





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  $^{31}\text{P}$  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  $P_A$  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 triphosphine. The  $^{31}\text{P}$  NMR spectrum of the product from the reaction of **1** with  $\text{W}(\text{CO})_4(\text{NHC}_5\text{H}_{10})_2$  (Scheme 1) showed signals featuring  $\text{AX}_2$  and  $\text{AMX}$  spin systems in 90 and 10% relative integrations, respectively. This spectral pattern can be rationalized in terms of two different coordination modes of  $\text{W}^0$  with **1**, as outlined in Scheme 1. The coordination of the phosphinoamine ( $\text{Me}_2\text{P}-\text{N}-\text{PMe}_2$ ) part of **1** is expected to generate an  $\text{AX}_2$  spin pattern for **2**, whereas the phosphanyl hydrazide coordination should result in an  $\text{AMX}$  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  $\text{W}(\text{CO})_4(\text{NHC}_5\text{H}_{10})_2$  in toluene under refluxing conditions, through  $^{31}\text{P}$  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

$\text{W}(\text{CO})_4(\text{NHC}_5\text{H}_{10})_2$ . The final confirmation of the four-membered metallacyclic structure proposed for **2** comes from an X-ray crystal structure analysis of its single crystals.† The ORTEP plot and the salient bonding parameters are summarised in Fig. 2. The structure consists of a  $\text{W}^0$  centre bonded to two  $-\text{PMe}_2$  groups in a *cis* fashion to afford the four-membered  $\text{W}-\text{P}-\text{N}-\text{P}$  metallacycle (Scheme 1). The structure of **2** is further characterised by a distorted octahedral geometry around  $\text{W}^0$  and an acute angle [ $66.5(1)^\circ$ ] around the  $\text{P}(1)-\text{W}-\text{P}(2)$  framework.

The predominance of **2** over **3** in the reaction of **1** with  $\text{W}(\text{CO})_4(\text{NHC}_5\text{H}_{10})_2$  is a significant feature in the coordination modes of this novel triphosphine. The interaction of  $\text{W}(\text{CO})_4(\text{NHC}_5\text{H}_{10})_2$  either *via*  $>P-N(\text{Me})-P<$  or  $>P-N(\text{Me})-N(\text{Me})-P<$  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

† 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,  $0.15 \times 0.20 \times 0.35 \text{ mm}$  obtained from dichloromethane/*n*-hexane at  $0^\circ \text{C}$  solution and measured at  $294 \text{ K}$ . Monoclinic, space group  $P2_1$ ;  $Z = 2$ ;  $a = 9.874(2)$ ,  $b = 12.153(2)$ ,  $c = 8.746(2) \text{ \AA}$ ,  $\beta = 112.45(7)^\circ$ ;  $V = 969.9(3) \text{ \AA}^3$ ;  $\rho_{\text{calcd}} = 1.788 \text{ g cm}^{-3}$ ;  $\mu = 6.34 \text{ mm}^2$ ;  $M = 522.06$ . 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.

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