Transition Metal Chemistry of Main Group Hydrazides, VI[1]

# New Directed Synthetic Strategies to Functionalized Heterocyclic Phosphorus(III) Hydrazides. First Examples of Crystal and Molecular Structures of $[RPN(Me)N(H)]_2$ (R = Et, Ph, and *t*Bu)

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The reactions of methylhydrazine with $RPCl_2$ (R = Et, *t*Bu, and Ph) produced the cyclic phosphorus(III) hydrazides (1,2,4,5,3,6-tetrazadiphosphorinanes) $[RPN(Me)N(H)]_2$ (R = Et, **1**; (Ph, **2**; *t*Bu, **3**) in good yields. The $^1H$- and $^{31}P$-NMR spectroscopic analysis indicated that **1** exists in chair and boat conformations. However, it crystallizes in the chair conformation exclusively. The X-ray crystallographic investigation of all the three *cyclo*-phosphorus hydrazides **1**–**3** confirms the existence of these compounds in the chair conformations in the solid state. The reaction of $Mo(CO)_4(NHC_5H_{10})_2$ with **1** and **2** gives the dinuclear Mo(0) complexes $[\{Mo(CO)_4(NHC_5H_{10})\}_2\{\mu\text{-}[RPN(Me)N(H)]_2\}]$ (R = Et, **5**; Ph, **6**). Based on $^1H$- and $^{31}P$-NMR spectroscopic data, a bridging dinuclear dimetallic formulation is proposed for **5** and **6**. The IR spectra indicate that the carbonyls are disposed in *cis*-geometry around the Mo(0) center.

Whereas the reactions of phosphorus trichloride with amines are nearly a century old, however, to date there are only limited reports on its corresponding reactions with hydrazines[2–7]. The pioneering effort of Nöth et al. involved the reaction of $P(NMe_2)_3$ with HNMeNHMe · 2 HCl to produce a cage compound $P[N(Me)N(Me)]_3P$ in near quantitative yield[2]. Gilje et al. have reported on the formation of $Cl_2PN(R')N(R')PCl_2$ by the reaction of $PCl_3$ with 1,1-dimethylhydrazine at −196°C[4]. In addition, the formation of $Cl_2PN(R')N(R')PCl_2$ from the reactions of $P[N(Me)N(Me)]_3P$ and $ClP[N(Me)N(Me)]_2PCl$ with $PCl_3$ have also been noted by Gilje et al.[5]. Despite the versatility of hydrazine bases towards nucleophilic substitution reactions, directed synthetic strategies to produce new phosphorus(III) compounds with the $R_2PN(R')N(R')PR_2$ frameworks are still rare. Efforts on the systematic investigations of $P^{III}$ halides with hydrazines are important in the context of enhancing the uitility and scope of main group chemistry of phosphorus hydrazides. In addition, a ready accesibility to the cyclic and acyclic phosphorus hydrazides [i.e. compounds with $R_2PN(R')N(R')PR_2$ linkages] may promote their subsequent use in the coordination chemistry with the transition metals. As part of our ongoing interest in the transition metal chemistry of main group hydrazides[1,8–13], we report herein: (i) a one-step reaction to the first examples of *cyclo*-bis(methylhydrazino)phosphanes $[RPN(Me)N(H)]_2$ (R = Et, **1**; Ph **2**; *t*Bu **3**). (ii) the X-ray structures of all the new compounds (**1**–**3**) and, (iii) the coordination chemistry of this new genre of ligands with Mo(0) precursor.

## Results and Discussion

The alkyl- and arylphosphorus(III) dihalides ($EtPCl_2$, $PhPCl_2$, and *t*$BuPCl_2$) reacted with methylhydrazine smoothly at 0°C in chloroform to give the *cyclo*-phosphorus hydrazides (1,2,4,5,3,6-tetrazadiphosphorinanes) $[RPN(Me)N(H)]_2$ (R = Et, **1**; Ph, **2**; *t*Bu, **3**) in good yields as outlined in Scheme 1. Compounds **1**–**3** are examples of *cyclo*-bis(methylhydrazino)phosphanes. The chemical constitutions of **1**–**3** were established by C, H, and N analytical data. Additional characterization was achieved by $^1H$- and $^{31}P$-NMR spectroscopy.

The formation of **3** is always accompanied by a small amount of the oxidized phosphorus(V) product [*t*BuP(O)N(Me)N(H)$]_2$ (**4**). This may be rationalized in terms of the extreme oxidative instability of **3** and may also be due to an inadvertent entry of oxygen during the reaction.

The $^1H$-NMR data of **1** has given insights into the conformational mobility of this heterocyclic compound (Figure 1). It appears that compound **1** is formed presumably as a mixture of chair and boat conformers as indicated by its proton NMR spectra. The $^1H$-NMR spectrum of the reaction mixture showed two sets of signals due to the P−Et and $NCH_3$ and NH protons (see Experimental). The doublet is deceptively simple due to the $A_3A'_3XX'$ spin system. A typical $^1H$-NMR spectrum which illustrates the presence

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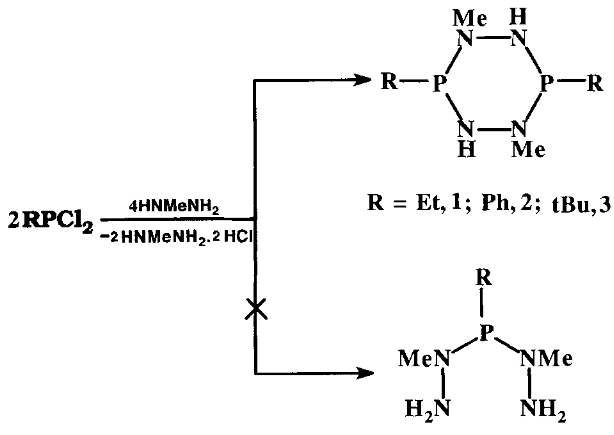
Scheme 1



[$t$BuP(O)N(Me)N(H)]$_2$ **4**

of chair and boat conformers of **1** is shown in Figure 1a. The assignments of the signals for the chair and boat forms are tentative, however, they were confirmed by the following experiments. The $^{31}$P-NMR spectrum consisted of three resonance signals at $\delta$ = 81.6, 89.2, and 94.1. The signal at $\delta$ = 89.2 was tentatively assigned to the chair conformer (which was later confirmed by X-ray crystallographic analysis as discussed below). The presence of two resonances at $\delta$ = 81.6 and 94.1 may indicate two dissimilar phosphorus centers in one conformer. It is important to note that the conformational mobility of **1** was lost upon crystallization of the mixture in dichloromethane/hexane. A nearly quantitative conversion, presumably, of a mixture of chair and boat to the chair form of **1** was achieved upon crystallization. The X-ray structural analysis of single crystals of **1** confirmed its chair configuration. The observation of a single resonance at $\delta$ = 89.2 in the $^{31}$P-NMR spectrum of **1** confirms the tentative assignment described above. The singularity of the chair species of **1** was also evident in its proton NMR spectrum, which consisted of a single set of resonance signal for the PEt, NMe, and NH protons (Figure 1b). Addition of solutions of pure chair compound **1** to the equilibrium mixture of chair and boat resulted in an increase in the intensities of the NH ($\delta$ = 4.40), NMe (2.85), and the Et (1.10 and 2.0–2.2) signals in the $^1$H-NMR spectrum. In addition, the signals that were tentatively assigned to the other conformer (Figure 1a), did not undergo any change in the relative intensities. This observation confirms the tentative assignments made for the chair and boat forms in Figure 1a. The corresponding $^{31}$P-NMR spectrum of the mixture of chair and boat forms to which solution of pure chair form of **1** was added showed an increase in the intensity of the signal at $\delta$ = 89.2, therefore, support the assignments made above.

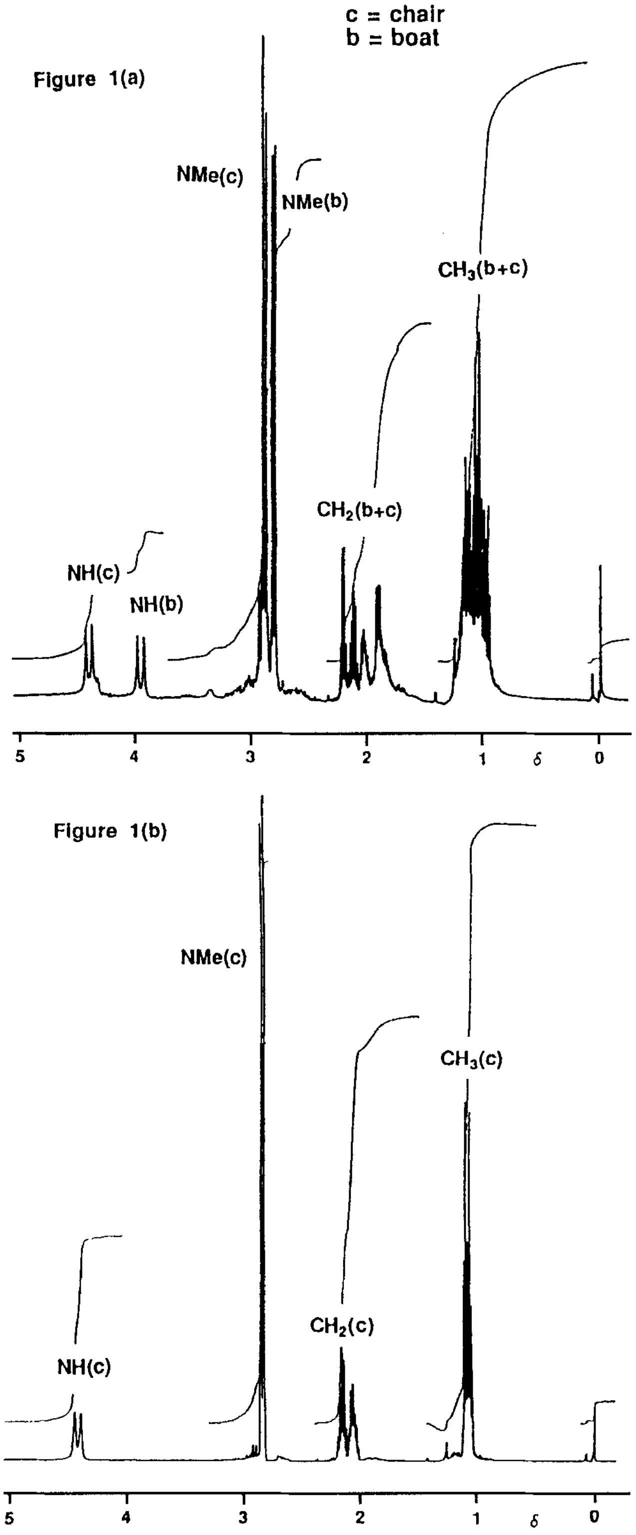


Figure 1 (a) $^1$H-NMR spectrum of a mixture of chair and, presumably, boat forms of **1**. (b) $^1$H-NMR spectrum of pure chair form of **1**. The doublets due to the NMe protons in (a) and (b) are deceptively simple despite the possible second-order effects arising from the possible $A_3A'_3XX'$ spin system

The solutions of pure chair form of **1** appear to undergo slow conversion to the boat form. These conversions were monitored by both $^1$H- and $^{31}$P-NMR spectroscopy. Typically, the $^{31}$P-NMR spectrum of **1** in CDCl$_3$ shows a signal at δ = 89.2, due to the chair conformer, which upon standing (1d) exhibits two additional signals at δ = 81.6 and 94.1, attributed to its boat form. The conversion of chair to the boat form of **1** was limited to 40% (as estimated from $^1$H- and $^{31}$P-NMR spectroscopy) even after 20 days at 25°C in $CDCl_3$. Heating the mixture did not accelerate the conversion from one form to the other.

The observation of additional signals in the $^1$H-NMR spectrum of **1** (Figure 1a) may not be due to the spanning of substituents of $P^{III}$ from the axial to equitorial sites because recent studies on related $P^{III}$ compounds have shown that such transformations generally involve large expense of energy[15]. The identification of preferred molecular shapes by $^{31}$P NMR is difficult[14]. In fact, phosphorus NMR does not provide an unambiguous distinction between the chair and boat forms. Therefore, an X-ray crystallographic investigation of **1**–**3** became necessary.

The exclusive formation of the six-membered $P_2N_4$ cyclic frameworks as observed in the present investigation is remarkable. It appears that the mixed primary and secondary amino bifunctionalities of methylhydrazine are presumably responsible for the formation of six-membered $P_2N_4$ type of cyclic dinitrogen-bridged diphosphanes **1**–**3**. It is important to note that the reactions of the pentavalent phosphorus halides [e.g., $RP(S)Cl_2$, R = Me, Et, Ph] with methylhydrazine gave exlusively the acyclic phosphorus hydrazides of the general formula $PR(S)(NMeNH_2)_2$[8–13]. In sharp contrast, the reactions of the trivalent phosphorus halides with methylhydrazine as outlined in Scheme 1 gave the cyclic phosphorus hydrazides exclusively.

The conformational mobility was not observed for the phenyl- and *tert*-butyl-substituted heterocyclic compounds **2** and **3**. Therefore, in order to understand if substituents on the phosphorus exert any effect on the conformations of **1**–**3**, we have undertaken a detailed X-ray crystallographic investigation of **1**–**3**.

## X-Ray Structures

The crystal structure of **1** consists of two molecules in the unit cell with no unusual intermolecular contacts. An ORTEP drawing of the molecule is shown in Figure 2. Bond distances and angles for selected non-hydrogen atoms are listed in Table 1. The $P_2N_4$ ring is in its chair conformation (Figure 3) and has a center of symmetry. The phosphorus atoms are above and below the plane formed by four nitrogen atoms by 0.583(3) Å (Figure 3). The mean P–N distance is 1.693(3) and the mean N–N distance 1.426(4) Å. The N–P–N angle is 106.0(1) Å. There are two types of geometries around nitrogen atoms N(1) and N(2), the geometry around N(1) is trigonal pyramidal, whereas around N(2) is trigonal planar.

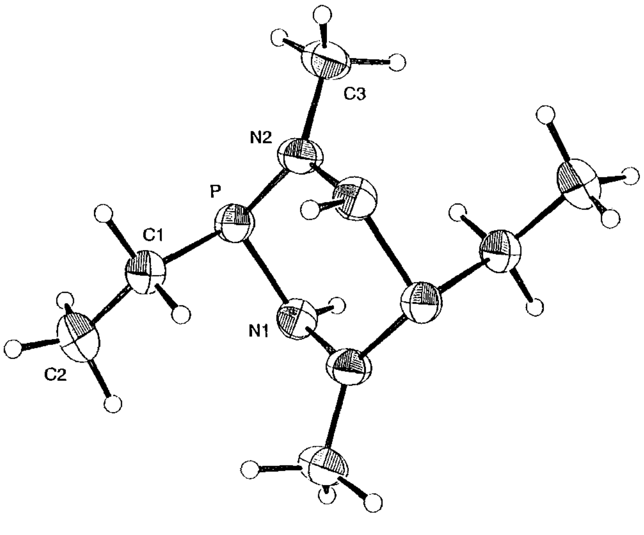


Figure 2. ORTEP representation of the structure **1**. The thermal ellipsoids are drawn at 50% probability level

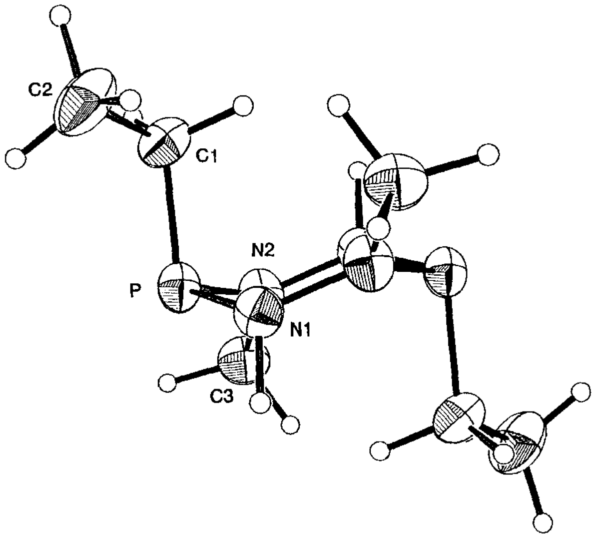


Figure 3. ORTEP representation showing the chair conformation of **1**. The thermal ellipsoids are drawn at 50% probability level

Table 1. Selected bond lengths [Å] and angles [°] for compound **1** ([a] indicates atom related by center of symmetry)

| | | | |
|---|---|---|---|
| P -- N1 | 1.700(3) | N2 -- N1$^a$ | 1.426(4) |
| P -- N2 | 1.687(3) | N2 -- C3 | 1.446(4) |
| P -- C1 | 1.820(4) | C1 -- C2 | 1.532(5) |
| N1 -- N2$^a$ | 1.425(4) | | |

| | | | |
|---|---|---|---|
| N1 -- P -- N2 | 106.0(1) | P -- N2 -- N1$^a$ | 120.2(2) |
| N1 -- P -- C1 | 99.5(2) | P -- N2 -- C3 | 123.0(2) |
| N2 -- P -- C1 | 100.2(2) | N1$^a$ -- N2 -- C3 | 115.3(3) |
| P -- N1 -- N2$^a$ | 118.9(2) | P -- C1 -- C2 | 112.0(3) |

An ORTEP diagram of **2** is shown in Figure 4. Bond distances and angles for selected non-hydrogen atoms are listed in Table 2. The crystal structure consists of eight molecules in the unit cell with no unusual intramolecular contacts. The molecule has a center of symmetry and the six-membered $P_2N_4$ ring is in its chair conformation. The phosphorus atoms are 0.563 Å above and below the plane of four nitrogen atoms (Figure 5). The mean P–N distance is 1.688(2) and the mean N–N distance 1.426(2) Å. The geometry around N(1) is trigonal pyramidal, whereas the geometry around N(2) is trigonal planar. The N–P–N angle is 106.3(7).

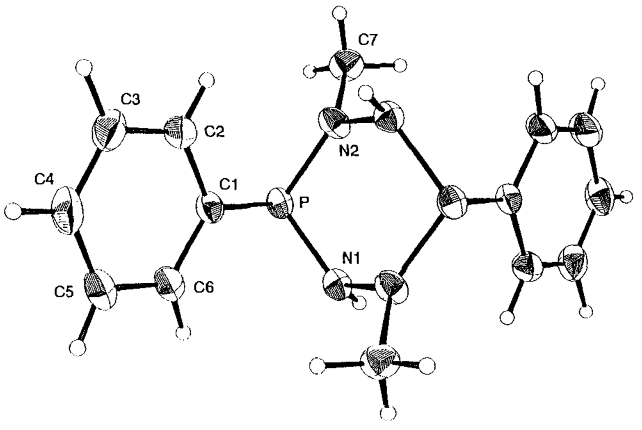


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Figure 4. ORTEP representation of the structure **2**. The thermal ellipsoids are drawn at 50% probability level

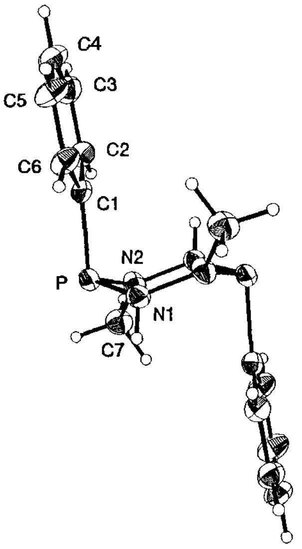

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Figure 5. ORTEP representation showing the chair conformation of **2**. The thermal ellipsoids are drawn at 50% probability level

Table 2. Selected bond lengths [Å] and angles [°] for compound **2** ($^a$ indicates atom related by center of symmetry)

| | | | |
|---|---|---|---|
| P -- N1 | 1.695(2) | N2 -- N1$^a$ | 1.426(2) |
| P -- N2 | 1.680(2) | N2 -- C7 | 1.448(2) |
| P -- C1 | 1.831(2) | N1 -- N2$^a$ | 1.426(2) |
| N1 -- P -- N2 | 106.3(1) | P -- N2 -- N1$^a$ | 120.6(1) |
| N1 -- P -- C1 | 98.8(1) | P -- N2 -- C7 | 123.3(2) |
| N2 -- P -- C1 | 101.6(1) | N1$^a$ -- N2 -- C7 | 114.8(1) |
| P -- N1 -- N2$^a$ | 119.2(1) | | |

The poor X-ray diffraction data for **3** resulted in a high final agreement factor ($R$). However, the X-ray analysis did confirm the existence of this compound in the chair conformation. The ORTEP plot is shown in Figure 6.

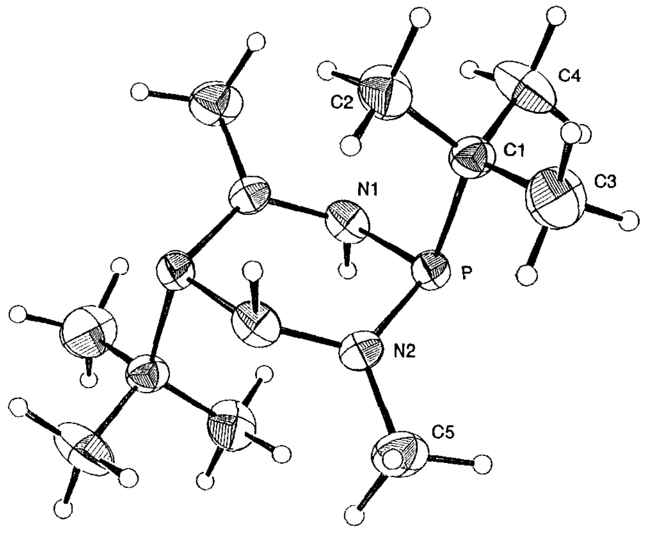
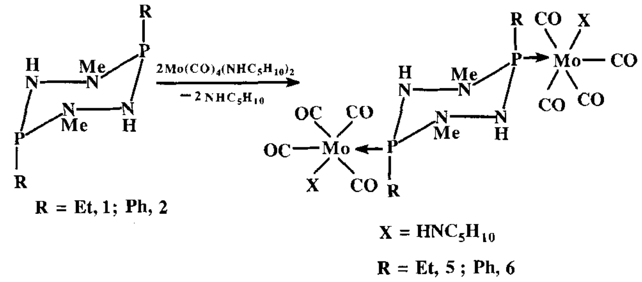


Figure 6. ORTEP representation of the structure **3**. The thermal ellipsoids are drawn at 50% probability level

## Coordination Chemistry of Cyclophosphorus Hydrazides

The presence of two trivalent phosphorus centers in **1**–**3** presents the possibility of using them as bidentate ligands towards transition metals. For example, **1** and **2** reacted smoothly with two molar equivalents of $Mo(CO)_4(NHC_5H_{10})_2$ to give the dinuclear complexes $[\{Mo(CO)_4(NHC_5H_{10})\}_2\{\mu\text{-}[RPN(Me)N(H)]_2\}]$ (R = Et, **5**; Ph, **6**) in good yields (Scheme 2). The chemical constitutions of **5** and **6** were confirmed by analytical and spectroscopic data. The disposition of the carbonyl groups in the octahedral complexes **5** and **6** is *cis* as confirmed by IR spectroscopy [νCO for **5**: 2016 (sh), 1923 (s), 1898 (vs), 1844 (s) $cm^{-1}$; for **6**: 2008 (sh), 1954 (s), 1867 (m), 1819 (vs) $cm^{-1}$]. The $^{31}P$-NMR spectra of the new molybdenum complexes **5** and **6** showed single resonance lines at $\delta = 125.5$ and 126.4 respectively. This clearly indicates the equivalence of both the phosphorus nuclei and also supports the proposed dinuclear formulation (Scheme 2). The spectroscopic data is also consistent with the two metal centers being bridged by the six-membered phosphorus hydrazide ligand. The $^1H$-NMR spectra of **5** and **6** are consistent with the proposed structures. The $^1H$-NMR spectrum of **5** shows two doublets at $\delta = 4.48$ [$^2J(PH) = 20.2$ Hz] and 3.20 [$^3J(PH) = 11.1$ Hz], attributed to the NH and NMe protons, respectively, of the six-membered $P_2N_4$ ring. The $^1H$-NMR spectrum of **6** shows two doublets at $\delta = 5.05$ [$^2J(PH) = 20.2$ Hz] and

Scheme 2



3.30 [$^3J$(PH) = 11.3 Hz], attributed to the NH and NMe protons, respectively. In addition, the $^1$H-NMR spectrum of **6** consisted of multiplets centered at $\delta$ = 0.7 and 1.32, respectively, and were assigned to the methylene protons of the 4- and 3-carbon atoms of the piperidine ring. The $NCH_2$ protons of this ring in **6** resonated as multiplets at $\delta$ = 3.32 and 3.76. A similar $^1$H-NMR spectroscopic pattern for the piperidine protons were observed for **5** (see experimental section).

## Conclusions

We have demonstrated that the nucleophilic substitution reactions of monoalkyl- and arylphosphorus dichlorides with methylhydrazine produce cyclic $RP[N(R')N(R'')]_2PR$ frameworks. This observation is in sharp contrast to acyclic $RP(E)[N(R')NH_2]_2$ (R = Me, Et, Ph; E = O, S) products that were formed in the corresponding reactions of the phosphorus(V) halides with methylhydrazine[8–13]. Why only the ethyl-substituted phosphorus hydrazide $[EtPN(Me)N(H)]_2$ (**1**) shows chair and boat conformational mobility is yet unclear. The utility of the new diphosphanes **1**–**3** to unravel their rich coordination chemistry is underway.

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## Experimental

All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. Reagents such as methylhydrazine, $PRCl_2$ (R = *t*Bu, Et, and Ph), and $[Mo(CO)_4(NHC_5H_{10})_2]$ were purchased from Aldrich Chemical Co. and were used without further purification. Triethylamine was distilled over KOH and stored over molecular sieves under $N_2$.

NMR: Bruker WH-500 spectrometer, $CDCl_3$ as solvent. The $^1$H NMR chemical shifts are given as $\delta$ values downfield from external standard $SiMe_4$. The $^{31}$P-NMR spectra were recorded with 85% $H_3PO_4$ as an external standard and positive chemical shifts lie downfield of the standard. Broad-band proton decoupling was used to run all $^{31}$P-NMR spectra. – IR: Nujol mulls and KBr cells, Mattson Galaxy 3000 spectrophotometer. – Elemental analyses: Oneida Research Services, Inc., New York.

*Synthesis of* $[EtPN(Me)N(H)]_2$ (**1**): A solution of methylhydrazine (10.0 g, 0.22 mol) in chloroform (100 ml) was added dropwise to a solution of $EtPCl_2$ (14.0 g, 0.11 mol) in chloroform (500 ml) at 0°C with constant stirring. The reaction mixture was stirred at 25°C for 12 h under a stream of dry nitrogen. The precipitate of methylhydrazine hydrochloride was filtered off and the filtrate upon evaporation in vacuo gave **1** as a mixture of boat and chair isomers in 80% (18.8 g) yield. Recrystallization of the mixture in dichloromethane/hexane (1:3 v/v) gave pure **1** in chair conformation, m.p. 69–71°C. – $C_6H_{16}N_4P_2$ (206.2): calcd. C 34.6, H 8.6, N 26.9; found C 34.2, H 8.77, N 26.3. – $^1$H NMR: $\delta$ = 1.10 [dt, $^3J$(PH) = 9.0, $^3J$(HH) = 7.5 Hz, 6H, $CH_2CH_3$], 2.0–2.2 (m, 4H, $PCH_2$), 2.85 [d, br, $^3J$(PH) = 12.2 Hz, 6H, $NCH_3$; the doublet is deceptively simple due to the $A_3A'_3XX'$ spin system], 4.40 [d, $^2J$(PH) = 26.2 Hz, 2H, NH). – $^{31}$P NMR: $\delta$ = 89.2 (s).

The synthesis of **2** and **3** were accomplished using a similar procedure as described for **1** above.

$[PhPN(Me)N(H)]_2$ (**2**): Yield 65%, m.p. 172–175°C. – $C_{14}H_{18}N_4P_2$ (304.3): calcd. C 55.2, H 5.9, N 18.4; found C 54.5, H 6.0, N 18.3. – $^1$H NMR: $\delta$ = 2.90 [d, br, $^3J$(PH) = 12.0 Hz, 6H, $NCH_3$; the doublet is deceptively simple due to the $A_3A'_3XX'$ spin system], 4.95 [d, $^2J$(PH) = 18.0 Hz, 2H, NH), 7.35–7.85 (m, 10H, Ph). – $^{31}$P NMR: $\delta$ = 90.0 (s).

$[tBuPN(Me)N(H)]_2$ (**3**): Yield 60%, m.p. 102–104°C. – $C_{10}H_{26}N_4P_2$ (264.3): calcd. C 45.5, H 9.8, N 21.2; found C 45.8, H 9.6, N 22.6. – $^1$H NMR: $\delta$ = 1.22 [d, $^3J$(PH) = 13.7 Hz, 18H, $CH_3$ (*t*Bu)], 2.90 [d, br, $^3J$(PH) = 11.0 Hz, 6H, $NCH_3$; the doublet is deceptively simple due to the $A_3A'_3XX'$ spin system], 4.62 [d, $^2J$(PH) = 26.2 Hz, 2H, NH). – $^{31}$P NMR: $\delta$ = 95.3 (s).

In addition, an oxidized product $[tBuP(O)N(Me)N(H)]_2$ (**4**), is also formed in ≈20% yield. – $C_{10}H_{26}N_4O_2P_2$ (296.3): calcd. C 40.8, H 8.7, N 18.9; found C 40.4, H 8.9, N 19.7. – $^1$H NMR: $\delta$ = 1.11 (br, 18H, *t*Bu), 2.65 (br, 6H, $NCH_3$), 3.10 (br, 2H, NH). – $^{31}$P NMR: $\delta$ = 44.1 (s, br).

**Caution: 3** caught fire while drying in vacuo at 50°C.

*Synthesis of* $[\{Mo(CO)_4(NHC_5H_{10})\}_2\{\mu\text{-}[EtPN(Me)N(H)]_2\}]$ (**5**): A solution of *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ (0.40 g, 1.058 mmol) in dichloromethane (25 ml) was added dropwise at 25°C to a solution of **1** (0.11 g, 0.529 mmol) also in dichloromethane (25 ml). The reaction mixture was heated under reflux for 12 h before the solvent was removed in vacuo to obtain a yellow microcrystalline powder. This residue was extracted with $CH_2Cl_2$/hexane (1:1), and the extracts (2 × 10 ml) were filtered through a column of silica gel (20 g). Evaporation of the solvent in vacuo gave the complex **5** in 62% (0.26 g) yield, m.p. 120°C (dec.). – $C_{46}H_{36}Mo_2N_6O_8P_4$ (1116.6): calcd. C 50.7, H 3.3, N 5.1; found C 49.6, H 3.4, N 5.1. – IR (nujol), (νCO): 2008 (sh), 1954 (s), 1867 (m), 1819 (vs) $cm^{-1}$. – $^1$H NMR: $\delta$ = 0.8–1.2 [m, 10H, $CH_3$ (Et), $CH_2$-4], 1.7 (m, 8H, $CH_2$-3). 2.0 [m, 4H, $CH_2$ (Et)], 2.55 (m, 4H, $CH_2$-2), 3.05 (m, 4H, $NCH_2$), 3.2 [d, br. $^3J$(PH) = 11.1 Hz, 6H, $NCH_3$; the doublet is deceptively simple due to the $A_3A'_3XX'$ spin system], 4.08 [d, $^2J$(PH) = 20.2 Hz, 2H, NH (PN ring)]. – $^{31}$P NMR: $\delta$ = 126.4 (s).

*Synthesis of* $[\{Mo(CO)_4(NHC_5H_{10})\}_2\{\mu\text{-}[PhPN(Me)N(H)]_2\}]$ (**6**): A solution of *cis*-$[Mo(CO)_4(NHC_5H_{10})]_2$ (0.40 g, 1.058 mmol) in dichloromethane (25 ml) was added dropwise at 25°C to a solution of **2** (0.16 g, 0.529 mmol) also in dichloromethane (25 ml). The reaction mixture was heated under reflux for 12 h before the solvent was removed in vacuo to obtain a yellow microcrystalline powder. This residue was extracted with $CH_2Cl_2$/hexane (1:1), and the extracts (2 × 10 ml) were filtered through a column of silica gel (20 g). Evaporation of the solvent in vacuo affords the complex **6** in 55% (0.25 g) yield, m.p. 140°C (dec.). – $C_{32}H_{40}Mo_2N_6O_8P_2$ (952.5): calcd. C 43.1, H 4.5, N 9.4; found C 41.3, H 4.3, N 8.9. – IR (nujol), (νCO): 2016 (sh), 1923 (s), 1898 (vs), 1844 (s) $cm^{-1}$. – $^1$H NMR: $\delta$ = 0.5–0.8 (m, 4H, $CH_2$-4), 1.2 (m, 8H, $CH_2$-3). 3.30 [d, br, $^3J$(PH) = 11.3 Hz, 6H, $NCH_3$; the doublet is deceptively simple due to the $A_3A'_3XX'$ spin system], 3.74 (m, 8H, $NCH_2$), 5.04 [d, $^2J$(PH) = 20.2 Hz, 2H, NH ($P_4N_2$ ring)], 7.4–7.8 (m, 10H, Ph). – $^{31}$P NMR: $\delta$ = 125.5.

*X-Ray Data Collection and Processing:* The crystal data and details of data collection for **1** and **2** are given in Table 3. The colorless crystals of both the compounds suitable for X-ray diffraction were obtained from $CH_2Cl_2$/hexane at 0°C. All X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo-$K_\alpha$ radiation and a graphite monochromator at 22(1)°C. The unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections. Both the crystals **1** and **2** exhibited no significant decay under X-ray irradiation. The structures were solved by direct methods and were subsequently refined by full-matrix least-square method which minimizes $\Sigma w/(|F_o| - |F_c|)^2)$ where $w^{-1} = [\sigma(\text{counting}) + (0.008(F_o)^2)/4F_o]$. Atomic scattering factors which included anomalous scattering contributions were from ref.[16]. All hydrogen atoms in both the structures were located in difference Fourier maps and refined with the fixed isotropic thermal parameters. The final cycle of the least-squares refinement gave an agreement factor *R* of 0.061 for **1** and 0.037 for **2**. The programs used for the crystallographic computations are reported in ref.[17]. Listing of full experimental details, coordinates, temperature factors and anisotropic temperature factors are deposited as supplementary material[18].

Table 3. Crystal data for compounds **1** and **2**

| | 1 | 2 |
|---|---|---|
| formula | $C_6H_{18}N_4P_2$ | $C_{14}H_{18}N_4P_2$ |
| crystal system | monoclinic | orthorhombic |
| space group | $P2_1/c$ | Pbca |
| fw | 208.18 | 152.13 |
| a, Å | 8.479(3) | 10.367(1) |
| b, Å | 6.714(1) | 7.353(1) |
| c, Å | 10.436(3) | 20.271(2) |
| β, deg | 103.35(2) | --- |
| Z | 2 | 8 |
| F(000) | 224 | 640 |
| V, Å$^3$ | 578.0(3) | 1545.2(2) |
| $d_{calc}$, g/cm$_3$ | 1.196 | 1.308 |
| crystal size, mm | 035 x 0.40 x 0.45 | 0.25 x 0.33 x 0.33 |
| μ, mm$^{-1}$ | 3.16 | 3.76 |
| no. of unique rflns | 855 | 1570 |
| no. of rflns with I>2σ | 790 | 1449 |
| no. of variables | 55 | 119 |
| R, $R_w$ | 0.061; 0.082 | 0.035; 0.059 |
| GOF | 2.65 | 2.19 |
| max shift/σ | 0.010 | 0.057 |
| res. electron density | 0.32e/Å$^3$ | 0.23e/Å$^3$ |

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[18] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57993, the names of the authors, and the journal citation.

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