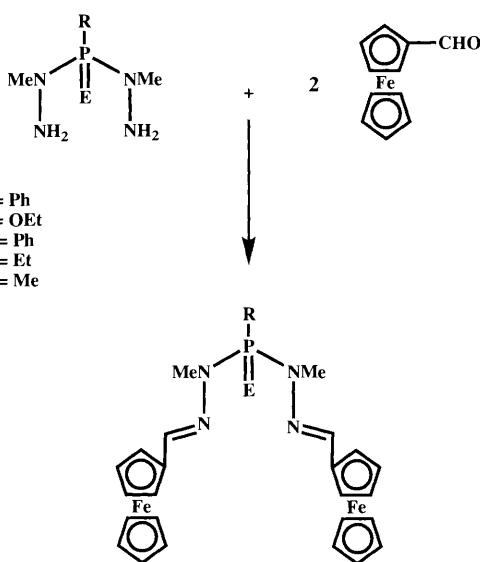
The Schiff base coupling reactions described in Scheme 8 demonstrate the diversity in terms of structure and properties of

the resulting phosphorus hydrazides. For example: (a) the hydroxy-[(58), (69), (80)], sulphydryl-[(59), (60)], and the piperazinyl-(70) functionalized phosphorus hydrazides present unique properties as a new generation of ligands in transition metal chemistry (discussed in the following sections);¹⁵ (b) the pyridoxyl phosphate-functionalized phosphorus hydrazides [e.g. (78)] are water soluble showing potential biochemical and biological applications, and (c) the carboxylate-containing

phosphorus hydrazides [*e.g.* (71), (72), and (76)] may be used as monomers in the synthesis of new polymers¹⁹

5.4 Organometallic Phosphorus Hydrazides

The reactions of ferrocenyl carboxaldehyde with the phosphorus hydrazides, as described in Scheme 9, demonstrate a new facet in the utility of Schiff base coupling reactions to produce phosphorus hydrazido compounds functionalized with organometallic units^{21 22} The ferrocenyl phosphorus hydrazides (81)–(85) are formed in near quantitative yields as air-stable and hydrolytically robust compounds. These compounds represent a new class of ‘organometallic ligands’ with potential for their use as synthons in coordination chemistry to produce multimetallic redox-active compounds (see Section 6)^{21 22}



Scheme 9

The ^{31}P NMR spectroscopic data for the ferrocenyl phosphorus hydrazides (81)–(85) (Table 6) indicate considerable upfield shifts (10–15 ppm) as compared to the free parent phosphorus hydrazides (63)–(67). It may be reasoned that the redox active ferrocenyl units in (81)–(85) inject electron density across the N–N–P–N–N frameworks, presumably, causing upfield chemical shifts for the interacting ^{31}P nuclei. X-Ray crystal structure of a representative ferrocenyl phosphorus hydrazide (82) has confirmed the absence of any inter or intra molecular contacts of the ferrocenyl sub units in these compounds²²

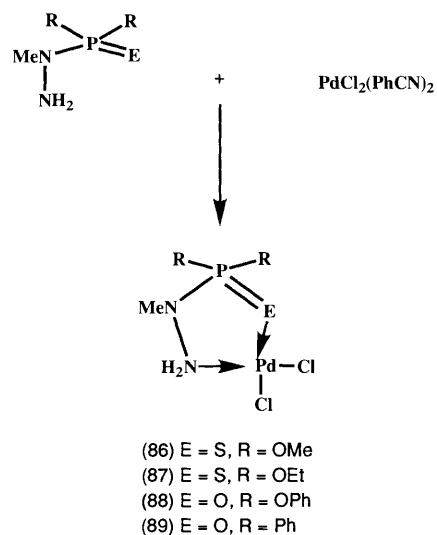
Table 6 ^{31}P NMR chemical shifts^a of organometallic phosphorus hydrazides

No	Formula	δ (ppm)
1	$\text{PhP(S)(NMeN=CHCp'FeCp)}_2$ (81)	77.8
2	$\text{EtOP(S)(NMeN=CHCp'FeCp)}_2$ (82)	71.8
3	$\text{PhP(O)(NMeN=CHCp'FeCp)}_2$ (83)	24.4
4	$\text{EtP(O)(NMeN=CHCp'FeCp)}_2$ (84)	41.7
5	$\text{MeP(O)(NMeN=CHCp'FeCp)}_2$ (85)	38.3
6	$cis-[\text{PdCl}_2\{\text{PhP(S)(NMeN=CHCp'FeCp)}_2\}]$ (109)	78.6
7	$cis-[\text{PdCl}_2\{\text{EtOP(S)(NMeN=CHCp'FeCp)}_2\}]$ (110)	71.1
8	$cis-[\text{PdCl}_2\{\text{PhP(O)(NMeN=CHCp'FeCp)}_2\}]$ (111)	22.3
9	$cis-[\text{PdCl}_2\{\text{EtP(O)(NMeN=CHCp'FeCp)}_2\}]$ (112)	36.5
10	$cis-[\text{PdCl}_2\{\text{MeP(O)(NMeN=CHCp'FeCp)}_2\}]$ (113)	32.6
11	$[\text{Cu}\{\text{PhP(S)(NMeN=CHCp'FeCp)}_2\}](\text{CF}_3\text{SO}_2)_2$ (114)	72.4

From ref 22 ^b From ref 21

6 Coordination Chemistry of Phosphorus(v) Hydrazides

The presence of chalcogenide centre(s) [*i.e.*, P(S) or P(O)], hard nitrogen base(s), and also the possibility of various functionalities (*e.g.* –OH, –SH, –NH₂, –NMe₂), at the terminal hydrazic nitrogens in the phosphorus hydrazides (*vide supra*) present attractive prospects for their utility as multifunctional ligands in the coordination chemistry of transition metals. Representative reactions, summarized in Scheme 10, illustrate the application of functionalized monophosphorus hydrazides to produce the new Pd^{II} metallacycles (86)–(91) involving the chelate interactions of P(S) or P(O) and the hydrazido nitrogen.¹⁷ Complexes of these ligands with Re^V have also been reported [(92), (93)]²⁰ All these compounds are monomeric and show remarkable hydrolytic and thermal stability. The ^{31}P NMR chemical shifts of all the Pd^{II} complexes (86)–(91) showed modest upfield shifts by 3–5 ppm as compared to the free ligands (Table 7). X-Ray crystallographic investigation of a representative compound (86) has confirmed the chelate interaction outlined in Scheme 10



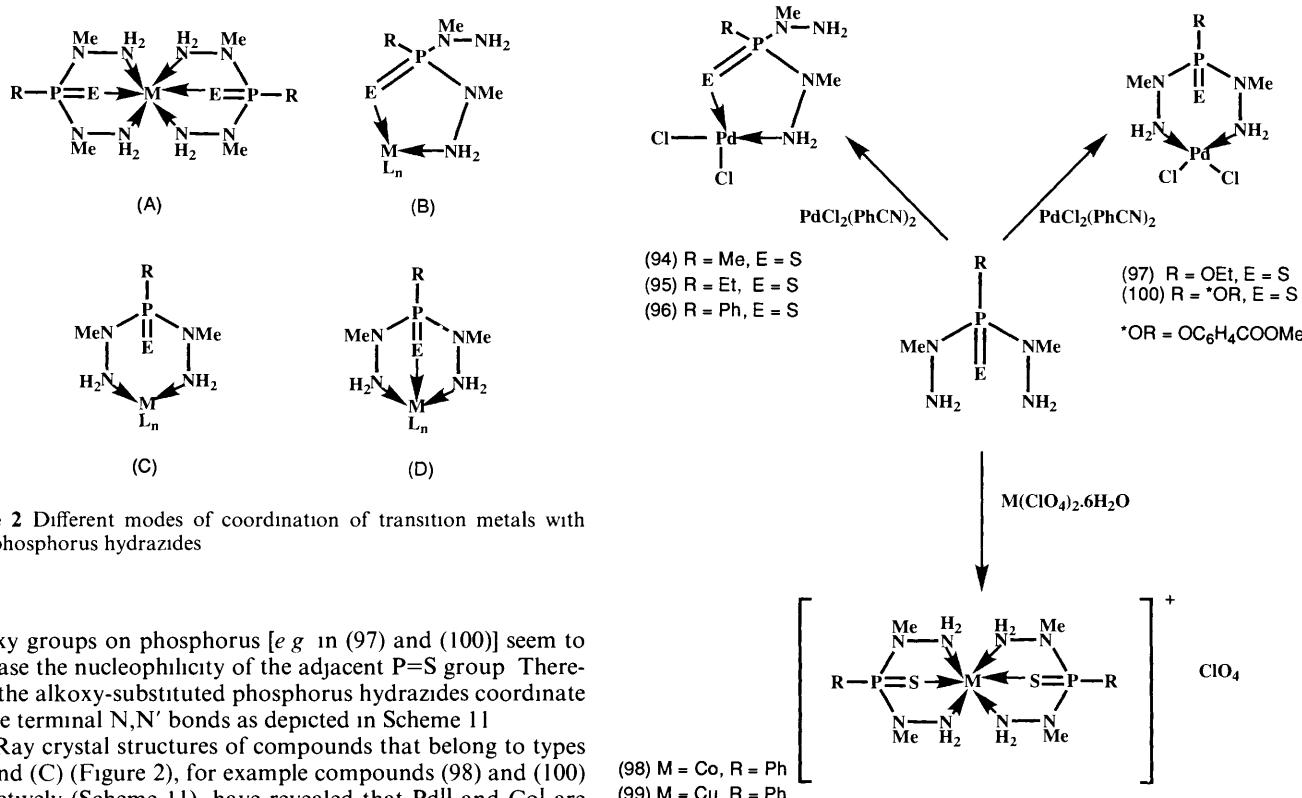
Scheme 10

Four different modes of coordination of transition metals with the bisphosphorus hydrazides RP(E)(NMeNH₂)₂ can be envisaged as depicted in Figure 2. Coordination types (A), (B), and (C) have been realized with various transition metals. The elusive nature of the (D)-type of coordination is yet unclear. Copper(II) and cobalt(II) precursors react with (63) and its derivatives through the coordination mode (A) exclusively to yield the metallacycles (98) and (99) in which the metals are reduced to +1 oxidation states (Scheme 11). A minimum of threefold excess of the phosphorus hydrazide (63) is required to reduce Co^{II} and Cu^{II} to their corresponding +1 oxidation states.¹⁵

The reactions of phosphorus hydrazides with the Pd^{II} precursors have been extensively investigated.^{23 24} Detailed spectroscopic and X-ray investigations of representative examples depicting different modes of coordinations are summarized in Scheme 11. A systematic investigation of the effect of substituents on phosphorus upon the mode of interaction with Pd^{II} has resulted in important insights on the regioselectivity of N,N' versus N,S coordination behaviour.^{15 17 23 25} For example, oxygen substituents on phosphorus [*e.g.* (RO)P(S)(NMeNH₂)₂, R = Et, Ph, C₆H₄COOMe-*p*] favoured N,N' coordination with Pd^{II} exclusively. In sharp contrast, carbon substituents on phosphorus [*e.g.* RP(E)(NMeNH₂)₂, R = Me, Et, Ph] produced Pd^{II} complexes *via* N,S coordination exclusively as outlined in Scheme 11. Conclusive proof for such distinct differences in the coordination modes has come from the detailed X-ray structural analysis of a number of Pd^{II} metal complexes.^{15 17 23 25}

Table 7 ^{31}P NMR chemical shifts for metal complexes of mono- and bis-phosphorus hydrazides

No	Formula	δ (ppm)	Ref
1	<i>cis</i> -[PdCl ₂ {(MeO) ₂ P(S)(NMeNH ₂)}] (86)	87.5	17
2	<i>cis</i> -[PdCl ₂ {(EtO) ₂ P(S)(NMeNH ₂)}] (87)	83.5	17
3	<i>cis</i> -[PdCl ₂ {(PhO) ₂ P(O)(NMeNH ₂)}] (88)	-4.0	17
4	<i>cis</i> -[PdCl ₂ {Ph ₂ P(O)(NMeNH ₂)}] (89)	25.9	17
5	<i>cis</i> -[PdCl ₂ {(MeO) ₂ P(S)(NMeN=CHC ₆ H ₄ COOH)}] (90)	77.3	24
6	<i>cis</i> -[PdCl ₂ {(MeO) ₂ P(S)(NMeN=CHC ₆ H ₄ O-)}] (91)	78.4	24
7	[Re(O)Cl{(MeO) ₂ P(S)(NMeNC ₆ H ₄ S-)(PPh ₃)}] (92)	81.3	20
8	[Re(O)Cl{(MeO) ₂ P(S)(NMeNCOC ₆ H ₄ S-)(PPh ₃)}] (93)	79.7	20
9	<i>cis</i> -[PdCl ₂ {MeP(S)(NMeNH ₂) ₂ }] (94)	95.4	24
10	<i>cis</i> -[PdCl ₂ {EtP(S)(NMeNH ₂) ₂ }] (95)	101.9	24
11	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeNH ₂) ₂ }] (96)	87.3	17
12	<i>cis</i> -[PdCl ₂ {EtOP(S)(NMeNH ₂) ₂ }] (97)	85.4	25
13	Co{[PhP(S)(NMeNH ₂) ₂]} ₂ ClO ₄ (98)	88.5	15
14	Cu{[PhP(S)(NMeNH ₂) ₂]} ₂ ClO ₄ (99)	—	15
15	<i>cis</i> -[PdCl ₂ {(MeOOC ₆ H ₅ O)P(S)(NMeNH ₂) ₂ }] (100)	74.2	25
16	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeN=CHC ₆ H ₄ OH)(NMeN=CHC ₆ H ₄ O)}] (101)	84.0	15
17	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeN=CHC ₅ H ₉ NH) ₂ }] (102)	81.8	15
18	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeNH ₂)(NMeN=CHC ₆ H ₄ COOH)}] (103)	84.4	19
19	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeN=CHC ₆ H ₄ COOH) ₂ }] (104)	82.8	19
20	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeN=CHC ₆ H ₄ F) ₂ }] (105)	81.1	25
21	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeNH ₂)(NMeN=CHC ₆ H ₅)}] (106)	83.9	25
22	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeNH ₂)(NMeN=CHC ₆ H ₅) ₂ }] (107)	81.8	25
23	<i>cis</i> -[PdCl ₂ {PhP(S)(NMeNH ₂)(NMeN=CHC ₆ H ₄ CH=CHCOOH)}] (108)	83.6	19

**Figure 2** Different modes of coordination of transition metals with bisphosphorus hydrazides

Alkoxy groups on phosphorus [*e.g.* in (97) and (100)] seem to decrease the nucleophilicity of the adjacent P=S group. Therefore, the alkoxy-substituted phosphorus hydrazides coordinate *via* the terminal N,N' bonds as depicted in Scheme 11

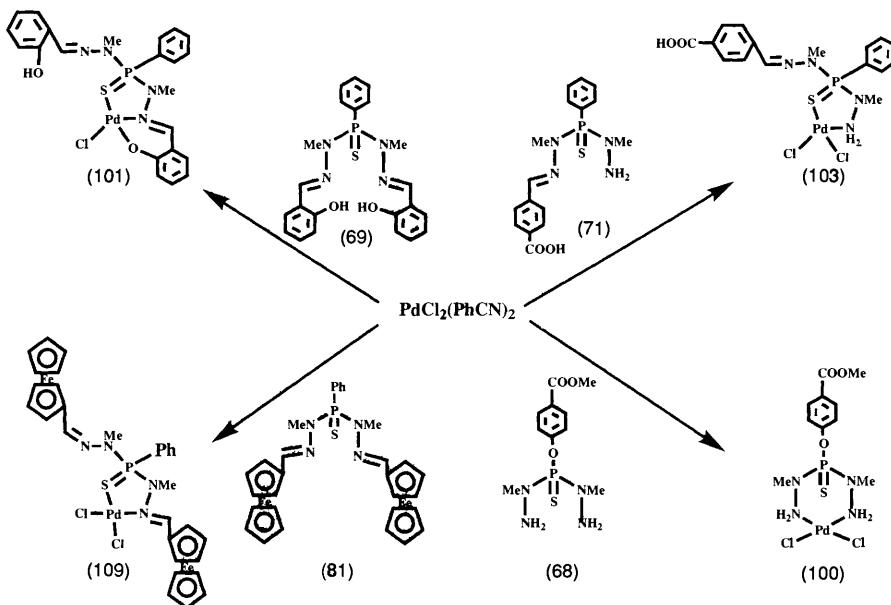
X-Ray crystal structures of compounds that belong to types (A) and (C) (Figure 2), for example compounds (98) and (100) respectively (Scheme 11), have revealed that Pd^{II} and Co^I are bound to the two nitrogens in a *cis* fashion. The ability of the oxygen substituents on the phosphorus to direct the incoming metal centre to bind *cis* to the two-hydrazine nitrogens is significant. This unique regioselectivity to produce *cis*-diaminopd^{II} (and also Pt^{II})⁸ complexes may be useful in the design of a new generation of *cis*-platin analogues.

Functionalized phosphorus hydrazides (69)–(85) (Tables 5 and 6) derived from the Schiff base coupling reactions of parent phosphorus hydrazides can be used as versatile ligands in transition metal chemistry. For example, the presence of hydroxy group [as in (69)] results in a dehydrochlorination reaction to produce a novel Pd^{II} complex (101) with Pd–O σ -bond (Scheme 12). A wide spectrum of functionalities (*e.g.* –COOH, piperidinyl, and ferrocenyl) on the phosphorus hydrazides

afford a new generation of mono and multimetallic transition metal compounds [(101)–(114)] as outlined in Scheme 12

7 Phosphorus Hydrazides as Building Blocks for Long-chain Phosphines

The –NH₂ functionalities of phosphorus hydrazides undergo facile nucleophilic substitution reactions with the alkylphosphorus(III) halides to give a new class of long-chain phosphines containing N–N–P^V–N–N– bridges as described in Scheme 13.²⁶ Recent studies have demonstrated the catalytic import-

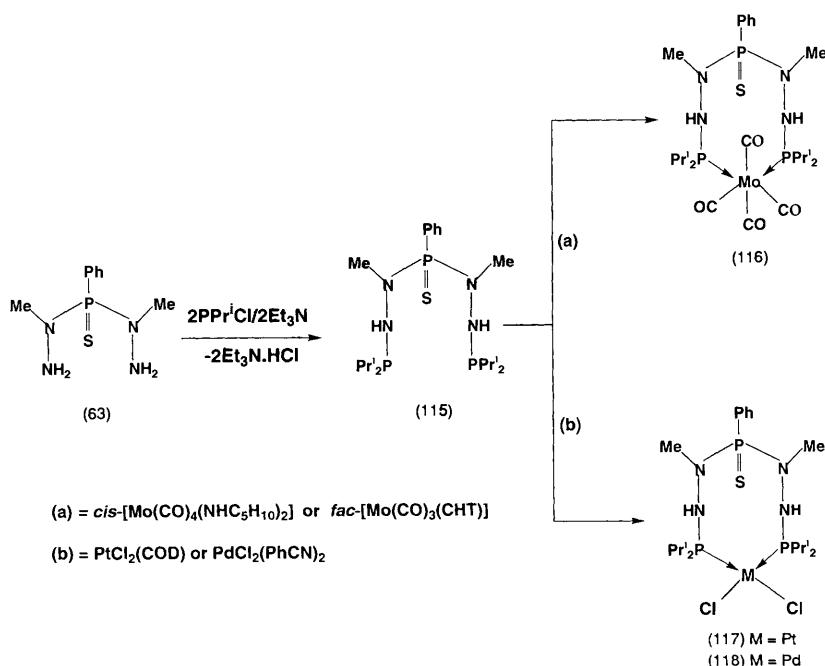


Scheme 12

ance of Pd^0 complexes of diphosphine ligands of various chain lengths.²⁷ It is also known that in certain Rh^1 complexes derived from alkane diphosphines, the size of the alkane chain exerts a profound influence on the catalytic activities of the metal complexes.²⁷ In this context, the application of the novel diphosphine (115) (Scheme 13) in transition metal chemistry raised two important questions: (a) what would be the mode of coordination (chelate, bridging, or non-chelate) of compounds of the type (115) with transition the metals; (b) is the chelation solely through the P^{III} centres or do the hetero atoms N or S of (115) also interact with the transition metals? The results of recent studies, summarized in Scheme 13, demonstrate the unusually large bite characteristics of (115).²⁶ The lack of interactions of $-\text{NH}$ and $\text{P}(\text{S})$ with Mo^0 (116), Pt^{II} (117), and Pd^{II} (118) have been confirmed through the *X*-ray crystallographic analysis of (116) and (117). The eight-membered ring in the compounds (116) and (117) are non-planar with twisted chair and crown conformations respectively.²⁶

8 X-Ray Crystallographic and Bonding Aspects of Phosphorus(v) Hydrazides and their Metal Complexes

Bonding parameters for the free phosphorus hydrazides and their metal complexes summarized in Table 8 indicate that no significant differences exist in the N–N bond lengths of the free ligands and their complexes. It is interesting to note that the $-\text{NMe}$ hydrazido nitrogens in the phosphorus hydrazides [e.g. (62), (63)] showed trigonal pyramidal geometry. However, all the Schiff base adducts [as in (73), (75), and (82)] showed trigonal planar geometries for the $-\text{NMe}$ hydrazido nitrogens.^{22–25} The $\text{M}–\text{N}–\text{N}$ ($\text{M} = \text{Pd}^{\text{II}}$ and Co^{I}) bond angles fall in the range 111–118° (Table 8), suggesting that the terminal hydrazido nitrogen in these compounds is involved in a two-electron donation with the metal centre. The $\text{P}^{\text{V}}–\text{N}$ bonds in the free phosphorus hydrazides and their Pd^{II} complexes fall in the range 1.61–1.68 Å indicating significant multiple bond character.^{22–25}



Scheme 13

Table 8 X-Ray crystallographic data for phosphorus(v) hydrazides and their metal complexes

No	Compounds	Bond distances in (Å)			Ref
		N—	P—N	P=S	
1	EtP(S)(NMeNH ₂) ₂ (62)	1.48, 1.45	1.67, 1.65	1.95	25
2	PhP(S)(NMeNH ₂) ₂ (63)	1.43, 1.42	1.67, 1.65	1.96	25
3	PhP(S){(NMeN=CHC ₆ H ₅) ₂ } (75)	1.38, 1.37	1.68, 1.68	1.93	25
4	PhP(S){(NMeN=CHC ₆ F ₅) ₂ } (73)	1.39, 1.38	1.68, 1.68	1.94	25
5	Co{PhP(S)(NMeNH ₂) ₂ } ₂ ClO ₄ (98)	1.46, 1.43	1.67, 1.65	1.98	15
6	PdCl{PhP(S){(NMeN=CHC ₆ H ₄ OH)(NMeN=CHC ₆ H ₄ O)}} (70)	1.46, 1.41	1.67, 1.65	1.98	15
7	[PdCl ₂ {PhP(S)(NMeNH ₂)(NMeN=CHC ₆ H ₄ COOH)}] (72)	1.44, 1.38	1.67, 1.64	1.99	19
8	EtOP(S){(NMeN=CHCp'FeCp) ₂ } (82)	1.39, 1.39	1.68, 1.66	1.94	22
9	[PdCl ₂ {EtOP(S)(NMeN=CHCp'FeCp) ₂ }] (84)	1.45, 1.43	1.68, 1.68	1.90	22
10	[PdCl ₂ {PhP(S)(NMeN=CHC ₆ H ₅) ₂ }] (75)	1.43, 1.39	1.67, 1.65	1.99	25
11	[PdCl ₂ {(MeO) ₂ P(S)(NMeNH ₂) ₂ }] (59)	1.43	1.61	1.96	17
12	[PdCl ₂ {(MeOC ₆ H ₅ O)P(S)(NMeNH ₂) ₂ }] (69)	1.44, 1.45	1.68, 1.67	1.90	25
13	Mo(CO) ₄ [PhP(S){(NMeNH ₂) ₂ } ₂] (116)	1.43, 1.42	1.69, 1.70	1.93	26
14	PtCl ₂ [PhP(S){(NMeNH ₂) ₂ } ₂] (117)	1.44, 1.42	1.71, 1.69	1.94	26

9 Conclusions

The main group chemistry of phosphorus(III) and phosphorus(V) hydrazides is extensive because of the various possibilities of functionalization at the phosphorus and nitrogen centres. The structural tuning affords phosphorus hydrazides that have hydrolytic stability and water solubility with potential biological applications. For example, (63), (71), and (78) have been used as ligands for ^{99m}Tc and Mn^{II} to design a new generation of potential radiopharmaceuticals and magnetic resonance imaging agents.^{28–31}

The development of viable synthetic pathways to bisphosphanyl hydrazides (OR)₂P—N(R¹)—N(R¹)—P(OR)₂ has opened up the main group and transition metal chemistry of a new class of chelating bis-phosphines. In sharp contrast to the well-known hydrolytic instability of the N—N bonds of simple hydrazines, such bonds in phosphorus(III) and phosphorus(V) hydrazides have demonstrated remarkable stabilities. The aforementioned unique features in conjunction with the versatile bonding and coordination modes displayed by phosphorus(III and V) hydrazides make it practical to produce transition metal complexes for specific catalytic applications. In fact, the development of a 16-electron Rh^I complex [*e.g.* (44)–(47)] which represents a new class of ‘hybrid’ Wilkinson catalysts, as outlined in Scheme 5, can be regarded as just a ‘tip of the iceberg’ towards the endeavour of developing catalytically useful compounds.

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