

A 4- to 7-Membered Chelate Ring Expansion in a $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) Derivative: X-Ray Crystal Structure of $[(\text{OC})_4\text{W}\{\text{Ph}_2\text{PNHN}=\text{C}(\text{Ph})\text{CH}_2\text{PPh}_2\}]$

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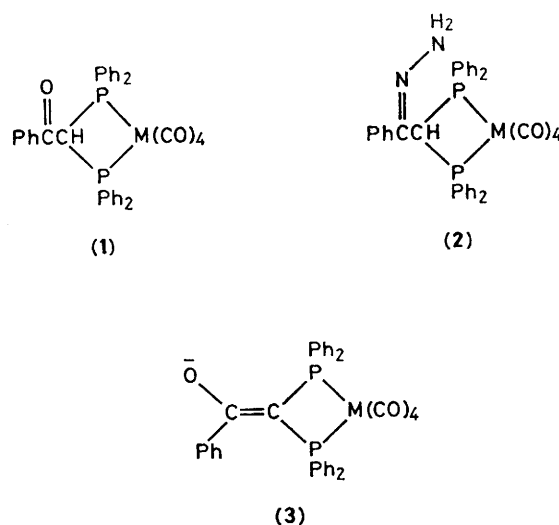
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Treatment of $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PCH}(\text{COPh})\text{PPh}_2\}]$ with hydrazine hydrate promotes a 4- to 7-membered ring expansion to give the title compound, the X-ray crystal structure of which has been determined.

There is a great deal of interest in the ligand $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm)¹ and its corresponding anion $[\text{Ph}_2\text{PCHPPh}_2]^-$ (ref. 2), but there have been few reports of the study of the corresponding compounds where $\text{CH}_2(\text{CH}^-)$ hydrogen atoms are replaced by other substituents.³ One might anticipate interesting steric, conformational, and electronic effects for such compounds as well as unusual reactions. Here we report a chelate ring expansion reaction, 4- to 7-membered, of a dppm derivative.

We have shown that dppm-substituted Group 6 metal carbonyls react with strong bases to give the anions $[\text{M}(\text{CO})_4(\text{Ph}_2\text{PCHPPh}_2)]^-$, which are attacked by nucleophiles (RX , $\text{X} = \text{halogen}$) at the central CH group.⁴ In this way we have made the benzoyl derivatives (1) ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$). We reasoned that the hydrazone derivatives (2) would have one nitrogen (NH_2) atom in a favourable position for an intramolecular nucleophilic attack and thought it most likely to occur at a co-ordinated carbonyl ($\text{C}=\text{O}$), or at the metal atom itself.

Complexes of type (1) when treated with base (*e.g.* OEt^-)



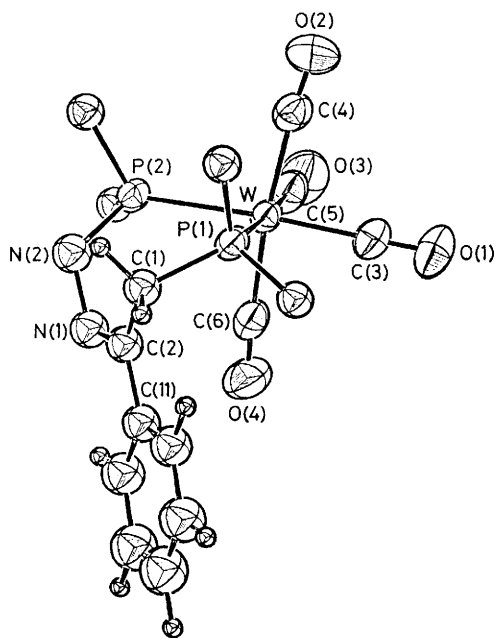
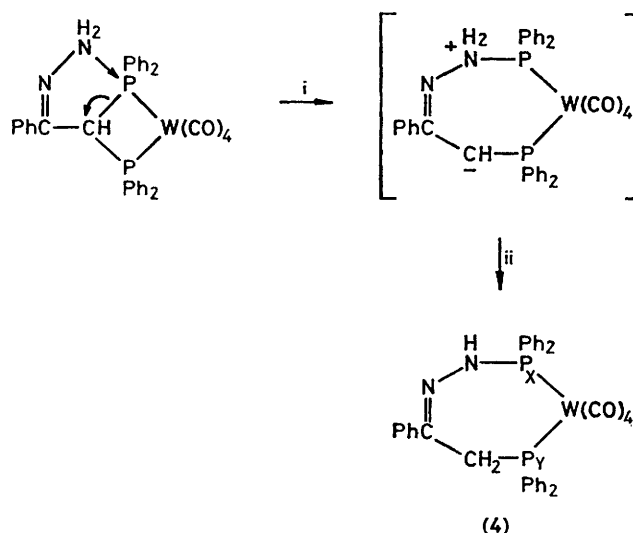


Figure 1. Molecular structure of $[\text{W}(\text{CO})_4(\text{Ph}_2\text{PNHN}=\text{C}(\text{Ph})\text{CH}_2\text{PPh}_2)]$. For clarity four phenyl groups (Ph_2) have been omitted. Bond lengths are $\text{W}-\text{P}(1)$, 251.3(2); $\text{W}-\text{P}(2)$, 249.7(1); $\text{P}(1)-\text{C}(1)$, 184.9(6); $\text{C}(1)-\text{C}(2)$, 149.7(8); $\text{C}(2)-\text{N}(1)$, 129.1(7); $\text{N}(1)-\text{N}(2)$, 143.8(7); $\text{N}(2)-\text{P}(2)$, 172.1(6) pm. Bond angles are $\text{W}-\text{P}(1)-\text{C}(1)$, 114.4(2); $\text{P}(1)-\text{C}(1)-\text{C}(2)$, 115.1(4); $\text{C}(1)-\text{C}(2)-\text{N}(1)$, 122.3(6); $\text{C}(2)-\text{N}(1)-\text{N}(2)$, 114.4(5); $\text{N}(1)-\text{N}(2)-\text{P}(2)$, 120.7(4); $\text{N}(2)-\text{P}(2)-\text{W}$, 116.9(2); $\text{P}(2)-\text{W}-\text{P}(1)$, 87.8(1)°.

are immediately converted into the enolate ion (3) and we found that the tungsten complex (1; $\text{M} = \text{W}$), when treated with hydrazine hydrate in ethanol, was immediately, and reversibly, converted into the ion (3), characterized by $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectroscopy, $\delta(\text{P}_\text{A}) = -10.3$, $\delta(\text{P}_\text{B}) = -12.7$ p.p.m.; $^2J(\text{P}_\text{A}-\text{P}_\text{B}) = 114$, $^1J(\text{P}_\text{A}-\text{W}) = 186$, and $^1J(\text{P}_\text{B}-\text{W}) = 187$ Hz. However, on heating the solution for a period of a few hours this enolate ion was completely replaced by a new species with $\delta(\text{P}_\text{X}) = 66.0$, $\delta(\text{P}_\text{Y}) = 4.5$ p.p.m.; $J(\text{P}_\text{X}-\text{P}_\text{Y}) = 29$, $J(\text{P}_\text{X}-\text{W}) = 255$, and $J(\text{P}_\text{Y}-\text{W}) = 236$ Hz. The new species was isolated as well-formed, pale yellow prisms in 77% yield. On the basis of microanalytical, molecular weight, and mass spectral data the new complex was found to have the molecular formula $\text{C}_{36}\text{H}_{28}\text{N}_2\text{O}_4\text{P}_2\text{W}$, i.e. isomeric with (2), ($\text{R} = \text{Ph}$, $\text{M} = \text{W}$) but various n.m.r. studies (see below) suggested that something very unusual had occurred and the structure was therefore determined by single crystal X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, with cell dimensions $a = 1.0592(2)$, $b = 1.6105(5)$, $c = 1.0343(2)$ nm, $\alpha = 95.12(3)$, $\beta = 107.14(2)$, $\gamma = 103.70(2)^\circ$, and $Z = 2$.†

The structure is shown in Figure 1, and bond lengths are given in the caption. The most interesting feature is the presence of a 7-membered ring. The 25 phenyl hydrogen atoms were included in calculated positions and the phenyl substituents refined as rigid groups. A difference map then revealed the two methylene hydrogen atoms but the remaining hydrogen



Scheme 1. A possible route for the conversion of the hydrazone (2) into the 7-membered ring chelate (4); i, nucleophilic attack by NH_2 on a co-ordinated phosphorus atom with C-P fission, ii, protonation and deprotonation steps.

atom could not be located. The final R is 0.032 for the 4045 F_o having $I > 2\sigma(I)$. There is strong crystallographic, i.e., and n.m.r. evidence that the remaining hydrogen atom is attached to $\text{N}(2)$, viz. the bond length $\text{C}(2)-\text{N}(1)$ of 129.1(7) pm indicates a C=N bond whereas the distances $\text{N}(1)-\text{N}(2)$ and $\text{N}(1)-\text{P}(2)$ suggest single bonds, i.e. $\text{N}(2)$ is sp^3 -hybridised and carries a hydrogen atom. In the i.r. spectrum (Nujol), $\nu(\text{N}-\text{H}) = 3294\text{ cm}^{-1}$. In the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum, the phosphorus resonance at 66.0 p.p.m. [P_X in (4)] is clearly due to $\text{NH}-\text{P}$. In the ^1H n.m.r. spectrum the doublet resonance at δ 5.87, $^2J(\text{P}_\text{X}-\text{H}) = 5.4$ Hz, due to NH , collapses to a singlet on doubly irradiating the frequency due to P_X and disappears on addition of D_2O . The CH_2 hydrogens occur as a doublet of doublets at δ 4.36; $^2J(\text{P}_\text{Y}-\text{H}) = 9$, $^4J(\text{P}_\text{X}-\text{H}) = 1.8$ Hz; confirmed by selective $^1\text{H}\{^{31}\text{P}\}$ experiments. In the $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum CH_2 gives a doublet at δ 35.6, $^1J(\text{P}_\text{Y}-\text{CH}_2) = 17$ Hz and a 1:2:1 triplet of doublets in an off-resonance $^{13}\text{C}\{^1\text{H}\}$ experiment. These data (all determined in CDCl_3) together with the structure determined by X-ray crystallography confirm the positions of the hydrogens to be as shown in (4).

We suggest that this remarkable ring expansion reaction is initiated by nucleophilic attack of NH_2 on co-ordinated PPh_2 , with $\text{P}-\text{CH}_2$ bond fission, as shown in Scheme 1. Protonation-deprotonation then gives the observed product (4). No intermediates could be detected by $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectroscopy and no other products seemed to be formed.

We thank the Government of Iraq for a studentship and the S.E.R.C. for financial support.

Received, 16th November 1981; Com. 1333

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23252 (24 pp.) from the British Library Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton or Perkin Trans.*, Index Issues.