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# Preparation and properties of molybdenum and tungsten dinitrogen complexes

## XXXII *. A series of novel carbonyl complexes of tungsten derived from the dinitrogen complex *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$

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**Abstract**

Treatment of *trans*-$[W(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with *N,N*-dimethylformamide (DMF) in benzene under reflux afforded *trans*-[W(CO)(DMF)(dppe)$_2$], together with a hydrido-carbamoyl complex [WH($\eta^2$-CONMe$_2$)(dppe)$_2$] as the intermediate stage of this decarbonylation reaction. The detailed structure of the latter complex was determined by X-ray crystallography. Reaction of *trans*-[W(CO)(DMF)(dppe)$_2$] with $N_2$ afforded *trans*-[W(CO)($N_2$)(dppe)$_2$], whose solution in benzene was further converted into a coordinatively unsaturated complex [W(CO)(dppe)$_2$] under reflux in an Ar atmosphere. Subsequent treatment of [W(CO)(dppe)$_2$] with $H_2$ gas gave a dihydrido complex [$WH_2$(CO)(dppe)$_2$].

## Introduction

Previously we have reported that the molybdenum dinitrogen complex *trans*-[Mo($N_2$)$_2$(dppe)$_2$] (**1a**, dppe = $Ph_2PCH_2CH_2PPh_2$) promotes decarbonylation of aldehydes and aldehydic compounds [2]. For example, **1a** reacts with excess *N,N*-dimethylformamide (DMF) in benzene under reflux to give a carbonyl complex *trans*-[Mo(CO)(DMF)(dppe)$_2$] (**2a**) together with a decarbonylated product $HNMe_2$. This carbonyl complex **2a** is converted into a carbonyl-dinitrogen complex *trans*-[Mo(CO)($N_2$)(dppe)$_2$] (**3a**) by recrystallizing **2a** from benzene/hexane under $N_2$ [3,4]. Moreover, when Ar gas is bubbled through a benzene solution of **3a** at 50 ° C, a coordinatively unsaturated complex [Mo(CO)(dppe)$_2$] (**4a**) is obtained from the resultant mixture (Scheme 1). An X-ray analysis has disclosed that the vacant site

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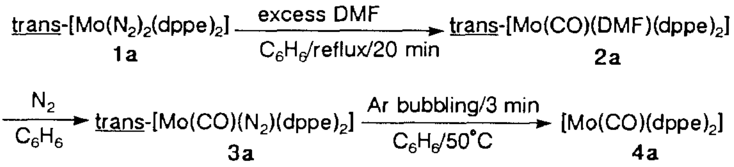
* For Part XXXI see ref. 1.



Scheme 1

*trans* to the CO ligand in **4a** is occupied by one agostic *ortho* hydrogen atom of the dppe ligand [4]. Interestingly, **4a** can bind a wide range of substrates including Lewis bases, ethylene, CO, and $N_2$ [5]. Recently Kubas et al. have also reported that **4a** reacts with $H_2$ to give an $\eta^2$-dihydrogen complex *trans*-[Mo($\eta^2$-$H_2$)(CO)(dppe)$_2$] [6].

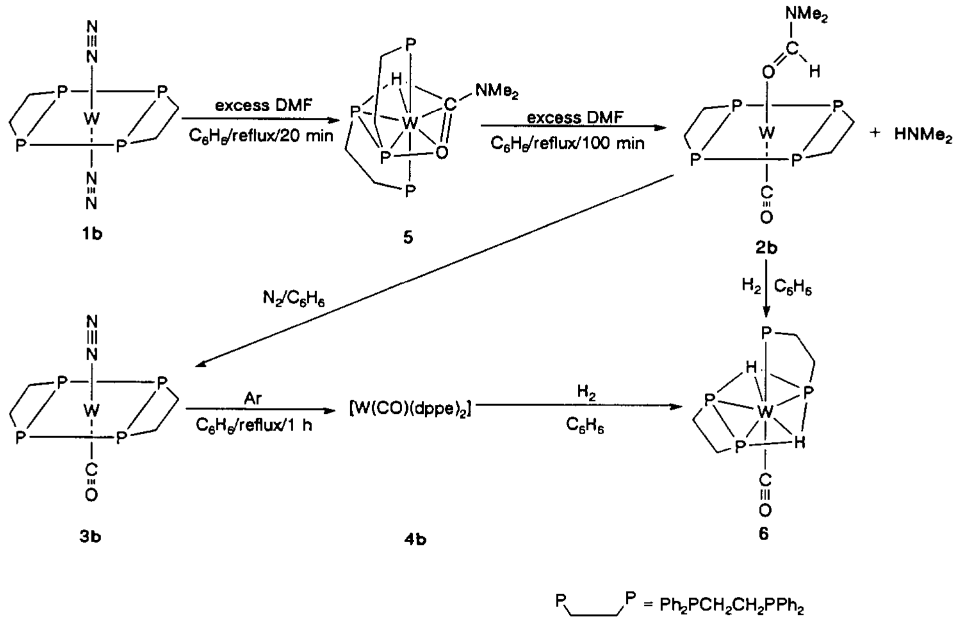
We have now extended our study to include the reaction of the tungsten analogue *trans*-[W($N_2$)$_2$(dppe)$_2$] (**1b**) with DMF and we have isolated a carbonyl complex *trans*-[W(CO)(DMF)(dppe)$_2$] (**2b**) as well as a hydrido-$\eta^2$-carbamoyl complex [WH($\eta^2$-CONMe$_2$)(dppe)$_2$] (**5**). We wish here to describe the details of these complexes and several tungsten carbonyl complexes derived from **2b**, extending previous brief accounts of this work [7,8].

## Results and discussion

### *Reaction of* trans-*[W(N$_2$)$_2$(dppe)$_2$] (1b) with DMF*

The tungsten complex **1b** in benzene reacts with DMF under refluxing conditions to give a carbonyl complex, *trans*-[W(CO)(DMF)(dppe)$_2$] (**2b**), as red crystals in 52% yield. The reaction is slower (2 h) for **1b** than for the molybdenum analogue **1a** (20 min). This can be ascribed to the weaker dissociating ability of the $N_2$ ligand in **1b**, a consequence of the presence of the $d\pi$–$p\pi^*$ interaction being stronger in the M–$N_2$ moiety in **1b** than in **1a**. Complex **2b** shows two characteristic bands in its IR spectrum at 1680 and 1638 cm$^{-1}$, assignable to $\nu$(C≡O) and $\nu$(C=O) respectively, which correspond well to those of **2a** observed at 1690 and 1630 cm$^{-1}$. The unusually low $\nu$(C≡O) values observed for **2** can be explained by the effective delocalization of the *d* electron density of the zero-valent metal toward the CO ligand due to the weak $\pi$-electron accepting ability of the DMF ligand in the *trans* position. This was confirmed by recent X-ray analysis of **2a** [9], which demonstrated a slightly long C≡O bond distance (1.18(2) Å) in the CO ligand as well as the absence of $d\pi$–$p\pi$ interaction between the Mo atom and the DMF ligand. In the $^{31}$P NMR spectra of **2** there were seen sharp singlets at 69.8 ppm for **2a** and 57.8 ppm for **2b** ($J$(W–P) = 314 Hz), consistent with the *trans* structure of these complexes.

On the other hand, when **1b** was reacted with DMF for only 20 min under the same conditions, a hydrido-$\eta^2$-carbamoyl complex [WH($\eta^2$-CONMe$_2$)(dppe)$_2$] (**5**) was isolated in 16% yield as dark red crystals in addition to **2b**. Clearly **5** corresponds to the intermediate stage of the conversion of **1b** to **2b**, since treatment of **5** with DMF in benzene under reflux afforded **2b** accompanied by the formation of HNMe$_2$ (Scheme 2). The yield of the latter, determined by the GLC analysis, was about 70% of the theoretical amount. To our knowledge, **5** is the first example of a hydrido-carbamoyl complex, although many other carbamoyl complexes are known.



Scheme 2

This complex may be regarded as a model for intermediates in the transition metal-catalyzed synthesis of DMF from CO and $HNMe_2$ [10]. In the IR spectrum of **5** there appeared a weak $\nu$(W–H) band at 1952 $cm^{-1}$ and a strong $\nu$(C=O) band at 1545 $cm^{-1}$, the former disappeared in the complex $[WD(\eta^2\text{-}CON(CD_3)_2)(dppe)_2]$ prepared from **1b** and DMF-$d_7$. The substantially low $\nu$(C=O) value observed for **5** is consistent with the $\eta^2$-coordination mode of the carbamoyl ligand (see below) *. The $^1H$ NMR spectrum of **5** recorded at room temperature shows a quintet at $-4.11$ ppm ($J$(P–H) = 33 Hz) assignable to the hydrido proton and two singlets at 3.14 and 2.45 ppm due to the $N$-methyl protons together with the resonances of the dppe ligands. The simple quintet for this hydrido proton can be interpreted by the dppe ligands in **5** having the same fluxional behaviour at this temperature that is commonly observed for Mo and W hydrido complexes of this type [12]. This was also confirmed by the $^{31}P$ NMR spectrum of **5** in toluene-$d_8$, showing only one broad singlet at 58.5 ppm at room temperature. On the other hand, when the temperature was lowered to $-78\,°C$, this broad singlet separated into four resonances with the same integrated intensities at 65.5, 63.4, 61.1, and 46.7 ppm, indicating that fluxional rotation is no longer present in **5** at this temperature.

### *X-ray structure of* $[WH(\eta^2\text{-}CONMe_2)(dppe)_2]$ *(5)*

An X-ray analysis was performed on a single crystal of **5** to clarify its structure. An ORTEP drawing with atom numbering scheme is shown in Fig. 1 and the selected bond distances and angles are gives in Table 1. The essentially planar $N,N$-dimethylcarbamoyl ligand is coordinated to the W atom at both C(11) and O(1) atoms. The

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* Common $\eta^1$-$N,N$-dimethylcarbamoyl complexes show the characteristic $\nu$(C=O) band in the range from 1565 to 1615 $cm^{-1}$ [11].

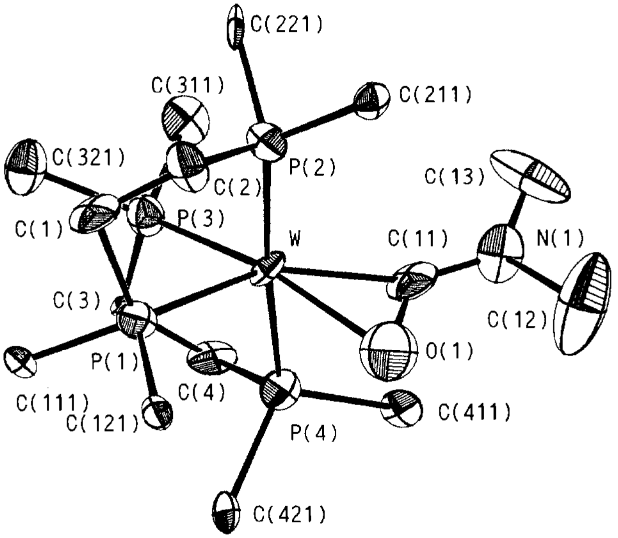


Fig. 1. ORTEP drawing and atom numbering scheme for [WH($\eta^2$-CONMe$_2$)(dppe)$_2$] (**5**). Carbon atoms in phenyl groups are omitted for clarity except for those attached to phosphorus atoms.

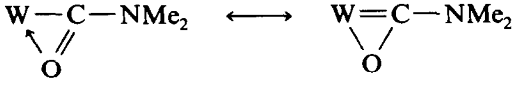
W atom is surrounded by two axial and two equatorial P atoms as well as by the C(11) and O(1) atoms of the carbamoyl ligand at the equatorial sites. Although the hydrido ligand could not be located by X-ray analysis, the equatorial site between C(11) and P(3) atoms is presumably occupied by the hydrogen atom, since the C(11)–W–P(3) angle of 140.1(10)° is greater than any of the other angles between neighbouring atoms around the W atom. Therefore **5** has overall a pentagonal bipyramidal structure, consisting of the hydrido and $\eta^2$-carbamoyl ligands produced

Table 1

Selected bond distances and angles in [WH($\eta^2$-CONMe$_2$)(dppe)$_2$] (**5**)

| | | | |
|---|---|---|---|
| *Distances (Å)* | | | |
| W–P(1) | 2.46(1) | W–P(2) | 2.47(1) |
| W–P(3) | 2.46(1) | W–P(4) | 2.39(1) |
| W–C(11) | 2.07(3) | W–O(1) | 2.37(2) |
| C(11)–N(1) | 1.33(4) | C(11)–O(1) | 1.43(4) |
| N(1)–C(12) | 1.50(4) | N(1)–C(13) | 1.37(5) |
| *Angles (deg)* | | | |
| P(1)–W–P(2) | 79.5(3) | P(1)–W–P(3) | 86.9(2) |
| P(1)–W–P(4) | 104.3(3) | P(1)–W–C(11) | 132.9(9) |
| P(1)–W–O(1) | 97.0(5) | P(2)–W–P(3) | 102.6(3) |
| P(2)–W–P(4) | 175.6(2) | P(2)–W–C(11) | 91.0(22) |
| P(2)–W–O(1) | 92.4(10) | P(3)–W–P(4) | 80.0(3) |
| P(3)–W–C(11) | 140.0(10) | P(3)–W–O(1) | 165.0(10) |
| P(4)–W–C(11) | 84.8(22) | P(4)–W–O(1) | 85.0(10) |
| C(11)–W–O(1) | 36.9(12) | W–C(11)–O(1) | 83.0(16) |
| W–O(1)–C(11) | 60.1(14) | W–C(11)–N(1) | 155.2(39) |
| C(11)–N(1)–C(12) | 123.2(30) | C(11)–N(1)–C(13) | 126.3(30) |
| C(12)–N(1)–C(13) | 110.4(26) | | |

by the oxidative addition of DMF after the cleavage of an aldehydic C–H bond, together with two dppe ligands with pseudo-*cis* configuration. Interestingly, the C(11)–O(1) bond length of 1.43(4) Å observed for **5** is about the same as that of a C–O single bond. This is much longer than that observed (1.322(7) Å) in the other mononuclear $\eta^2$-carbamoyl complex with a *d*-element metal centre $[Ph_4P]_2$-$[Mo(NO)(\eta^2\text{-}CONMe_2)(NCS)_4]$ to have been studied [13], although such an elongated C=O bond has been observed for the $\eta^2$-carbamoyl ligand coordinated to the *f*-element $[Th(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}CONEt_2)Cl]$ (1.44(3) and 1.53(4) Å) [14]. The W–C(11) bond length of 2.07(3) Å is much shorter than the sum of the bonding radii of the W and C atoms (2.4 Å) and is indicative of some multiple bond character. These features may be explained by assuming the structure I tends towards structure II in the $\eta^2$-carbamoyl complex **5**, presumably as a result of the stronger donating ability of the W atom in **5** than that of the Mo atom in $[Ph_4P]_2[Mo(NO)(\eta^2\text{-}CONMe_2)(NCS)_4]$.



(I) (II)

### *Preparation of* trans-*[W(CO)(N₂)(dppe)₂] (3b) and [W(CO)(dppe)₂] (4b)*

Recrystallization of **2b** from benzene/hexane under $N_2$ gave a carbonyl-dinitrogen complex *trans*-$[W(CO)(N_2)(dppe)_2]$ (**3b**) as orange crystals in 75% yield (Scheme 2). In **2b** the DMF ligand is more easily replaced by $N_2$ than it is in **2a**, and this is confirmed by the fact that if the reaction of **1a** with excess DMF is carried out under $N_2$, only **2a** can be isolated in the case of molybdenum, whereas the tungsten complex **1b** affords a mixture of **2b** and **3b**. This is presumably due to tungsten being more electron-rich than molybdenum, which results in dissociation of the weak $\pi$-accepting DMF ligand in **2b** (see above) [9]. Complex **3b** shows medium and weak $\nu(N{\equiv}N)$ bands at 2070 and 2030 $cm^{-1}$ and strong $\nu(C{\equiv}O)$ bands at 1817 and 1795 $cm^{-1}$, respectively. The splitting of $\nu(N{\equiv}N)$ and $\nu(C{\equiv}O)$ is due to a crystal effect and these data correspond well to those obtained by X-ray crystallography for **3a** ($\nu(N{\equiv}N)$: 2110m, 2080m; $\nu(C{\equiv}O)$: 1812s, 1791s) [4]. The $^{31}P$ NMR spectrum of **3b** (50.0 ppm, s; $J(W–P) = 302$ Hz) also confirms the expected *trans* structure (**3a**: 69 ppm, s [4]).

When Ar gas is bubbled through a benzene solution of **3a** at 50 °C for 3 min, **3a** can be smoothly converted into $[Mo(CO)(dppe)_2]$ (**4a**) as already described [4]. However, under the same reaction conditions **3b** did not give the corresponding carbonyl complex $[W(CO)(dppe)_2]$ (**4b**), but afforded a mixture of *cis*-$[W(CO)_2(dppe)_2]$ and uncharacterizable tungsten-dppe complex(es).

Complex **4b** can be isolated in moderate yield as extremely air-sensitive dark green crystals by refluxing a benzene solution of **3b** under Ar for 1 h.

Complex **4b** shows one broad and strong $\nu(C{\equiv}O)$ band at 1716 $cm^{-1}$ (Nujol), as observed for **4a** at 1721 $cm^{-1}$ *. Thus **4b** in solid state possibly has the same

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* The $\nu(C{\equiv}O)$ frequency for **4a** reported at 1807 $cm^{-1}$ [4] is ascribed to the species formed by the contact of the KBr pellet of **4a** with air during IR spectroscopy. The spectrum recorded in the absence of air for a nujol mull of **4a** carefully prepared under Ar results in the appearance of the $\nu(C{\equiv}O)$ band at 1721 $cm^{-1}$ as claimed by Kubas and coworkers [6].

structure as that demonstrated for **4a** by an X-ray analysis, i.e. with one CO and two dppe ligands together with an agostic *ortho* hydrogen atom of the dppe ligand in *trans* position to the CO ligand [4]. However, the structural features of **4** in solution are more complicated: a preliminary examination of IR and NMR work has shown that the structure of **4a** in benzene-$d_6$ is basically the same as that in the solid form but **4b** is present as a mixture of the species with an agostic hydrogen atom as well as the *ortho*-metallated species [8]. Further work is now in progress to clarify the structure of **4** in solution and to prepare analogous complexes containing a wider range of diphosphine ligands, which will be reported in a subsequent paper.

### *Reaction of [W(CO)(dppe)$_2$] (4b) with H$_2$ gas*

In contrast to the formation of the $\eta^2$-$H_2$ complex [Mo($\eta^2$-$H_2$)(CO)(dppe)$_2$] by the reaction of **4a** and $H_2$ gas [6], treatment of the tungsten complex **4b** with $H_2$ gas in benzene at room temperature for 0.5 h gives a dihydrido complex [$WH_2$(CO)(dppe)$_2$] (**6**) as yellow crystals in 42% yield. The reaction of **2b** with $H_2$ gas in benzene for 1 h also afforded **6** in 81% yield. It is noteworthy that the molybdenum analogue **2a** does not react with $H_2$ gas under the same reaction conditions and the unreacted **2a** can be recovered even after 24 h. The IR spectrum of **6** features a strong $\nu$(C≡O) band at 1777 $cm^{-1}$ and a medium $\nu$(W–H) band at 1726 $cm^{-1}$, the latter shifting to 1235 $cm^{-1}$ in [$WD_2$(CO)(dppe)$_2$]. The $^1$H NMR spectrum of **6** at room temperature shows a quintet with W satellites at −3.70 ppm ($J$(P–H) = 34 Hz, $J$(W–P) = 34 Hz). When the temperature is lowered to −78 °C, this quintet changes to a slightly broadened multiplet which is interpreted as having $A_2BCX_2$ pattern. This can be simulated by talking the coupling constants of $J$(P–H) with 18, 47, and 47 Hz. The $^{31}$P NMR spectrum of **6** in toluene-$d_8$ at room temperature shows one broad singlet at 58.3 ppm, which separates into three broad singlets at 64.5, 63.6, and 39.4 ppm at −78 °C. The intensity ratio observed for these resonances is 2 : 1 : 1. These NMR data are indicative of the fluxional behaviour of dppe ligands in **6** at room temperature; in contrast the molecule becomes rigid at low temperature, as observed for **5**. The data at −78 °C are consistent with the pentagonal bipyramidal structure shown in Scheme 2, which is quite similar to that of the closely related dihydrido complex [$MoH_2(CO)(Et_2PCH_2CH_2PEt_2)_2$] recently reported by Kubas et al. [15]. The dihydrido character of **6** is also confirmed by the large $T_1$ value measured for the high-field signal by inversion-recovery pulse sequence (0.52 s at room temperature and 1.7 s at −78 °C) [16].

The way in which hydrogen is added, whether in the form of $\eta^2$-$H_2$ or dihydride, is now known to be determined by electronic and steric factors [17]. Regarding the $d^6$ $ML_5$ fragment, Extended Hückel calculations predict that the formation of the dihydride is much easier for a metal with high $d$ orbitals than for a metal with low $d$ orbitals [18]. The result obtained here confirms this theoretical prediction.

Morris et al. [19] have tried to quantify the tendency of poor $\pi$-donor metal sites favouring $\eta^2$-$H_2$ and good $\pi$-donor sites a dihydrido structure by comparing $\nu$(N≡N) of the corresponding octahedral $d^6$ $N_2$ complexes. They concluded that $H_2$ binds as an $\eta^2$-ligand where $\nu$(N≡N) is between about 2060 and 2150 $cm^{-1}$, while a dihydrido structure is adopted if $\nu$(N≡N) is less than 2050 $cm^{-1}$ [19]. The fact that **3a** shows $\nu$(N≡N) at 2095 $cm^{-1}$ and **3b** at 2050 $cm^{-1}$ is consistent with this relationship.

Analogous findings showing how the mode of hydrogen addition is controlled by the nature of metal have been reported for complexes including the iron triad, $[MH_4(PR_3)_3]$ [20], and the cobalt triad, $[MH_2\{P(CH_2CH_2PPh_2)_3\}]^+$ [21], where the dihydrido character also increases as 1st row metals are replaced by 2nd and then 3rd row metals.

## Experimental

All manipulations were carried out under dry $N_2$ or Ar atmosphere as appropriate, using Schlenk tube techniques. Solvents were purified according to standard methods and stored under an inert atmosphere. Complex **1b** was prepared as previously reported [22]. NMR spectra were recorded on a JEOL JMN-GX-400 spectrometer at 400 MHz for $^1H$ or 162 MHz for $^{31}P$ nuclei and the chemical shifts are referred to the impurity in $C_6D_6$ at 7.20 ppm or 85% $H_3PO_4$, respectively. IR spectra were measured by a Shimadzu IR-408 spectrometer. $HNMe_2$ was determined by an Ohkura Model 103 Gas Chromatograph equipped with a 3 mm × 2 m glass column packed with Amipack 118 (Gasukuro Kogyo Inc.). Analyses were performed at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, University of Tokyo.

### *Preparation of* trans-*[W(CO)(DMF)(dppe)$_2$] (**2b**)*

To a solution of **1b** (1.00 g, 0.97 mmol) in benzene (20 ml) was added DMF (5.0 ml, 64 mmol) under Ar and the solution was refluxed for 2 h. After cooling to room temperature, addition of hexane (50 ml) precipitated red crystals, which were filtered off, washed with hexane and dried *in vacuo*. Yield 540 mg, 52%. IR (KBr, $cm^{-1}$): 1680s ($\nu$(C≡O)), 1638s ($\nu$(C=O)); $^{31}P\{^1H\}$ NMR ($C_6D_6/C_6H_6$/DMF, r.t.): $\delta$ 57.8 (s, $J(W-P) = 314$ hz). Anal. Found: C, 61.99; H, 5.17; N, 1.53. $C_{56}H_{55}NO_2P_4W$ calc.: C, 62.17; H, 5.13; N, 1.30%.

### *Preparation of [WH($\eta^2$-CONMe$_2$)(dppe)$_2$] (5)*

A solution of **1b** (100 mg, 0.97 mmol) and DMF (1.0 ml, 13 mmol) in benzene (4 ml) was refluxed for 20 min and the resultant dark red solution was dried *in vacuo*. Benzene (1–2 ml) was added to the residue and the mixture stirred. Hexane (2–4 ml) was then added slowly to the suspension. On standing, dark red crystals of **5** appeared with precipitate of **2b**. Crystals of **5** were separated from **2b** by suspending **2b** as a slurry in benzene/hexane for removal with a syringe. The crystals were washed with hexane and dried in vacuo. Yield 16 mg, 16%. It is essential to use freshly distilled benzene and DMF to obtain **5**. IR (KBr, $cm^{-1}$): 1952w ($\nu$(W–H)), 1545s ($\nu$(C=O)); $^1H$ NMR ($C_6D_6$, r.t.): $\delta$ 3.14 (s, 3H, $NCH_3$); 2.45 (s, 3H, $NCH_3$); −4.11 (quintet, 1H, $J(P-H) = 33$ Hz, WH). Anal. Found: C, 61.94; H, 4.93; N, 0.79. $C_{55}H_{55}NOP_4W$ calc.: C, 62.28; H, 5.27; N, 1.34%.

### *Preparation of* trans-*[W(CO)(N$_2$)(dppe)$_2$] (**3b**)*

After dissolving **2b** (200 mg, 0.18 mmol) in benzene (8 ml) with stirring under $N_2$, hexane (16 ml) was added to the resultant solution. Orange crystals were deposited and filtered off, washed with hexane and dried *in vacuo*. Yield 140 mg, 75%. IR (KBr, $cm^{-1}$): 2070m ($\nu$(N≡N)), 2030w ($\nu$(N≡N)), 1817s ($\nu$(C≡O)), 1795s ($\nu$(C≡O));

$^{31}P\{^1H\}$ NMR ($C_6D_6/C_6H_6$, r.t.): $\delta$ 50.0 (s, $J(W-P) = 302$ Hz). Anal. Found: C, 61.70; H, 4.89; N, 2.62. $C_{53}H_{48}N_2OP_4W$ calc.: C, 61.40; H, 4.68; N, 2.70%.

### *Preparation of [W(CO)(dppe)$_2$] (**4b**)*

A solution of **3b** (100 mg, 0.092 mmol) in benzene (4 ml) was refluxed for 1 h under Ar and to the resultant dark green solution was added hexane (8 ml). Dark green crystals were deposited and filtered off, washed with hexane and dried *in vacuo*. Yield 79 mg, 81%. IR (Nujol, $cm^{-1}$): 1716s ($\nu(C\equiv O)$). Anal. Found: C, 62.17; H, 4.95. $C_{53}H_{48}OP_4W$: C, 63.10; H, 4.81%.

### *Preparation of [WH$_2$(CO)(dppe)$_2$] (**6**) from **2b***

A solution of **2b** (100 mg, 0.092 mmol) in benzene (4 ml) was stirred under $H_2$ for 1 h and hexane (8 ml) was added to the product solution. Yellow crystals were precipitated and filtered off, washed with hexane and dried *in vacuo*. Yield 76 mg, 81%. IR (KBr, $cm^{-1}$): 1777s ($\nu(C\equiv O)$), 1726m ($\nu$(W-H)); $^1H$ NMR ($C_6D_6$, r.t.): $\delta$ $-3.70$ (quintet, 2H, $J(P-H) = J(W-P) = 34$ Hz, WH). Anal. Found: C, 62.42; H, 4.93. $C_{53}H_{50}OP_4W$ calc. C, 62.98; H, 5.00.

Table 2

Crystallographic data for [WH($\eta^2$-CONMe$_2$)(dppe)$_2$] (5)

| | |
|---|---|
| *(a) Crystal data* | |
| Formula | $WP_4ONC_{55}H_{55}$ |
| Molecular weight | 1053.8 |
| Crystal dimensions, mm | 0.16×0.16×0.74 |
| Space group (crystal system) | *Cc* (monoclinic) |
| *a*, Å | 19.722(5) |
| *b*, Å | 16.067(4) |
| *c*, Å | 21.949(10) |
| *β*, deg | 135.96(2) |
| Cell volume, Å$^3$ | 4834.9 |
| *Z* | 4 |
| $D_{calcd}$, g cm$^{-3}$ | 1.448 |
| *F*(000), electrons | 2136 |
| $\mu_{calcd}$, cm$^{-1}$ | 26.1 |
| *(b) Data collection* | |
| Diffractometer | Rigaku AFC-5 |
| Monochromator | graphite |
| Radiation (λ/Å) | Mo-$K_\alpha$ (0.7107) |
| $2\theta$ range, deg | $2 < 2\theta < 60$ |
| Scan method | $\omega$ ($2 < 2\theta < 30°$), $\omega$-$2\theta$ ($30 < 2\theta < 60°$) |
| Scan speed, deg min$^{-1}$ | 2 |
| Reflections measured | 5733 |
| data, $\lvert F_o \rvert > 3\sigma(F_o)$ | 4215 |
| *(c) Solution and refinement* | |
| No. of parameters refined | 752 |
| *R* | 0.059 |
| $R_w$ | 0.070 |
| max residuals, e Å$^{-3}$ | 2.0 (around W atom) |

Table 3

Atomic coordinates and equivalent temperature factors for [$WH(\eta^2\text{-}CONMe_2)(dppe)_2$] (5) [a]

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| W | 0(3) | 176(0) | 0(3) | 2.1 |
| P(1) | 1130(4) | −938(3) | 1026(3) | 2.6 |
| P(2) | −148(3) | 238(4) | 1024(3) | 2.6 |
| P(3) | −1160(4) | −931(3) | −1022(3) | 2.6 |
| P(4) | 117(4) | 227(4) | −1012(3) | 2.8 |
| O(1) | 1157(16) | 1267(14) | 730(14) | 6.1 |
| N(1) | −167(16) | 2235(11) | −112(15) | 3.4 |
| C(1) | 877(18) | −1260(16) | 1721(17) | 4.2 |
| C(2) | 765(14) | −422(13) | 2012(14) | 3.5 |
| C(3) | −1040(9) | −1185(9) | −1738(10) | 1.2 |
| C(4) | −872(15) | −413(13) | −2020(12) | 2.7 |
| C(11) | 139(29) | 1455(17) | 42(31) | 4.4 |
| C(12) | 506(28) | 2972(23) | 293(24) | 9.6 |
| C(13) | −1110(24) | 2490(25) | −625(21) | 7.1 |
| C(111) | 2470(13) | −731(11) | 1918(13) | 2.4 |
| C(112) | 3160(13) | −1323(15) | 2241(13) | 3.2 |
| C(113) | 4210(19) | −870(18) | 2993(18) | 4.9 |
| C(114) | 4415(11) | −289(14) | 3300(12) | 3.7 |
| C(115) | 3673(12) | 342(9) | 2969(13) | 2.6 |
| C(116) | 2774(13) | 76(12) | 2231(11) | 2.7 |
| C(121) | 1195(13) | −1985(11) | 722(12) | 2.1 |
| C(122) | 1173(18) | −2716(14) | 1086(19) | 4.9 |
| C(123) | 1353(19) | −3495(16) | 771(19) | 4.8 |
| C(124) | 1497(15) | −3510(14) | 313(15) | 3.4 |
| C(125) | 1623(17) | −2772(13) | 53(18) | 4.0 |
| C(126) | 1436(17) | −2012(14) | 240(15) | 3.8 |
| C(211) | −82(12) | 1190(11) | 1494(11) | 2.2 |
| C(212) | 868(15) | 1698(13) | 2040(15) | 3.0 |
| C(213) | 931(18) | 2449(15) | 2375(16) | 4.1 |
| C(214) | 135(21) | 2787(21) | 2155(16) | 6.0 |
| C(215) | −646(30) | 2353(24) | 1728(27) | 7.7 |
| C(216) | −715(23) | 1553(18) | 1443(20) | 5.5 |
| C(221) | −1268(14) | −38(7) | 651(11) | 1.9 |
| C(222) | −2167(15) | 179(17) | −252(13) | 4.1 |
| C(223) | −3048(19) | −215(20) | −598(19) | 5.2 |
| C(224) | −3130(12) | −743(13) | −150(14) | 3.1 |
| C(225) | −2273(21) | −905(19) | 741(21) | 5.2 |
| C(226) | −1371(11) | −642(12) | 1092(12) | 2.5 |
| C(311) | −2471(16) | −602(14) | −1865(12) | 3.2 |
| C(312) | −2707(16) | 205(16) | −2279(15) | 3.6 |
| C(313) | −3847(27) | 277(28) | −2941(24) | 8.2 |
| C(314) | −4541(27) | −198(23) | −3326(25) | 7.0 |
| C(315) | −4183(13) | −1143(10) | −2885(12) | 2.1 |
| C(316) | −3248(15) | −1193(13) | −2223(14) | 3.1 |
| C(321) | −1301(16) | −1971(14) | −728(14) | 3.7 |
| C(322) | −1436(17) | −2027(14) | −215(15) | 3.6 |
| C(323) | −1580(21) | −2764(19) | −39(18) | 5.2 |
| C(324) | −1692(21) | −3470(17) | −423(18) | 5.2 |
| C(325) | −1340(16) | −3463(13) | −858(14) | 2.9 |
| C(326) | −1195(15) | −2721(12) | −967(13) | 2.6 |
| C(411) | 1303(14) | −253(12) | −622(14) | 3.0 |
| C(412) | 1260(27) | −616(23) | −1159(23) | 6.6 |
| C(413) | 2215(22) | −987(17) | −688(21) | 4.8 |

Table 3 (continued)

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| C(414) | 2992(26) | −795(22) | 110(26) | 6.9 |
| C(415) | 3040(15) | −255(17) | 634(15) | 4.1 |
| C(416) | 2123(15) | 34(13) | 210(14) | 3.2 |
| C(421) | −147(12) | 1271(12) | −1564(11) | 2.5 |
| C(422) | 674(16) | 1645(14) | −1389(16) | 3.7 |
| C(423) | 471(21) | 2388(15) | −1824(22) | 5.2 |
| C(424) | −460(15) | 2747(13) | −2363(16) | 3.5 |
| C(425) | −1175(15) | 2427(14) | −2412(15) | 3.3 |
| C(426) | −986(22) | 1633(20) | −2022(17) | 5.2 |

[a] Multiplied by $10^4$.

*Preparation of **6** from **4b***

Complex **6** was also prepared by the analogous treatment of **4b** (50 mg, 0.050 mmol) in benzene (2 ml) with $H_2$ for 30 min. Yield 21 mg, 42%.

*X-Ray structure determination of* $[WH(\eta^2\text{-}CONMe_2)(dppe)_2]$ *(5)*

Data collection was performed at room temperature by using a single crystal of **5** sealed in a glass capillary under Ar. Crystallographic data are summarized in Table 2. The orientation matrix and unit cell parameters were derived from the least squares fit of 20 machine-centred reflections with $2\theta$ values between 20 and 25°. No significant decay of three check reflections was observed during the data collection. Intensity data were corrected for Lorentz and polarization effects and absorption correction was made.

Structure solution and refinement were performed using a UNIX-III program package [23] at the Computer Centre of the University of Tokyo. The W atom was found by the direct method program MULTAN 78 and subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, which were refined anisotropically by block-diagonal least square techniques. Published atomic scattering factors were used [24]. Many hydrogen atoms were located from the difference Fourier map, and the remaining hydrogen atoms were placed at the calculated positions, which were included in the final stage of the refinement with isotropic thermal parameters. Final atomic coordinates of nonhydrogen atoms are shown in Table 3. Further data are available from the authors, in the form of tables of bond lengths and angles, hydrogen atom parameters, anisotropic thermal parameters for non-hydrogen atoms, and structure factors together with an ORTEP drawing of the molecule with a full atomic numbering scheme.

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