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P–H bond activation at a tungsten(0) centre: synthesis and characterisation of $WH(PPh_2)(dppe)_2$

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Abstract

Irradiation of the dinitrogen complex $W(N_2)_2(dppe)_2$ **1** [dppe = bis-1,2-(diphenylphosphino)ethane] in the presence of diphenylphosphine results in P–H bond activation to give the phosphido complex $WH(PPh_2)(dppe)_2$ **2**. The X-ray crystal structure of the phosphido complex **2** indicates a W–P bond length of 2.28 Å that is consistent with a W–P double bond. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten; Phosphide; Crystal structure; Hydride

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1. Introduction

Complexes containing terminal phosphido groups as ligands are well known and some of the chemistry of the formal metal–phosphorus double bond has been investigated [1]. Phosphido complexes of tungsten have previously been prepared via several approaches including: (i) halide metathesis reactions between lithium phosphides ($LiPR_2$) and metal halides [2], (ii) 1,2-elimination of HX from a $MX–PHR_2$ complex [1], and (iii) oxidative addition of a P–H bond to a tungsten (IV) complex accompanied by ligand dissociation [3].

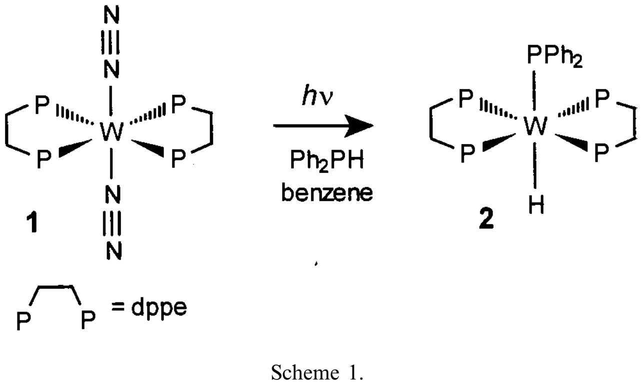
In 1973, Schunn reported the reversible oxidative addition of a P–H bond in PH_3 at iridium diphosphine centres to form $[Ir(dppe)_2(PH_2)H]^+$ and $[Ir(dmpe)_2(PH_2)H]^+$ [dppe = bis-1,2-(diphenylphosphino)ethane, dmpe = bis-1,2-(dimethylphosphino)ethane] [4], while in 1988 Baker et al. [5] observed reversible P–H bond activation at a rhenium–palladium bimetallic system.

In this paper we report the preparation and structural characterisation of $WH(PPh_2)(dppe)_2$ **2** from the dinitrogen complex $W(N_2)_2(dppe)_2$ [6], **1** (Scheme 1). To our knowledge this is the first reported example of P–H bond activation at a tungsten(0) centre.

2. Experimental

2.1. General procedures

All manipulations were carried out under an inert atmosphere of nitrogen, either by use of standard Schlenk and vacuum line techniques or by carrying out



Scheme 1.

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reactions in a nitrogen-filled dry box. All solvents were degassed and distilled under a nitrogen atmosphere from a suitable drying agent. $W(N_2)_2(dppe)_2$ **1** was synthesised following the method of Hussain et al. [6]. NMR spectra were recorded using a Bruker AMX400 spectrometer at 300 K. ^1H-NMR (400.13 MHz) chemical shifts were referenced to internal solvent residuals. ^{31}P-NMR (161.98 MHz) chemical shifts were referenced to external, neat trimethyl phosphite taken as δ 140.85 ppm. Elemental analyses were carried out at Campbell Microanalytical Laboratories, University of Otago (Dunedin, New Zealand).

2.2. Synthesis of WH(PPh$_2$)(dppe)$_2$ **2**

$W(N_2)_2(dppe)_2$ **1** (64 mg, 0.062 mmol) was dissolved in benzene (10 ml) and Ph_2PH (12 mg, 0.065 mmol) was added. The reaction mixture was irradiated for 2 h at room temperature using an Oriel 66033 high pressure mercury lamp, to give a bright green solution. The solution was filtered through celite, and hexane (5 ml) was added. The product crystallised from the solution on standing at room temperature for 2 days. $WH(PPh_2)(dppe)_2$ **2** (46 mg, 67%) was isolated as a green crystalline solid. (mp > 220°C (dec), Found C, 65.8; H, 5.25; $C_{64}H_{59}P_5W$ requires C, 65.9; H, 5.10%). ^1H-NMR (C_6D_6): δ -3.62 (quin, 1H, $^2J_{HP} = 42.1$ Hz, W**H**), δ 2.66 (m, 4H, PC**H**$_2$), δ 2.99 (m, 4H, PC**H**$_2$), δ 6.97–7.74 (m, 50H, P**Ph**) ppm. $^{31}P\{^1H\}$-NMR (C_6D_6): δ 62.3 (d, $^2J_{PP} = 25.4$ Hz, 4P, $^1J_{WP} = 136.5$ Hz, W(**dppe**)$_2$), δ 136.4 (quin, $^2J_{PP} = 25.4$ Hz, 1P, W**P**Ph$_2$) ppm.

2.3. X-ray crystal structure of WH(PPh$_2$)(dppe)$_2$ **2**

Crystals of $WH(PPh)_2(dppe)_2$ **2**, suitable for X-ray crystallography were grown by slow evaporation of a benzene solution of the complex. The crystals decomposed rapidly on removal from the mother liquor and data was collected at low temperature. A small green prismatic crystal of the complex was attached to a glass fibre with Exxon Paratone N. The crystal was quenched in a nitrogen cold stream at − 120°C after mounting on a Rigaku AFC7R diffractometer equipped with a Molecular Structure Corporation flexible tube low temperature system (Table 1).

Table 1
Crystallographic data for $WH(PPh)_2(dppe)_2$ **2**

Empirical formula	$C_{76}H_{71}P_5W$
Formula weight	1323.12
Crystal colour, habit	Green, prism
Crystal dimensions	0.10 × 0.08 × 0.04 mm
Lattice parameters	
a (Å)	14.045(4)
b (Å)	19.020(4)
c (Å)	13.076(5)
α (°)	106.31(3)
β (°)	110.84(3)
γ (°)	76.98(2)
V (Å^3)	3102(1)
Space group	$P\bar{1}$ (#2)
Z-value	2
$D_{calc.}$ (g cm^{-3})	1.416
F(000)	1352.00
μ(Cu–K$_\alpha$) (cm^{-1})	50.01
Radiation	Cu–K$_\alpha$ ($\lambda = 1.54178$ Å) graphite monochromated
Temperature	−120.0°C
$2\theta_{max}$	119.5°
HKL range	$0 \rightarrow 8$, $-11 \rightarrow 11$, $-8 \rightarrow 8$
Number of reflections measured	3447
Unique reflections	3254 ($R_{int} = 0.184$)
Number of observations ($I > 2.0\sigma(I)$)	2495
Number of variables	359
Residuals: R; Rw[a]	0.075; 0.072
Goodness of fit indicator	3.59
Maximum peak in final difference map	2.09 (e$^-$ Å^{-3})
Minimum peak in final difference map	−2.45 (e$^-$ Å^{-3})

[a] $R = \Sigma(|Fo| - |Fc|)^2/\Sigma|Fo|$; $Rw = (\Sigma w(|Fo| - |Fc|^2/\Sigma w|Fo|^2)^{1/2}$; $w = 1/\sigma^2(Fo)$.

Graphite monochromated Cu–K$_\alpha$ radiation was generated with a 12 kW direct drive rotating anode. Triclinic cell constants were obtained from a least-squares refinement against the setting angles of 24 reflections in the range $45.48 < 2\theta < 74.28°$. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.40°. Data were collected with ω-2θ scans of $(1.78 + 0.35 \tan\theta)°$ width at a speed of 16.0° min^{-1} (in ω). Reflections with $I < 15.0\sigma(I)$ were rescanned up to ten times. Stationary background counts were recorded on each side of the reflections, with a peak to background counting time ratio of 2:1. The intensities of three representative reflections measured every 150 reflections did not change significantly during the data collection. An empirical absorption correction based on azimuthal scans of three reflections was applied to the data, and the data were also corrected for Lorentz and polarisation effects.

All calculations were carried out using the teXsan [7] crystallographic software package. The structure was solved by direct methods [8] in the space group $P\bar{1}$ and expanded using Fourier techniques [9]. Neutral atom scattering factors were taken from Cromer and Waber [10]. Anomalous dispersion effects were included in the structure factor calculation [11] and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [12]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [13].

The number of data collected beyond 70° 2θ was approximately 15% of the maximum number of reflections theoretically available between 70 and 120° 2θ. Consequently only the atoms heavier than carbon were refined anisotropically. The hydrogen atoms were included in the full matrix least squares refinement at calculated positions with group temperature factors. The hydride site could not be located and the hydride was included in the model at an idealised position *trans* to the axial phosphido ligand.

The lattice has channels approximately parallel to the *a* axis that contain benzene, and the benzene rapidly escapes on removing the crystals from the mother liquor.

3. Results and discussion

The dinitrogen complex $W(N_2)_2(dppe)_2$ **1** has been examined closely as an important model for understanding nitrogen fixation [14]. The photochemistry of **1** has been studied in some detail [15] and it is known that dinitrogen dissociation is the initial step that occurs when **1** is irradiated [16,17]. $W(N_2)_2(dppe)_2$ is a potentially useful precursor to the coordinatively unsaturated W(0) moiety $[W(dppe)_2]$.

Irradiation of a benzene solution of the dinitrogen complex **1** in the presence of diphenylphosphine resulted in the formation of the complex $WH(PPh_2)(dppe)_2$ **2**. The reaction was quantitative by ^{31}P-NMR spectroscopy and the product was also isolated as an analytically pure green crystalline solid in reasonable yield (67%). The phosphido complex **2** was unambiguously characterised by multinuclear NMR and X-ray crystallographic studies.

The ^{31}P-NMR spectrum exhibited two resonances in the ratio 4:1 at δ 62.3 and δ 136.4 ppm, respectively. The high field resonance appeared as a doublet ($^2J_{PP} =$ 25.4 Hz) and tungsten satellites ($^1J_{WP} = 136.5$ Hz) and was assigned to the four equivalent phosphorus atoms of the dppe ligands, occupying the four equatorial coordination sites around the octahedral tungsten centre. The low field signal appeared as a quintet ($^2J_{PP} =$ 25.4 Hz). The resonance was assigned to the diphenylphosphido moiety and the observed multiplicity is due to coupling through the metal centre to the four equivalent phosphorus atoms of the dppe ligands.

In addition to the resonances of the dppe and diphenylphosphido ligands, the ^1H-NMR spectrum of complex **2** exhibited a quintet at δ -3.62 ppm ($^2J_{HP} =$ 42.1 Hz) for the tungsten-bound hydride. The multiplicity of the signal is due to coupling through the metal centre to the four equivalent *cis* phosphorus atoms of the dppe ligands. The coupling to the *trans* phosphido ligand and the tungsten satellites were not observed.

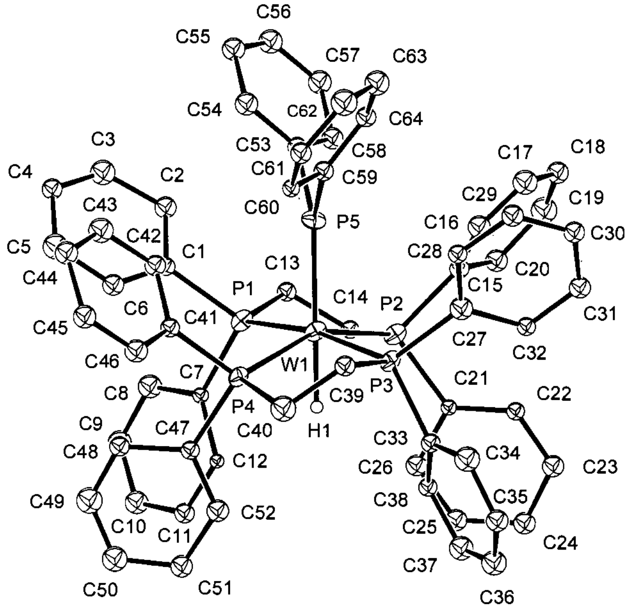


Fig. 1. ORTEP diagram of $WH(PPh_2)(dppe)_2$ **2**, showing atom labeling (25% ellipsoids). The metal-bound hydride was not located in the analysis and has been included at an idealised position.

From X-ray crystallography, the complex adopts a slightly distorted octahedral geometry about the tungsten centre with the tungsten displaced from the least squares equatorial plane by 0.36 Å towards the phosphido axial ligand (Fig. 1).

Selected bond distances and angles are shown in Table 2. The four phosphorus atoms of the dppe ligands occupy the equatorial coordination sites of the tungsten centre and have similar bond lengths. The diphenylphosphido ligand occupies an axial coordination site. The hydride was not located in the analysis and was assumed to be axially coordinated *trans* to the diphenylphosphide ligand. The hydride is included at an idealised position in Fig. 1.

The W(1)–P(5) distance of 2.28 Å is typical of known tungsten–phosphorus double bonds [1] (Table 3). The P(5)–W(1)–P bond angles are all greater than 90°. This distortion from octahedral geometry is probably the result of steric interactions between the phenyl residues of the phosphido and dppe ligands—the C(2) to C(53) distance is 3.47(4) Å, the C(28)–C(59) distance is 3.36(3) Å, and the C(42)–(C60) distance is 3.37 Å.

Table 2
Selected bond distances (Å) and angles (°) for $WH(PPh_2)(dppe)_2$ **2**

W(1)–P(1)	2.414(7)	W(1)–P(2)	2.457(7)
W(1)–P(3)	2.439(7)	W(1)–P(4)	2.433(8)
W(1)–P(5)	2.283(7)		
P(1)–W(1)–P(2)	79.2(2)	P(1)–W(1)–P(3)	107.5(2)
P(1)–W(1)–P(4)	99.2(2)	P(1)–W(1)–P(5)	92.5(2)
P(2)–W(1)–P(3)	98.8(2)	P(2)–W(1)–P(4)	155.9(2)
P(2)–W(1)–P(5)	100.0(3)	P(3)–W(1)–P(4)	78.8(2)
P(3)–W(1)–P(5)	96.9(2)	P(4)–W(1)–P(5)	104.1(2)
W(1)–P(1)–C(1)	122.7(7)	W(1)–P(1)–C(7)	120.6(8)
W(1)–P(5)–C(53)	131.0(7)	W(1)–P(5)–C(59)	131.9(8)

Table 3
W–P bond lengths (Å) of selected tungsten complexes [18]

Complex	W–P (Å)
$W(P)[N(CH_2CH_2NSiMe_3)_3]$[16]	2.162(4)
$Cp^*WH(PPh_2)_2(PMe_3)$[3]	2.325(2) and 2.322(2)
1,2-$W_2(PCy_2)_2(NMe_2)_4$[2a]	2.401(6)
$W_2(NMe_2)_5(PPh_2)$[2b]	2.432(4)
$CpW(CO)_2(P^tBu_2)$[1]	2.284(4)
$WH(PPh_2)(dppe)_2$**2**	2.283(7)

The W(1)–P(5)–C(53) and W(1)–P(5)–C(59) bond angles are approximately 10° larger than for the dppe ligands. The phenyl residues of the phosphido ligand may be bent back to minimise steric interaction with the dppe ligands or the larger bond angle may be indicative of the different hybridisation at the P(5) centre.

The unit cell for complex **2** indicated that the crystal lattice contained channels of benzene (Fig. 2). The benzene rapidly escaped from the crystals once they were removed from the mother liquor resulting in collapse of the lattice.

There are very few reports of thermal loss of dinitrogen from **1**. The dinitrogen complex **1** thermally activates the aldehydic C–H bond in *N*,*N*-dimethylformamide to form a tungsten hydride which is an intermediate in the decarbonylation of DMF [19]. Thermal activation of the S–H bond in bulky thiols has also been observed in the analogous molybdenum complex $[Mo(N_2)_2(dppe)_2]$. The isolated thiolate hydride complexes exhibited a *cis* geometry and readily eliminated thiols in the presence of less bulky substrates [20].

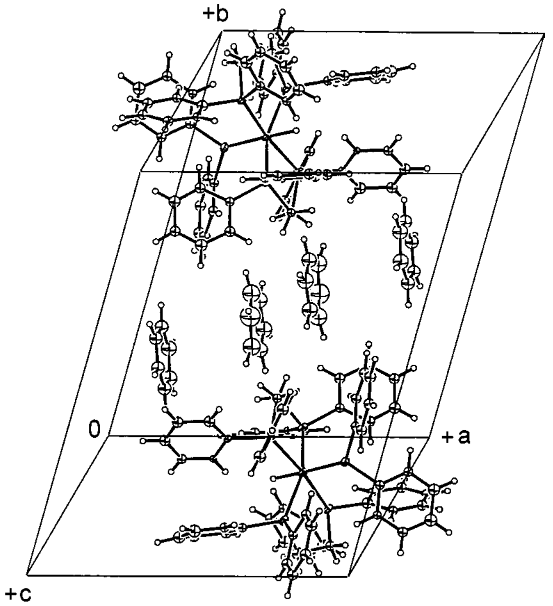
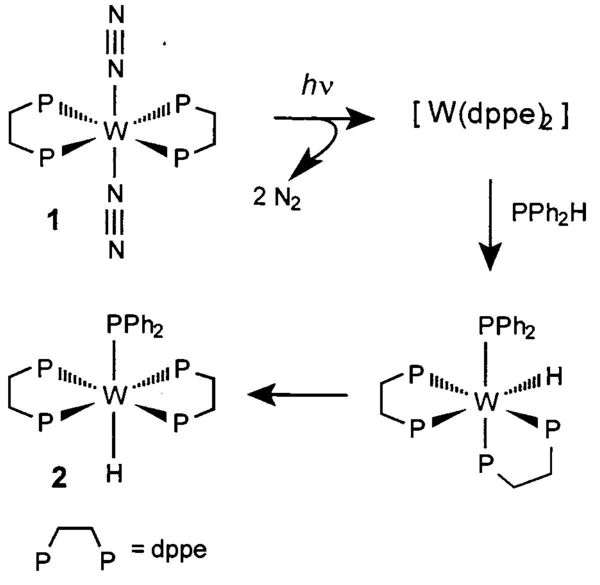


Fig. 2. Unit cell for $WH(PPh_2)(dppe)_2$ **2** showing benzene channels.



Scheme 2.

Flash photolysis studies [17] of complex **1** have indicated that, on irradiation, initial loss of one dinitrogen ligand is followed rapidly by the rapid dissociation of a second N_2 to give the doubly coordinatively unsaturated species $[W(dppe)_2]$. In the absence of other substrates, the unsaturated species re-coordinates N_2 to re-form the starting complex. Photochemical P–H bond activation observed with **1**, probably proceeds via the doubly unsaturated W(0) species which oxidatively adds the P–H bond of the substrate to give initially a *cis* complex which isomerises rapidly to the observed *trans* complex **2** (Scheme 2).

4. Summary

The phosphido complex $WH(PPh_2)(dppe)_2$ **2** was synthesised via the irradiation of a benzene solution of the dinitrogen complex $W(N_2)_2(dppe)_2$ **1** in the presence of diphenylphosphine. Under photochemical conditions, the dinitrogen complex **1** acts as a synthetic equivalent to the electron rich and coordinatively unsaturated $W(dppe)_2$ moiety. The product results from the oxidative addition of the P–H bond to the tungsten centre and represents one of the first examples of P–H bond activation at a tungsten(0) centre.

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References

[1] K. Jörg, W. Malisch, W. Reich, A. Meyer, U. Schubert, Angew. Chem. Int. Ed. Engl. 25 (1986) 92.

[2] (a) W.E. Buhro, M.H. Chisholm, K. Folting, J.C. Huffman, J.D. Martin, W.E. Streib, J. Am. Chem. Soc. 1988, 110, 6563. (b) H. Schultz, K. Folting, J.C. Huffman, W.E. Streib, M.H. Chisholm, Inorg. Chem. 1993, 32, 6056.

[3] R.T. Baker, J.C. Calabrese, R.L. Harlow, I.D. Williams, Organometallics 12 (1993) 830.

[4] R.A. Schunn, Inorg. Chem. 12 (1973) 1573.

[5] R.T. Baker, J.C. Calabrese, T.E. Glassman, Organometallics 7 (1988) 1889.

[6] W. Hussain, G.J. Leigh, H.M. Ali, C.J. Pickett, D.A. Rankin, J. Chem. Soc., Dalton Trans. 1984, 1703.

[7] teXsan, Crystal Structure Analysis Package, Molecular Structure Corporation 1985, The Woodlands, TX, 1992.

[8] A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Cryst. 26 (1993) 343.

[9] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-94 Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.

[10] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A.

[11] J.A. Ibers, W.C. Hamilton, Acta Crystallogr. 17 (1964) 781.

[12] D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer, Boston, 1992, pp. 219–222.

[13] D.C. Creagh, J.H. Hubbell, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer, Boston, 1992, pp. 200–206.

[14] M.H. Hidai, Y. Mizobe, Chem. Rev. 95 (1995) 1115.

[15] J.G. Brummer, G.A. Crosby, Inorg. Chem. 24 (1985) 552.

[16] (a) G.J. Leigh, C.J.J. Pickett, J. Chem. Soc. Dalton Trans. 1977, 1797. (b) J. Chatt, G.J. Leigh, C.J.J. Pickett, J. Chem. Soc. Dalton Trans. 1978, 1638.

[17] A. Caruana, H. Hermann, H.J. Kisch, J. Organomet. Chem. 187 (1980) 349.

[18] N.C. Zanetti, R.R. Schrock, W.M. Davis, Angew. Chem. Int. Ed. Engl. 34 (1995) 2044.

[19] T. Ishida, Y. Mizobe, T. Tanase, M. Hidai, Chem. Lett. 1988, 441.

[20] R.A. Henderson, D.L. Hughes, R.L. Richards, C.J. Shortman, J. Chem. Soc. Dalton Trans. 1978, 1638.