## Methyl Hydrazine as a Building Block for a Bridge Between Phosphinoamine $[R_2P-N(R)-PR_2]$ and Phosphorus Hydrazide $[R_2P-N(R)-N(R)-PR_2]$ . Synthesis and Coordination Chemistry of a Novel Triphosphine $[(Me_2P)_2N-N(Me)(PMe_2)]^{\dagger}$

## V. Sreenivasa Reddy,<sup>a</sup> Kattesh V. Katti\*<sup>a</sup> and Charles L. Barnes<sup>b</sup>

<sup>a</sup> Center for Radiological Research and MU Research Reactor, Allton Building Laboratories, 301 Business Loop 70 West, Columbia, MO 65203, USA

<sup>b</sup> Department of Chemistry, University of Missouri, Columbia, MO 65211, USA

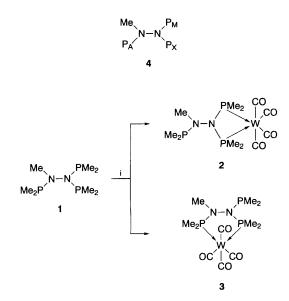
The reaction of methylhydrazine with dimethylchlorophosphine in the presence of triethylamine affords the new triphosphine  $(Me_2P)_2N-N(Me)(PMe_2)$  **1** in near quantitative yields, which represents a bridge between phosphinoamine [>P-N(R)-P<] and phosphanyl hydrazide [>P-N(R)-N(R)-P<] backbones; reaction of **1** with *cis*-[W(CO)<sub>4</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>2</sub>] proceeds *via* two coordination modes to give M-P-N-P and M-P-N-P metallacyclic frameworks; the structure of the phosphinoamine coordinated part of **1** has been demonstrated by X-ray crystallographic investigation of **2**.

The main group chemistry of phosphinoamines [*i.e.* compounds with R<sub>2</sub>P–N(R)–PR<sub>2</sub> framework] has been the subject of extensive research in the last three decades.<sup>1</sup> In sharp contrast, the chemistry of phosphanyl hydrazides consisting of >P–N(R)–N(R)–P< backbones is surprisingly limited to a few reports.<sup>2</sup> We have recently reported a novel synthetic route to Cl<sub>2</sub>P–N(Me)–N(Me)–PCl<sub>2</sub> and also demonstrated that this compound can be used as a versatile precursor to several unexplored series of >P–N(R)–N(R)–P<-based new bisphosphines.<sup>3</sup> The phosphanyl hydrazides with the >P–N(R)–N(R)–P< backbones can be considered as the next homologues to phosphinoamines [*e.g.* R<sub>2</sub>P–N(R)–PR<sub>2</sub>]. Herein, we report the synthesis and characterisation of a novel triphosphine, (Me<sub>2</sub>P)<sub>2</sub>N–N(Me)(PMe<sub>2</sub>) 1 *via* the full phosphinilation of *N*-methylhydrazine [eqn. (1)].

NHMeNH<sub>2</sub> + 3 PMe<sub>2</sub>Cl + 3 Et<sub>3</sub>N  $\rightarrow$  (Me<sub>2</sub>P)<sub>2</sub>N–N(Me)(PMe<sub>2</sub>) (1)

This triphosphine 1 represents an important and unprecedented facet in the main group chemistry of polyphosphines because this compound features the combination of >P-N-P< and >P-N-N-P< frameworks thus establishing a bridge between potentially useful phosphine-containing ligand systems. The skeletal flexibility and the coordination chemistry of this dinitrogen-bridged triphosphine are also addressed.

Treatment of methylhydrazine with a threefold excess of dimethylchlorophosphine in the presence of triethylamine in *n*-hexane at 0 °C afforded the new triphosphine  $[(Me_2P)_2N-N(Me)(PMe_2)]$ , 1, in near quantitative yields (Scheme 1). The <sup>31</sup>P NMR spectrum of 1 consisted of a doublet centred at  $\delta$  34.5



Scheme 1 Reagents: i, W(CO)<sub>4</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>2</sub>

[attributed to  $-N(PMe_2)_2$ ] and a triplet centred at  $\delta$  50.7 [attributed to  $-N(Me)(PMe_2)$ ] with  ${}^{3}J(PP) = 18.0$  Hz [Fig. 1(*a*)]. Further characterisation of 1 was provided by <sup>1</sup>H NMR spectroscopy.

The complete substitution of the > NH and  $-NH_2$  groups of methylhydrazine by  $-PMe_2$  substituents is unique, because, (a) it represents a rare example of full functionalisation of methyl hydrazine by main group centres although its substitution reactions with various aliphatic and aromatic groups are extensively known, and, (b) the  $NH_2$  nitrogen of methyl hydrazine provides a bridge between the two distinct types of >P-N-P< and >P-N-N-P<-based bisphosphines.

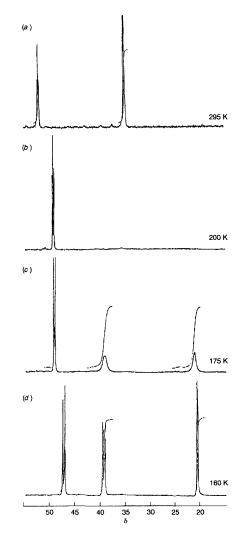


Fig. 1 Variable temperature <sup>31</sup>P NMR (121.5 MHz) spectra of 1

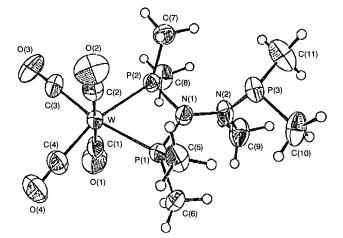


Fig. 2 ORTEP diagram of 2 showing 50% probability ellipsoids. Salient bond distances (Å) and bond angles (°): W-P(1) 2.481(2), W-P(2) 2.484(2), W-C(1) 2.005(8), W-C(2) 2.024(9), W-C(3) 2.016(8), W-C(4) 1.993(8), P(1)-N(1) 1.700(6), P(2)-N(1) 1.699(6), P(3)-N(2) 1.708(7); P(1)-W-P(2) 66.5(1), W-P(1)-N(1) 93.5(2), W-P(2)-N(1) 93.4(2), P(1)-N(1)-P(2) 106.5(3), P(1)-N(1)-N(2) 127.7(5), P(2)-N(1)-N(2) 125.7(5).

The <sup>31</sup>P NMR spectra of 1 recorded at four different temperatures (297, 200, 175 and 160 K) (Fig. 1) demonstrate restricted rotation of the N-N bond at 160 K. For example, at 297 K, because of the free rotation across the N-N bond in 1, the cis  $(P_X)$  and the trans  $(P_M)$  disposed phosphines are seen to be equivalent in the form of a triplet fine structure for  $P_A$  [Fig. 1(*a*)  $\{\delta P_A = 50.7; J[PAP(M + X)] = 18.0 \text{ Hz}\}]$ . However, coalescence is reached at 200 K resulting in the total collapse of the resonances due to  $P_X$  and  $P_M$  and accompanied by a small upfield shift of  $P_A [\delta P_A = 49.2; Fig. 1(b)]$ . Distinct signals for  $P_X$  and  $P_M$  begin to appear at 175 K and the triplet splitting for P<sub>A</sub> which was seen at 297 K appears to slowly transform into a doublet signal, presumably as a result of  $J(P_A P_M)$  splitting [Fig. 1(c)]. The N–N bond rotation in 1 appears to collapse at 160 K as evidenced by the distinct signals and splitting patterns for  $P_A$ ,  $P_M$  and  $P_X$  in the form of a doublet at  $\delta$  47.5, a doublet of doublets at  $\delta$  39.6 and an additional doublet at  $\delta$  20.7, respectively [Fig. 1(d)].

The presence of the phosphinoamine (>P-N-P<) and phosphanyl hydrazide (>P-N-N-P<) backbones within the same molecule 1 is of particular interest in the context of establishing the preferred coordination modes of this tri-phosphine. The <sup>31</sup>P NMR spectrum of the product from the reaction of 1 with  $W(CO)_4(NHC_5H_{10})_2$  (Scheme 1) showed signals featuring AX<sub>2</sub> and AMX spin systems in 90 and 10% relative integrations, respectively. This spectral pattern can be rationalized in terms of two different coordination modes of Wo with 1, as outlined in Scheme 1. The coordination of the phosphinoamine (Me<sub>2</sub>P-N-PMe<sub>2</sub>) part of 1 is expected to generate an  $AX_2$  spin pattern for 2, whereas the phosphanyl hydrazide coordination should result in an AMX spin system for 3. Fractional crystallisation afforded the separation of 2 and 3. Prolonged reaction times (24 h) in dichloromethane and also refluxing the reaction mixture did not result in any changes in the proportions of 2 and 3. Examination of the reaction of 1 with  $W(CO)_4(NHC_5H_{10})_2$  in toluene under refluxing conditions, through <sup>31</sup>P NMR spectroscopy, at 5, 30 and 60 min indicated that 2 and 3 were formed in a ratio of 75 and 25%, respectively, at all these time intervals. Only a slight increase in the proportion of 3 (28%) was noted upon stirring the reaction mixture in toluene for 24 h under refluxing temperatures. The triphosphine 1 was found to be stable in refluxing toluene. It may be conceived that the five-membered chelate 3 is the thermodynamically preferred product. However, the observed strong propensity for the four-membered metallacycle 2 suggests an unusual kinetic control in the reaction of 1 with  $W(CO)_4(NHC_5H_{10})_2$ . The final confirmation of the fourmembered metallacyclic structure proposed for 2 comes from an X-ray crystal structure analysis of its single crystals.<sup>‡</sup> The ORTEP plot and the salient bonding parameters are summarised in Fig. 2. The structure consists of a W<sup>0</sup> centre bonded to two -PMe<sub>2</sub> groups in a *cis* fashion to afford the four-membered W-P-N-P metallacycle (Scheme 1). The structure of 2 is further characterised by a distorted octahedral geometry around W<sup>0</sup> and an acute angle [66.5(1)<sup>o</sup>] around the P(1)-W-P(2) framework.

The predominance of 2 over 3 in the reaction of 1 with  $W(CO)_4(NHC_5H_{10})_2$  is a significant feature in the coordination modes of this novel triphosphine. The interaction of  $W(CO)_4(NHC_5H_{10})_2$  either *via* >P–N(Me)–P< or >P–N(Me)–N(Me)–P< skeletons of 1 will leave one phosphine unit uncoordinated for further reactions with similar or dissimilar metal centres to be carried out. Therefore, the coordination chemistry of this class of novel triphosphines may open up new avenues in the development of homo- or hetero-bimetallic organometallic compounds.

Received, 26th September 1994; Com. 4/05878J

## Footnotes

<sup>†</sup> Part 12 in the series 'Transition Metal Chemistry of Main Group Hydrazides'. For Part 11, see: V. S. Reddy, K. V. Katti and C. L. Barnes, *Inorg. Chem.*, in the press.

‡ Crystal data for 2: yellow crystals,  $0.15 \times 0.20 \times 0.35$  mm obtained from dichloromethane/n-hexane at 0 °C solution and measured at 294 K. Monoclinic, space group P2<sub>1</sub>; Z = 2; a = 9.874(2), b = 12.153(2), c = 8.746(2) Å, β = 112.45(7)°; V = 969.9(3) Å<sup>3</sup>; ρ<sub>calcd</sub> = 1.788 g cm<sup>-3</sup>; μ = 6.34 mm<sup>1</sup>; M = 522.06. Absorption corrections were made, the min. and max. transmission factors are 0.557446 and 0.997254. 1429 Unique reflections were measured and 1386 with  $I > 2\sigma(I)$  were used in the refinement to R = 0.017,  $R_w = 0.023$ . Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.<sup>4</sup> The structure was solved by direct methods using NRCVAX program.<sup>5</sup> Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

## References

- For leading reviews in this area see for example: M. S. Balakrishna, V. S. Reddy, S. S. Krishnamurthy, J. C. T. R. Burckett St. Laurent and J. F. Nixon, *Coord. Chem. Rev.*, 1993, **129**, 1; R. B. King, *Acc. Chem. Res.*, 1980, **13**, 243; A. R. Davis, A. T. Dronsfield, R. N. Haszeldine and D. R. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1973, 379; R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat and L. Stobbs, *J. Chem. Soc., Dalton Trans.*, 1973, 1414; J. F. Nixon, *J. Chem. Soc. A*, 1968, 2689.
- T. T. Bopp, M. D. Havlicek and J. W. Gilje, J. Am. Chem. Soc., 1971, 93, 3051; M. D. Havlicek and J. W. Gilje, Inorg. Chem., 1972, 11, 1624; H. Nöth and R. Ullmann, Chem. Ber., 1974, 107, 1019; H. Nöth and R. Ullmann, Chem. Ber., 1976, 109, 1963; S. F. Spangenberg and H. H. Sisler, Inorg. Chem., 1969, 8, 1004.
- 3 V. S. Reddy and K. V. Katti, *Inorg. Chem.*, 1994, **33**, 2695; V. S. Reddy, K. V. Katti and C. L. Barnes, *Chem. Ber.*, 1994, **127**, 979; 1994, **127**, 1355.
- 4 International Tables For X-ray Crystallography, Kynoch Press, Birmingham, 1974, vol.4.
- 5 The following references are relevant to the NRCVAX system: E. J. Gabe, Y. L. Page, J.-P. Charland, F. L. Lee and P. S. White, J. Appl. Crystallogr., 1989, 22, 384; H. Flack, Acta Crystallogr., Sect. A, 1983, 39, 876; C. K. Johnson, ORTEP-A Fortran Thermal Ellipsoid Plot Program, Technical Report ORNL-5138, Oak Ridge, 1976; A. C. Larson, Crystallographic Computing, Munksgaard, Copenhagen, 1970, 293; Y. L. Page, J. Appl. Crystallogr., 1988, 21, 983; Y. L. Page and E. J. Gabe, J. Appl. Crystallogr., 1979, 12, 464; D. Rogers, Acta Crystallogr, Sect. A, 1981, 37, 734.