Journal of Organometallic Chemistry, 431 (1992) 65–80
Elsevier Sequoia S.A., Lausanne
JOM 22584

Reactivity of dinuclear tungsten carbonyls bridged both by hydride and by bidentate phosphine ligands, $(\mu\text{-H})(\mu\text{-Ph}_2P(CH_2)_nPPh_2)W_2(CO)_7(NO)$ ($n = 1$–3)

Jiann T. Lin [a], Kuo-Yang Chang [a,b], Ming L. Gong [a,c], Chung-Cheng Chang [b], Han-Mou Gau [c], Li-Hong Tsen [a] and Yuh S. Wen [a]

[a] *Institute of Chemistry, Academia Sinica, Nankang, Taipei (Taiwan)*
[b] *Department of Chemistry, National Sun Yat-Sen University, Kaohsiung (Taiwan)*
[c] *Department of Chemistry, National Chung-Hsin University, Taichung (Taiwan)*

(Received November 1, 1991)

Abstract

The ligand substitution of $(\mu\text{-H})(\mu\text{-Ph}_2P(CH_2)_nPPh_2)W_2(CO)_7(NO)$ ($n = 1$–3, designated as **1**, **2** and **3**) provides complexes $(\mu\text{-H})(\mu\text{-Ph}_2P(CH_2)_nPPh_2)W_2(CO)_6(L)(NO)$ (L = $PhPH_2$, $n = 1$–3, designated as **4**, **5** and **6**: L = ^nPrNC, $n = 1$–3, designated as **7**, **8** and **9**). Michael addition towards several conjugate olefins following the deprotonation of $PhPH_2$ in **4** results in the formation of the complexes $(\mu\text{-H})(\mu\text{-dppm})W_2(CO)_6(PhPH(CH_2CH_2X))(NO)$ (**10**, X = CN; **11**, X = C(O)H; **12**, X = C(O)Me). Diastereomers are found in complexes **10–12** and the interconversion of the isomers is established for **10**. The isomerization involves the dissociation of $PhPH(CH_2CH_2CN)$. X-ray crystal structure analyses for complexes $(\mu\text{-H})(\mu\text{-dppm})W_2(CO)_6(Ph_2PH)(NO)$ (**13**) and **10** were carried out. **13**: orthorhombic, *Pbca*, $Z = 8$, a 19.428(5), b 36.100(8), c 12.025(1) Å, V 8438 (3) Å^3, $R = 0.041$, $R_w = 0.059$. **10**: triclinic, $P\bar{1}$, $Z = 4$, a 9.883(2), b 20.429(4), c 21.137(3) Å, α 91.24(1), β 91.87(1), γ 99.86(2)°, V 4200(1) Å^3, $R = 0.042$, $R_w = 0.044$.

Introduction

Complexes with three-center, two-electron (3c-2e) metal–hydrogen–metal bonds constitute an important class [1] among transition-metal hydrides. A theoretical study on metal complexes containing an unsupported M–H–M linkage concluded that M–H–M bonds were intrinsically flexible and subject to small changes in their environment [2]. Previous studies by us [3] and others [4] indicated that substantial variation of the M–H–M linkage indeed occurred in quite a few dimeric group VI metal complexes.

Diphosphine ligands were frequently used to prevent rupture of the dimeric metal complexes [5], including those containing M–H–M linkages [6]. We recently applied this strategy to improve the stability of $HW_2(CO)_9(NO)$. Complexes

---

Correspondence to: Dr. J.T. Lin, Institute of Chemistry, Academica Sinica, Nankang, Taipei, Taiwan.

(μ-H)(μ-$Ph_2P \sim PPh_2$)$W_2(CO)_7(NO)$ were synthesized and their chemical reactivities briefly examined [7]. In that report we described that substitution of Ph_2PH for the CO ligand in (μ-H)(μ-$Ph_2P(CH_2)_nPPh_2$)$W_2(CO)_7(NO)$ ($n = 1$–3, designated as **1**, **2** and **3**) occurred readily with the assistance of Me_3NO. In this paper, the ligand substitution of **1**–**3** is given in more detail. Activation of $PhPH_2$ by compound **1** as well as the interesting isomerization of (μ-H)(μ-dppm)$W_2(CO)_6$($PhPH(CH_2CH_2CN)$)(NO) are also included. The results of a structural study on (μ-H)(μ-dppm)$W_2(CO)_6(Ph_2PH)(NO)$ and (μ-H)(μ-dppm)$W_2(CO)_6$($PhPH(CH_2CH_2(CN)$)(NO) are also reported.

Experimental

General procedure

All manipulations were carried out under an atmosphere of N_2 using standard Schlenk techniques or a N_2-filled glovebox. All solvents were dried and degassed with use of standard procedures. All the column chromatography was performed under N_2 by use of silica gel (230–400 mesh ASTM, Merck) as the stationary phase in a column of 2.5 cm in diameter. Complexes (μ-H)(μ-$Ph_2P(CH_2)_nPPh_2$)W_2-$(CO)_7(NO)$ ($n = 1$–3, designated as **1**, **2** and **3**) were prepared as previously described [7]. Ph_3PN^nPr was prepared by the published procedure [8]. Elemental analyses were performed on a Perkin–Elmer 2400 CHN analyzer. Infrared measurements were made on a Perkin–Elmer 880 spectrometer. Nuclear magnetic resonance spectra were run on a Bruker MSL-200 or AM-200 instrument. The ^1H and ^{31}P NMR spectra were referenced to TMS and external 85% H_3PO_4, respectively.

*(μ-H)(μ-dppm)$W_2(CO)_6(PhPH_2)(NO)$ (**4**).* Complex **1** (300 mg, 0.31 mmol) was dissolved in THF at −50°C and stirred for 3 h. One equivalent of $PhPH_2$ (0.033 ml) was then added and the solution was stirred at the same temperature for another 2 h. The reaction mixture was then removed from the cooling bath and the solvent removed in vacuo. The resulting yellow-orange residue was chromatographed. Complex **4** was obtained from the yellow-orange band eluted by CH_2Cl_2/hexane (1/2 v/v) in a yield of 46%. Anal. Found: C, 42.18; H, 2.68; N, 1.23. $C_{37}H_{30}NO_7P_3W_2$ calc.: C, 41.88; H, 2.85; N, 1.32%.

*(μ-H)(μ-dppe)$W_2(CO)_6(PhPH_2)(NO)$ (**5**).* Complex **2** (300 mg, 0.30 mmol) in 75 ml of CH_3CN prechilled to −30°C was added dropwise an CH_3CN solution of Me_3NO (23 mg, 0.31 mmol) chilled at −30°C. After 3 h at the same temperature the solution was added $PhPH_2$ (0.033 ml, 0.31 mmol) and stirred for another 2 h. The solution was then warmed to room temperature and the solvent removed under vacuum. The crude product was chromatographed. The yellow-orange crystals of **5** (30%) were obtained from the second, major band (CH_2Cl_2/hexane 1/2.5 v/v). Anal. Found: C, 41.98; H, 2.81; N, 1.25. $C_{38}H_{32}NO_7P_3W_2$ calc.: C, 42.44; H, 2.99; N, 1.30%.

*(μ-H)(μ-dppp)$W_2(CO)_6(PhPH_2)(NO)$ (**6**).* Essentially the same procedure for the synthesis of **5** was followed except that acetone was used as the solvent. Complex **6** has a yield of 40%. Anal. Found: C, 42.87; H, 3.02; N, 1.20. $C_{39}H_{34}NO_7P_3W_2$ calc.: C, 43.00; H, 3.15; N, 1.29%.

*(μ-H)(μ-dppm)$W_2(CO)_6(^nPrNC)(NO)$ (**7**).* To a CH_2Cl_2 solution of **1** (300 mg, 0.306 mmol) prechilled to −35°C was added Ph_3PN^nPr (147 mg, 0.459 mmol).

After 1 h the reaction mixture was removed from the cooling bath and stirred for another 2 h, during which time the color changed from orange to orange-yellow. The solvent was removed in vacuo and the residue was chromatographed. Yellow-orange powdery **7** was obtained from the band eluted by CH_2Cl_2/hexane (1/2 v/v) in a yield of 60%. Anal. Found: C, 41.11; H, 2.85; N, 2.67. $C_{35}H_{30}N_2O_7P_2W_2$ calc.: C, 41.20; H, 2.96; N, 2.75%.

(μ-H)(μ-dppe)$W_2(CO)_6(^nPrNC)(NO)$ (8) and (μ-H)(μ-dppp)$W_2(CO)_6(^nPrNC)(NO)$ (9) were prepared by essentially the same procedure except the reaction time was 4 and 12 h, respectively.

Complex **8** has a yield of 59%. Anal. Found: C, 41.33; H, 2.95; N, 2.82. $C_{36}H_{32}N_2O_7P_2W_2$ calc.: C, 41.81; H, 3.12; N, 2.71%.

Complex **9** has a yield of 58%. Anal. Found: C, 42.05; H, 3.22; N, 2.52. $C_{37}H_{34}N_2O_7P_2W_2$ calc.: C, 42.39; H, 3.27; N, 2.67%.

(μ-H)(μ-dppm)$W_2(CO)_6(PhPH(CH_2CH_2CN))(NO)$ (10). A solution of **4** (150 mg, 0.141 mmol) in THF prechilled to −50°C was treated with a stoichiometric amount of NEt_3 in THF also at −50°C. After stirring at −50°C for 1 h, a solution of CH_2=CHCN (9.3 μl, 0.141 mmol) in THF was added. Stirring was maintained at −50°C for another 1 h and then the reaction mixture was removed from the cooling bath and stirred for a further 1 h. The solvent was removed *in vacuo* and the residue was chromatographed. Yellow-orange powdery **10** was obtained from the band eluted by CH_2Cl_2/hexane (5/3 v/v) in a yield of 65%. Anal. Found: C, 42.97; H, 2.91; N, 2.25. $C_{40}H_{33}N_2O_7P_3W_2$ calc.: C, 43.11; H, 2.98; N, 2.51%.

(μ-H)(μ-dppm)$W_2(CO)_6(PhPH(CH_2CH_2X))(NO)$ (11, X = C(O)H; 12, X = C(O)Me). Identical procedures were used for the formation of compounds **11** and **12** as were used for **10**, except that CH_2=CHC(O)H and CH_2 = CHC(O)Me were used instead of CH_2=CHCN.

Complex **11** has a yield of 29%. Anal. Found: C, 43.13; H, 2.79; N, 1.26. $C_{40}H_{34}NO_8P_3W_2$ calc.: C, 43.00; H, 3.07; N, 1.25%.

Complex **12** has a yield of 44%. Anal. Found: C, 43.30; H, 3.11; N, 1.34. $C_{41}H_{36}NO_8P_3W_2$ calc.: C, 43.53; H, 3.21; N, 1.25%.

Exchange studies of (μ-H)(μ-dppm)$W_2(CO)_6(L)(NO)$ with L′

A NMR tube of 5 mm in diameter was loaded with suitable amounts (20–30 mg) of (μ-H)(μ-dppm)$W_2(CO)_6$(L)(NO) in 0.5 ml of acetone-d_6. The tube was cooled by liquid nitrogen and a 100-fold excess of L′ was added. The tube was then sealed in vacuo and rapidly warmed to room temperature. The exchange reaction was monitored by ^{31}P NMR spectra with a Bruker MSL-200 spectrometer operating at 80 MHz. The spectra were taken for every hour, and the results were collected in Table 1.

Crystallographic studies

Crystals of (μ-H)(μ-dppm)$W_2(CO)_6(Ph_2PH)$(NO) (**13**) were obtained by cooling a concentrated solution of the complex in acetone at −5°C for several days. Crystals of (μ-H)(μ-dppm)$W_2(CO)_6(PhPH(CH_2CH_2CN))$(NO) (**10**) (isomer **1**) were grown by slow diffusion of hexane into a concentrated solution of **10** in a mixture of CH_2Cl_2 and Et_2O. Crystals were mounted in the thin wall glass capillary tubes. Diffraction measurements were made on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ 0.7107 Å) for **10**, or on a

Table 1

Exchange of L′ for L in (μ-H)(μ-dppm)$W_2(CO)_6(NO)(L)$ [a]

L	L′	Results based on $^{31}P\{H\}$ NMR
$PhPH(CH_2CH_2CN)$	$PhPH_2$	the exchange is complete after 24 h
$PhPH(CH_2CH_2CN)$	^tBuNC	the exchange is complete after 22 h
Ph_2PH	$PhPH_2$	less than 10% exchange after 8 d
$PhPH_2$	Ph_2PH	the exchange is complete after 1/2 h
^tBuNC	$PhPH_2$	there is no exchange
$PhPH(CH_2CH_2CN)$	PPh_3	there is no exchange

[a] The concentration of L′ is in 100 times excess to that of (μ-H)(μ-dppm)$W_2(CO)_6(NO)(L)$.

Rigaku AFC5R diffractometer using monochromated Cu-K_α radiation (λ 1.5405 Å), with the θ–2θ scan mode. Unit cells were determined from centering 25 reflections in the suitable 2θ range. Other relevant experimental details are listed in Table 2. Absorption corrections according to ψ scans of three reflections were applied. All the data processing was carried out on a Micro VAX 3600 using the NRCC SDP program [9]. The coordinates of tungsten atoms were obtained from Patterson syntheses. The coordinates of all the remaining atoms except hydrogen

Table 2

Crystal data for compounds **10** and **13**

	10	**13**
Formula	$C_{40}H_{33}N_2O_7P_3W_2$	$C_{43}H_{34}NO_7P_3W_2$
Formula weight	1114.3	1137.4
a (Å)	9.883(2)	19.428(5)
b (Å)	20.429(4)	36.100(8)
c (Å)	21.137(3)	12.025(1)
α (°)	91.24(1)	
β (°)	91.87(1)	
γ (°)	99.86(2)	
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pbca$
Z	4	8
V (Å^3)	4200(1)	8434(3)
D_{calc} (g/cm^3)	1.762	1.792
Crystal size (mm)	0.25×0.17×0.13	0.31×0.23×0.42
Radiation	Mo-K_α (λ = 0.7107 Å)	Cu-K_α (λ = 1.5405 Å)
μ (mm^{-1})	5.75	11.6
Transmission factors (max; min)	1.00; 0.75	1.00; 0.45
2θ-range	0–45	0–120
Octants	$\pm h, +k, \pm l$ $-10 \sim 10$ $0 \sim 21$ $-22 \sim 22$	$+h, +k, +l$ $0 \sim 19$ $0 \sim 40$ $0 \sim 13$
No. of unique reflections	10954	6149
Reflections with $I > n\sigma$	6265 (n = 2)	5027 (n = 2.5)
No. of variables	981	509
R; R_w	0.042; 0.044	0.041; 0.059
GOF	1.51	1.83
max Δ/σ	0.342	0.093

atoms were obtained from a series of structure factor calculations and Fourier syntheses. The structures were refined by minimizing $\Sigma\omega(|F_o|-|F_c|)^2$, where $\omega = 1/\sigma(F_o)^2$ was calculated from the counting statistics. The atomic scattering factors f_0 and anomalous dispersion terms f', f'' were taken from ref. 10. All nonhydrogen atoms were refined anisotropically. The position of the bridging hydrogen atom was located from the final difference Fourier maps for **13** and refined. Other hydrogen atoms were included in the structure factor calculation in idealized position with d_{C-H} 0.98 Å. The final positional parameters for the atoms in **13** and **10** are in Table 3. Selected interatomic distances and bond angles are in Table 4.

Results and discussion

The high CO stretching frequencies of (μ-H)(μ-$Ph_2P \sim PPh_2$)$W_2(CO)_7(NO)$ suggest that nucleophilic attack at CO may be facile [11*]. Therefore, while in refluxing THF fragmentation of all complexes (μ-H)(μ-$Ph_2P \sim PPh_2$)$W_2(CO)_7(NO)$ occur to yield $W(CO)_4(\eta^2$-$Ph_2P \sim PPh_2)$ similarly to the behavior of (μ-H)(μ-$Ph_2P \sim PPh_2$)$Mo_2(CO)_8^-$ described by Darensbourg [12], trimethylamine oxide reacts with them rapidly in CH_3CN at low temperature without causing the rupture of the dimeric units. Trapping the presumed intermediate, (μ-H)(μ-$Ph_2P \sim PPh_2$)$W_2(CO)_6(CH_3CN)(NO)$, with various ligands yielded several complexes, (μ-H)(μ-$Ph_2P(CH_2)_nPPh_2$)$W_2(CO)_6(L)(NO)$ ($n = 1$–3; L = Ph_2PH [7], $PhPH_2$, ^tBuNC [13*]). Triphenylphosphinpropylimine, Ph_3PN^nPr, also readily reacts with **1**–**3** to yield (μ-H)(μ-$Ph_2P(CH_2)_nPPh_2$)$W_2(CO)_6(^nPrNC)(NO)$ ($n = 1$–3, designated as **4**–**6**). Deoxygenation of the carbonyl ligand likely proceeds via initial addition of the phosphinimine to the carbonyl carbon with subsequent elimination of $Ph_3P{=}O$, similar to those reported in literature [14]. In the conversion of (μ-H)(μ-$Ph_2P \sim PPh_2$)$W_2(CO)_7(NO)$ to (μ-H)(μ-$Ph_2 \sim PPh_2$)$W_2(CO)_6(L)(NO)$, one might expect that the CO ligand reacted was initially coordinated to the tungsten atom containing the NO ligand, a common feature for metal nitrosyl complexes [15]. Indeed, this has been confirmed by X-ray structural determination on (μ-H)(μ-dppm)$W_2(CO)_6(Ph_2PH)(NO)$ (**13**) and (μ-H)(μ-dppm)$W_2(CO)_6(PhPH(CH_2CH_2CN))(NO)$ (**10**) (see below).

The spectroscopic properties of **4**–**9** (Table 5) are consistent with formulation: one hydride chemical shift around -10 to *ca.* -12 ppm (δ value) with two sets of tungsten satellites in the ^1H NMR, three (complexes **4**, **5** and **6**) or two (complexes **7**, **8** and **9**) different chemical shifts for the phosphorus atoms in the ^{31}P NMR, and a ν(NO) stretching around 1650 cm^{-1}. The CO stretchings appear at lower frequencies than those of **1**–**3**, as expected. The methylene protons in (μ-H)(μ-dppm)$W_2(CO)_6(L)(NO)$ always appear to be diastereotopic, indicating the asymmetric nature of these complexes. The two hydrogen atoms of $PhPH_2$ in **4**, **5** and **6** are also diastereotopic.

It is interesting to note that although (μ-H)(μ-dppm)$W_2(CO)_7(NO)$ (**1**) is indefinitely stable in CH_2Cl_2 under N_2, it readily loses one CO in THF even at low temperature. Thus ligand substitution of **1** could be performed conveniently in

---

* Reference number with asterisk indicates a note in the list of references.

Table 3

Positional parameters and B_{iso} values for the atoms in **10** and **13**

Atom	x	y	z	B_{iso}
Compound **10**				
W1	0.53036(8)	0.35587(3)	0.10288(3)	3.03(3)
W2	0.39774(8)	0.19094(3)	0.08655(3)	2.65(3)
W1A	−0.09536(10)	0.83894(3)	0.34560(3)	4.23(4)
W2A	−0.07813(9)	0.69911(3)	0.42650(3)	3.91(3)
P1	0.28767(49)	0.36665(18)	0.12916(16)	2.89(19)
P2	0.15987(47)	0.22011(19)	0.09273(16)	2.77(19)
P3	0.37383(54)	0.19113(20)	−0.03182(17)	3.70(22)
P1A	0.15408(58)	0.86847(20)	0.38319(17)	4.07(23)
P2A	0.18116(52)	0.72656(20)	0.42543(16)	3.41(21)
P3A	−0.08343(88)	0.62328(25)	0.32951(21)	8.04(39)
N1	0.3400(15)	0.1057(6)	0.0899(5)	4.0(7)
N64	0.7354(21)	0.2730(8)	−0.1967(6)	8.0(11)
N1A	−0.0795(16)	0.6290(6)	0.4805(5)	5.0(7)
N64A	−0.1584(30)	0.6544(10)	0.1013(10)	15.5(19)
O1	0.4713(15)	0.4156(6)	−0.0296(5)	7.2(8)
O2	0.6640(14)	0.3200(5)	0.2326(5)	6.1(7)
O3	0.8186(14)	0.3370(6)	0.0588(6)	7.4(8)
O4	0.6456(18)	0.5013(5)	0.1440(5)	8.5(9)
O5	0.7059(14)	0.1748(5)	0.0723(5)	6.2(7)
O6	0.4531(15)	0.1946(5)	0.2328(4)	5.9(7)
O7	0.2952(14)	0.0453(5)	0.0912(5)	5.4(6)
O1A	0.0105(21)	0.8201(8)	0.2087(5)	11.6(13)
O2A	−0.2674(17)	0.8774(7)	0.4614(6)	9.0(9)
O3A	−0.3922(18)	0.7853(8)	0.2915(7)	11.0(11)
O4A	−0.1100(19)	0.9798(6)	0.3003(5)	8.5(10)
O5A	−0.4024(18)	0.6751(9)	0.4092(8)	12.2(12)
O6A	−0.1143(14)	0.7901(5)	0.5446(5)	6.1(7)
O7A	−0.0783(17)	0.5852(5)	0.5161(5)	7.1(8)
C1	0.4874(21)	0.3925(7)	0.0180(7)	4.8(9)
C2	0.6040(19)	0.3306(7)	0.1863(7)	4.2(9)
C3	0.7073(19)	0.3456(8)	0.0742(7)	4.7(9)
C4	0.5976(21)	0.4464(7)	0.1293(7)	5.0(9)
C5	0.5884(20)	0.1832(8)	0.0780(6)	4.8(9)
C6	0.4325(19)	0.1992(7)	0.1814(6)	3.7(8)
C8	0.1601(17)	0.3087(6)	0.0822(5)	2.9(7)
C11	0.2180(18)	0.3590(7)	0.2082(5)	3.4(8)
C12	0.0940(22)	0.3777(9)	0.2204(7)	5.7(11)
C13	0.0375(24)	0.3745(10)	0.2806(8)	7.2(12)
C14	0.1113(24)	0.3486(9)	0.3266(7)	7.0(12)
C15	0.2380(24)	0.3311(9)	0.3175(7)	6.5(12)
C16	0.2920(23)	0.3369(8)	0.2565(7)	5.9(11)
C21	0.2458(17)	0.4464(7)	0.1068(6)	3.3(7)
C22	0.1927(21)	0.4579(7)	0.0480(7)	4.7(9)
C23	0.1721(21)	0.5221(8)	0.0334(7)	5.3(10)
C24	0.1978(21)	0.5728(7)	0.0770(8)	5.6(10)
C25	0.2560(26)	0.5606(8)	0.1336(7)	7.1(13)
C26	0.2859(22)	0.4993(7)	0.1488(7)	5.2(10)
C31	0.0625(17)	0.1969(6)	0.1639(6)	3.0(7)
C32	−0.0546(19)	0.2211(7)	0.1777(7)	4.2(9)
C33	−0.1306(20)	0.1996(9)	0.2290(7)	5.4(10)
C34	−0.0920(20)	0.1535(9)	0.2663(7)	5.5(10)
C35	0.0275(22)	0.1281(8)	0.2554(7)	5.9(11)
C36	0.1031(20)	0.1491(8)	0.2028(7)	5.0(10)

Table 3 (continued)

Atom	x	y	z	B_{iso}
Compound 10				
C41	0.0379(15)	0.1814(6)	0.0311(6)	2.7(7)
C42	−0.0020(18)	0.1125(8)	0.0329(6)	3.9(8)
C43	−0.0929(20)	0.0768(8)	−0.0114(7)	4.9(9)
C44	−0.1036(18)	0.1794(7)	−0.0651(6)	3.9(8)
C45	−0.1438(20)	0.1113(8)	−0.0607(6)	5.1(9)
C46	−0.0129(17)	0.2149(7)	−0.0180(6)	3.2(7)
C51	0.3269(17)	0.1120(7)	−0.0723(6)	3.3(8)
C52	0.4115(21)	0.0652(8)	−0.0653(7)	5.1(10)
C53	0.3763(24)	0.0024(9)	−0.0969(7)	6.5(12)
C54	0.2613(25)	−0.0098(8)	−0.1314(7)	6.8(12)
C55	0.1712(22)	0.0350(9)	−0.1387(7)	6.1(10)
C56	0.2069(22)	0.0970(8)	−0.1092(7)	5.5(10)
C61	0.5284(20)	0.2305(7)	−0.0705(6)	4.2(8)
C62	0.5049(24)	0.2373(10)	−0.1443(8)	7.3(13)
C63	0.6341(21)	0.2553(7)	−0.1740(7)	5.1(10)
C1A	−0.0235(22)	0.8244(8)	0.2587(8)	5.8(10)
C2A	−0.2027(21)	0.8611(8)	0.4196(8)	5.6(10)
C3A	−0.2768(25)	0.8002(10)	0.3084(10)	8.2(13)
C4A	−0.1003(23)	0.9268(8)	0.3194(7)	5.6(11)
C5A	−0.2837(24)	0.6846(9)	0.4141(8)	7.1(13)
C6A	−0.0951(19)	0.7593(8)	0.5011(7)	4.4(9)
C8A	0.2409(20)	0.7949(7)	0.3757(6)	4.1(9)
C11A	0.2104(21)	0.9035(7)	0.4624(6)	4.8(10)
C12A	0.1121(23)	0.9186(8)	0.5026(7)	6.1(11)
C13A	0.1535(27)	0.9458(9)	0.5636(7)	8.1(14)
C14A	0.2904(27)	0.9518(9)	0.5806(7)	7.7(14)
C15A	0.3916(23)	0.9371(9)	0.5428(7)	7.0(12)
C16A	0.3514(23)	0.9123(8)	0.4822(7)	6.0(11)
C21A	0.2581(22)	0.9297(8)	0.3336(6)	5.2(10)
C22A	0.2647(26)	0.9955(8)	0.3460(8)	7.0(13)
C23A	0.3406(25)	1.0431(9)	0.3075(8)	7.3(13)
C24A	0.4093(32)	1.0225(9)	0.2609(10)	10.2(18)
C25A	0.4104(36)	0.9594(11)	0.2493(9)	14.1(23)
C26A	0.3284(30)	0.9108(9)	0.2846(9)	9.7(16)
C31A	0.2784(18)	0.7425(7)	0.5000(6)	3.5(8)
C32A	0.2167(21)	0.7407(9)	0.5578(7)	5.5(10)
C33A	0.2904(22)	0.7516(10)	0.6140(7)	6.6(12)
C34A	0.4313(26)	0.7673(8)	0.6111(6)	6.8(13)
C35A	0.5011(22)	0.7707(10)	0.5562(7)	7.1(12)
C36A	0.4221(21)	0.7583(9)	0.4992(7)	5.7(10)
C41A	0.2536(20)	0.6571(8)	0.3911(6)	4.6(9)
C42A	0.3199(21)	0.6576(7)	0.3349(6)	5.0(10)
C43A	0.3554(25)	0.6005(9)	0.3111(7)	6.8(12)
C44A	0.3241(25)	0.5446(9)	0.3402(9)	7.9(13)
C45A	0.2586(25)	0.5407(8)	0.3964(8)	7.0(12)
C46A	0.2210(23)	0.5977(8)	0.4229(7)	6.2(11)
C51A	−0.1861(21)	0.5423(8)	0.3385(7)	5.4(10)
C52A	−0.1427(24)	0.4983(8)	0.3753(8)	6.5(11)
C53A	−0.2178(30)	0.4360(9)	0.3843(9)	9.1(16)
C54A	−0.3369(32)	0.4230(10)	0.3562(11)	10.9(18)
C55A	−0.3873(28)	0.4592(10)	0.3109(10)	9.3(15)
C56A	−0.3089(28)	0.5235(9)	0.3055(9)	8.4(14)
C61A	−0.0770(46)	0.6424(11)	0.2581(9)	19.4(31)
C62A	−0.0768(26)	0.6047(10)	0.1993(7)	8.1(14)
C63A	−0.1302(43)	0.6380(12)	0.1515(12)	18.4(27)

Table 3 (continued)

Atom	x	y	z	B_{iso}
Compound **13**				
W1	0.74551(2)	0.10905(1)	0.08026(4)	3.63(2)
W2	0.63552(2)	0.16651(1)	0.21607(3)	3.52(2)
P1	0.67270(12)	0.12301(6)	−0.08935(17)	3.19(9)
P2	0.55488(11)	0.15301(6)	0.05819(18)	3.24(9)
P3	0.57109(13)	0.12464(7)	0.34817(19)	3.72(10)
N	0.5882(5)	0.2049(2)	0.2738(6)	5.1(4)
O1	0.6862(5)	0.0284(2)	0.1294(8)	7.3(5)
O2	0.8549(4)	0.0763(2)	−0.0841(9)	8.3(5)
O3	0.8344(4)	0.1824(2)	0.0774(7)	6.8(4)
O4	0.8425(6)	0.0919(3)	0.2788(9)	11.8(7)
O5	0.6992(4)	0.2284(2)	0.0631(6)	6.2(4)
O6	0.7609(5)	0.1758(4)	0.3761(7)	11.1(7)
O7	0.5573(5)	0.2306(2)	0.3100(7)	8.3(5)
C1	0.7058(5)	0.0575(3)	0.1085(9)	5.2(5)
C2	0.8153(5)	0.0881(3)	−0.0204(9)	5.0(5)
C3	0.7985(5)	0.1569(3)	0.0745(9)	5.0(5)
C4	0.8060(6)	0.0974(3)	0.2088(10)	6.6(6)
C5	0.6790(5)	0.2041(3)	0.1144(7)	4.2(4)
C6	0.7151(6)	0.1720(4)	0.3210(9)	6.7(7)
C8	0.6006(4)	0.1567(2)	−0.0755(7)	3.4(4)
C11	0.6340(5)	0.0837(2)	−0.1648(8)	3.9(4)
C12	0.6672(6)	0.0496(3)	−0.1564(9)	5.5(5)
C13	0.6436(7)	0.0192(3)	−0.2159(9)	6.4(7)
C14	0.5870(8)	0.0225(3)	−0.2811(10)	7.4(7)
C15	0.5549(6)	0.0573(4)	−0.2904(10)	7.1(6)
C16	0.5794(6)	0.0870(3)	−0.2354(9)	5.2(5)
C21	0.7222(5)	0.1456(2)	−0.2029(7)	3.3(3)
C22	0.7438(5)	0.1263(3)	−0.2919(8)	4.7(5)
C23	0.7840(6)	0.1434(3)	−0.3744(9)	5.9(6)
C24	0.8014(5)	0.1803(3)	−0.3653(8)	5.0(5)
C25	0.7805(6)	0.1993(3)	−0.2720(9)	5.6(5)
C26	0.7416(6)	0.1817(3)	−0.1912(9)	5.3(5)
C31	0.4890(4)	0.1891(2)	0.0538(7)	3.3(3)
C32	0.4881(5)	0.2164(3)	−0.0246(8)	4.1(4)
C33	0.4409(5)	0.2455(3)	−0.0151(9)	5.0(5)
C34	0.3938(5)	0.2458(3)	0.0715(8)	4.6(5)
C35	0.3944(5)	0.2173(3)	0.1476(9)	5.0(5)
C36	0.4415(5)	0.1896(3)	0.1410(8)	4.6(4)
C41	0.5067(4)	0.1101(2)	0.0412(7)	3.4(4)
C42	0.4513(5)	0.1092(3)	−0.0304(9)	4.8(5)
C43	0.4185(6)	0.0750(3)	−0.0475(11)	6.5(6)
C44	0.4370(6)	0.0437(3)	0.0076(10)	5.8(5)
C45	0.4920(6)	0.0450(3)	0.0768(10)	5.6(5)
C46	0.5272(5)	0.0782(2)	0.0968(8)	4.0(4)
C51	0.5433(5)	0.1469(3)	0.4779(7)	4.0(4)
C52	0.5853(5)	0.1721(3)	0.5335(8)	4.9(5)
C53	0.5592(7)	0.1888(3)	0.6274(9)	6.1(6)
C54	0.4959(7)	0.1808(3)	0.6706(9)	6.0(6)
C55	0.4564(6)	0.1564(4)	0.6169(10)	6.6(6)
C56	0.4777(5)	0.1381(3)	0.5210(8)	5.0(5)
C61	0.6096(5)	0.0809(2)	0.3877(8)	4.1(4)
C62	0.5733(6)	0.0482(3)	0.3819(10)	5.8(6)
C63	0.6056(8)	0.0150(3)	0.4121(12)	7.9(8)
C64	0.6712(7)	0.0152(3)	0.4526(11)	6.8(7)
C65	0.7063(6)	0.0472(3)	0.4608(11)	6.7(7)
C66	0.6753(6)	0.0797(3)	0.4269(11)	6.4(6)
H	0.685(4)	0.122(2)	0.187(7)	4.1(21)

THF (see Experimental section). Similar substitution of CO by THF was observed for $HW_2(CO)_9(NO)$ [3b]. Presently we do not know the reason of the decreased stability of **1** relative to **2** and **3**.

Deprotonation of primary or secondary phosphine ligands is a well known strategy to construct phosphido-bridged metal complexes [16]. The $PhPH_2$ ligand in **4** could also be easily deprotonated by NEt_3, and the resulting phosphide ligand was then able to undergo Michael addition [17] toward conjugated olefins CH_2=CHX (X = CN, C(O)H, C(O)Me) to form complexes (μ-H)(μ-dppm)$W_2(CO)_6(PhPH(CH_2CH_2X))(NO)$ (**10**, X = CN; **11**, X = C(O)H; **12**, X = C(O)Me).

There are two diastereomers for each of the complexes **10–12**, and the two isomers exist in approximately equal amounts. One isomer of **10** was characterized by X-ray structural determination (see below). The spectroscopic properties of these compounds appear to be normal: one hydride chemical shift around -10 to *ca.* -12 ppm (δ value) with two sets of tungsten satellites in the ^1H NMR, three different chemical shifts for the phosphorus atoms in the ^{31}P NMR, and a ν(NO) stretching around 1650 cm^{-1}. We reason that the presence of two isomers for **10–12** are due to the presence of two asymmetric centers in the complexes: the W_2 unit and the chiral phosphine ligand. Consequently, four possible isomers designated as *RR*, *SS*, *RS* and *SR* (the first letter represents the chirality of W_2 unit and the second letter represents the chirality of PhPH(Y)), will be produced from the reaction. Based on the structure of complex **13**, one would expect that the small hydrogen atom, **H**, in PhPH(Y) in **10–12** also leans towards $Ph_2P \sim PPh_2$. This together with approximate equal steric congestion for Ph and CH_2CH_2CN [18] would then make no preference for the chirality of $PhPH(CH_2CH_2CN)$ in **10–12**. Therefore, *RR*(*SS*) and *RS*(*SR*) are approximately in equal amounts for **10–12**.

We were able to grow single crystals for one of the diastereomers of **10**. Interesting isomerization occurred when these crystals were dissolved in acetone-d_6. It took less than 48 h for the equilibrium between the two diastereomers to be reached. The isomerization most likely involved the dissociation of $PhPH(CH_2CH_2CN)$ followed by the cross-over recombination, *i.e.*,

$$W_2(R)/\text{phosphine}(R) \rightarrow W_2(R) + \text{phosphine}(R)$$

$$W_2(S)/\text{phosphine}(S) \rightarrow W_2(S) + \text{phosphine}(S)$$

$$W_2(R) + \text{phosphine}(S) \rightarrow W_2(R)/\text{phosphine}(S)$$

$$W_2(S) + \text{phosphine}(R) \rightarrow W_2(S)/\text{phosphine}(R)$$

The lability of coordinated mono-dentate phosphines has been confirmed from our exchange experiments (Table 1). For example, $PhPH(CH_2CH_2CN)$ in **10** could be readily displaced by $PhPH_2$ and ^tBuNC, and so is $PhPH_2$ in (μ-H)(μ-dppm)$W_2(CO)_6(PhPH_2)(NO)$ by Ph_2PH. On the contrary, ^tBuNC in (μ-H)(μ-dppm)$W_2(CO)_6(^tBuNC)(NO)$ was found to be sufficiently robust. The facile dissociation of phosphine ligands might be owing to the steric crowdness in the dimer. The deprotonation of $PhPH_2$ in **4** with subsequent Michael addition, and then displacement of the newly formed phosphine ligand by $PhPH_2$ thus constitute a catalytic cycle. The turnover number in a one-pot reaction was found to be greater than 100. A blank experiment indicated that base-catalyzed addition of free phosphine ($PhPH_2$) to acrylonitrile [19] was negligible. Our future target will be

Table 4

Selected bond distances (Å) and angles (°) for complexes **10** and **13**

	10	**13**
W(1)–W(2); W(1A)–W(2A)	3.405(1); 3.387(1)	3.3966(7)
W(1)–C(1); W(1A)–C(1A)	2.02(2); 2.03(2)	2.04(1)
W(1)–C(2); W(1A)–C(2A)	2.00(2) 2.00(2)	1.97(1)
W(1)–C(3); W(1A)–C(3A)	1.91(2); 1.96(2)	2.01(1)
W(1)–C(4); W(1A)–C(4A)	1.92(2); 1.90(2)	1.99(1)
W(1)–P(1); W(1A)–P(1A)	2.524(5); 2.533(5)	2.533(2)
W(2)–C(5); W(2A)–C(5A)	1.93(2); 2.01(2)	2.012(9)
W(2)–C(6); W(2A)–C(6A)	2.02(1); 2.01(2)	2.01(1)
W(2)–P(2); W(2A)–P(2A)	2.529(5); 2.529(5)	2.509(2)
W(2)–P(3); W(2A)–P(3A)	2.506(4); 2.536(5)	2.525(2)
W(2)–N(1); W(2A)–N(1A)	1.74(1); 1.85(1)	
W(2)–N		1.803(8)
W(1)–H		1.81(8)
W(2)–H		1.89(8)
C(1)–O(1); C(1A)–O(1A)	1.14(2); 1.12(2)	1.14(1)
C(2)–O(2); C(2A)–O(2A)	1.17(2); 1.18(2)	1.17(1)
C(3)–O(3); C(3A)–O(3A)	1.20(2); 1.17(3)	1.16(1)
C(4)–O(4); C(4A)–O(4A)	1.17(2); 1.18(2)	1.12(1)
C(5)–O(5); C(5A)–O(5A)	1.21(2); 1.16(3)	1.14(1)
C(6)–O(6); C(6A)–O(6A)	1.11(2); 1.14(2)	1.12(1)
N(1)–O(7); N(1A)–O(7A)	1.24(2); 1.18(2)	
N–O(7)		1.19(1)
W(1)–C(1)–O(1); W(1A)–C(1A)–O(1A)	176(2); 174(2)	176(1)
W(1)–C(2)–O(2); W(1A)–C(2A)–O(2A)	171(2); 176(1)	177(1)
W(1)–C(3)–O(3); W(1A)–C(3A)–O(3A)	177(1); 169(2)	172.7(9)
W(1)–C(4)–O(4); W(1A)–C(4A)–O(4A)	176(2); 176(2)	177(1)
W(2)–C(5)–O(5); W(2A)–C(5A)–O(5A)	177(1); 177(2)	172.1(8)
W(2)–C(6)–O(6); W(2A)–C(6A)–O(6A)	170(1); 174(2)	177(1)
W(2)–N(1)–O(7); W(2A)–N(1A)–O(7A)	178(1); 178(1)	
W(2)–N–O(7)		178.8(8)
C(1)–W(1)–C(2); C(1A)–W(1A)–C(2A)	170.0(7); 166.2(7)	90.7(4)
C(1)–W(1)–C(3); C(1A)–W(1A)–C(3A)	83.8(7); 85.9(8)	168.8(4)
C(1)–W(1)–C(4); C(1A)–W(1A)–C(4A)	86.2(2); 85.4(7)	84.4(5)
C(1)–W(1)–P(1); C(1A)–W(1A)–P(1A)	85.8(6); 86.4(6)	96.0(3)
C(2)–W(1)–C(3); C(2A)–W(1A)–C(3A)	83.8(7); 84.0(8)	87.5(4)
C(2)–W(1)–C(4); C(2A)–W(1A)–C(4A)	86.6(6); 86.1(7)	89.4(4)
C(2)–W(1)–P(1); C(2A)–W(1A)–P(1A)	101.4(5); 104.9(6)	88.0(3)
C(3)–W(1)–C(4); C(3A)–W(1A)–C(4A)	91.3(8); 95.6(9)	84.6(5)
C(3)–W(1)–P(1); C(3A)–W(1A)–P(1A)	174.1(5); 158.3(6)	95.0(3)
C(4)–W(1)–P(1); C(4A)–W(1A)–P(1A)	91.6(6); 92.5(7)	177.4(4)
C(5)–W(2)–C(6); C(5A)–W(2A)–C(6A)	88.6(7); 88.6(7)	89.5(4)
C(5)–W(2)–P(2); C(5A)–W(2A)–P(2A)	170.8(5); 170.8(5)	86.2(3)
C(5)–W(2)–P(3); C(5A)–W(2A)–P(3A)	88.3(4); 85.5(5)	173.7(3)
C(5)–W(2)–N(1); C(5A)–W(2A)–N(1A)	94.8(7); 94.2(7)	
C(5)–W(2)–N		85.9(4)
C(6)–W(2)–P(2); C(6A)–W(2A)–P(2A)	93.2(5); 95.1(5)	167.6(4)
C(6)–W(2)–P(3); C(6A)–W(2A)–P(3A)	174.0(4); 173.9(6)	92.6(3)
C(6)–W(2)–N(1); C(6A)–W(2A)–N(1A)	91.9(5); 89.6(6)	
C(6)–W(2)–N		94.3(5)
P(2)–W(2)–P(3); P(2A)–W(2A)–P(3A)	89.1(2); 90.7(2)	92.88(7)
P(2)–W(2)–N(1); P(2A)–W(2A)–N(1A)	94.2(5); 94.2(5)	
P(2)–W(2)–N		97.0(3)
P(3)–W(2)–N(1); P(3A)–W(2A)–N(1A)	93.4(3); 91.9(4)	
P(3)–W(2)–N		88.0(3)
W(1)–H–W(2)		133(5)

Table 5

IR spectra in the ν(CO) region and ^{1}H and ^{31}P {H} NMR spectra of (μ-H)(μ-Ph$_2$ ~ PPh$_2$)W$_2$(CO)$_6$(L)(NO)

Compound	ν(CO), ν*(NO)* ^{a} (cm^{-1})	δ(ppm) ^{b,c}, J(Hz)	δ(ppm) ^{b,d}, J(Hz)
4	2030s, 2001m, 1958s, 1905sh, 1886s, 1879sh, *1628m*	*Ph* (7.75–6.84, m, 25H); P*H* (5.96, dm, 1H, ^{1}J(P–H) = 350); P*H* (5.05, (dm, 1H, ^{1}J(P–H) = 276); CH_2 (4.98, m, 1H); CH_2 (4.04, m, 1H); W–*H* (−10.2, m, 1H, ^{1}J(W–H) = 39.2)	*P*Ph$_2$ (23.6, d, 1P, ^{2}J(P–P) = 64.0, ^{1}J(W–P) = 232); *P*Ph$_2$ (11.6, dd, 1P, ^{2}J(P–P) = 64.0, 19.7; ^{1}J(W–P) = 208); Ph*P*H$_2$ (−72.6, d, 1P, ^{2}J(P–P) = 19.7; ^{1}J(W–P) = 211)
5	2028s, 2002m, 1955s, 1904sh, 1885s, 1867sh, *1639m*	*Ph* (7.80–7.42, m, 25H); P*H* (6.1, dm, 1H, ^{1}J(P–H) = 354); P*H* (5.0, dm, 1H, ^{1}J(P–H) = 346); CH_2 (3.3–2.6, br, m, 4H); W–*H* (−11.5, (pseudo quartet, ^{2}J(P–H) = 18.0, ^{1}J(W–H) = 42.0, 38.0)	*P*Ph$_2$ (23.7, br, 1P, ^{1}J(W–P) = 230); *P*Ph$_2$(16.6, dd, 1P, ^{2}J(P–P) = 18.9, 8.4; ^{1}J(W–P) = 226); Ph*P*H$_2$ (−67.2, br, 1P, ^{1}J(W–P) = 218)
6	2026s, 1998m, 1939m, 1896sh, 1870s, 1848sh, *1642m*	*Ph* (7.61–7.31, m, 25H); P*H* (6.0, dm, 1H, ^{1}J(P–H) = 353); P*H* (5.10, dm, 1H, ^{1}J(P–H) = 345); CH_2 (3.25, m, 2H); CH_2 (2.70, m, 2H); CH_2 (2.00, m, overlapping with acetone-d_6; W–*H*(−10.5, m, 1H, ^{1}J(W–H) = 44.1)	*P*Ph$_2$ (11.1, s, 1P, ^{1}J(W–P) = 207); *P*Ph$_2$ (5.45, d, 1P, ^{2}J(P–P) = 20.1, ^{1}J(W–P) = 230); Ph*P*H$_2$ (−66.3, d, 1P, ^{2}J(P–P) = 2.01; ^{1}J(W–P) = 221)
7	2030ms, 2003ms, 1964ms, 1906sh, 1884s, *1638m*, 2190w–m (ν(CN))	*Ph* (7.60–7.20, m, 20H); CH_aH$_b$ (4.40, m, 1H); CH$_a$$H_b$ (4.20, m, 1H); CH_2CH$_2$Me (3.58, t, 2H, ^{3}J(H–H) = 6.4); CH$_2$CH_2Me (1.55, m, 2H); CH$_2$CH$_2$*Me* (0.88, t, 2H, ^{3}J(H–H) 7.4); W–*H* (−10.8, pseudo triplet, ^{2}J(P–H) = 15.5, ^{1}J(W–H) = 35.0)	*P*Ph$_2$ (23.3, d, 1P, ^{2}J(P–P) = 57.9, ^{1}J(W–P) = 222); *P*Ph$_2$ (14.2, d, 1P, ^{2}J(P–P) = 57.9; ^{1}J(W–P) = 245)
8	2029ms, 2003m, 1959ms, 1899sh, 1878s, *1632m* 2194w–m (ν(CN))	*Ph* (7.68–7.41, m, 20H); NCH_2 (3.64, m, 2H); P CH_2 (3.10, br, 4H); NCH$_2$CH_2 (1.42, m, 2H); CH$_2$*Me* (0.75, t, 3H); W–*H* (−11.4, pseudo triplet, 1H, ^{2}J(P–H) = 18.0, ^{1}J(W–H) = 36.0)	*P*Ph$_2$ (24.8, d, 1P, ^{2}J(P–P) = 10.0, ^{1}J(W–P) = 215); *P*Ph$_2$ (17.2, d, 1P, ^{2}J(P–P) = 10.0; ^{1}J(W–P) = 226)

Table 5 (continued)

Compound	ν(CO), *ν(NO)* [a] (cm^{-1})	δ(ppm) [b,c], J(Hz)	δ(ppm) [b,d], J(Hz)
9	2027ms, 2001m, 1960ms, 1902m, 1876s, *1646m* 2197w–m (ν(CN))	Ph (7.66–7.36, m, 20H); NCH_2 (3.58, m, 2H); PCH_2 (3.17, m, 2H); PCH_2 (2.72, m, 2H); PCH$_2$CH_2 (1.90, m, 2H); NCH$_2$CH_2 (1.56, m, 2H); CH$_2$*Me* (0.86, t, 3H); W–*H* (−10.4, pseudo triplet, ^2J(P–H) = 18.0, ^1J(W–H) = 32.0)	*P*Ph$_2$ (11.6, s, 1P, ^1J(W–P) = 206); *P*Ph$_2$ (5.68, s, 1P, ^1J(W–P) = 232)
10	2025s, 1999m, 1954s 1928sh, 1885sh, 1905s *1632m*	Ph (7.48–7.38, m, 50H, isomers 1 & 2); P*H* (5.28, m, 2H, ^1J(P–H) = 357, isomers 1 & 2); PC H_aH$_b$P (4.94, m, 1H, isomer 1); PCH$_a$$H_b$P (4.74, m, 1H, isomer 2); PCH_aH$_b$P (3.60, m, 1H, isomer 1); PCH$_a$$H_b$P (3.55, m, 1H, isomer 2); CH_2 (2.50, m, 4H, isomers 1 & 2); CH_2 (2.20, m, 4H, isomers 1 & 2); W–*H* (−10.3, dddm, 1H, ^2J(P–H) = 26.5, 15.6, 11.0; ^1J(W–H) = 46.8, isomer 1); W–*H* (−10.0, dddm, 1H, ^2J(P–H) = 23.0, 15.3, 8.8; ^1J(W–H) = 41.9, isomer 2)	*P*Ph$_2$ (22.0, two overlapping doublets 2P, ^1J(W–P) = 229, isomers 1 & 2); *P*Ph$_2$ (11.6, dd, 1P, ^2J(P–P) = 64.8, 17.8; ^1J(W–P) = 251, isomer 1); *P*Ph$_2$ (10.1, dd, 1P, ^2J(P–P) = 63.9, 17.3; ^1J(W–P) = 251, isomer 2); Ph*P*H(Y) (−14.8, two overlapping doublets, 2P, ^1J(W–P) = 215, isomers 1 & 2)
11	2025s, 1999m, 1949s, 1904sh, 1885s, 1869sh, *1630m* 1724m (ν(C=O))	C(O)*H* (9.45, s, 1H, isomer 1(2)); C(O)*H* (9.32, s, 1H, isomer 1(2)); *Ph* (7.48–6.98, m, 50H, isomers 1 & 2); P*H* (5.15, dm, 2H, ^2J(P–H) = 340, isomer 1 & 2); PCH_aH$_b$ (4.80, m, 1H, isomer 1(2)); PCH_aH$_b$ (4.55, m, 1H, isomer 1(2)); PCH$_a$$H_b$ (3.6, m, 2H, isomers 1 & 2); CH_2 (2.45, m, 4H, isomers 1 & 2); CH_2 (2.14,	*P*Ph$_2$ (21.6, two overlapping doublets, 2P, ^2J(P–P) = 64.8; ^1J(W–P) = 227, isomers 1 & 2); *P*Ph$_2$ (11.9, dd, 1P, ^2J(P–P) = 64.8, 17.8; J(W–P) = 240, isomer 1(2)); *P*Ph$_2$ (10.5, dd, 1P, ^2J(P–P) = 64.0, 18.6; ^1J(W–P) = 246, isomer 1(2)); *P*Ph(Y) (−11.7, d, 2P, ^1J(W–P) = 224, isomers 1 & 2)

		m, 4H, isomer 1 & 2); W–*H* (−10.0, dddm, 1H, ^2J(P–H) = 24.0, 15.4, 8.5; ^1J(W–H) = 41.2, isomer 1(2)); W–*H* (−10.3, dddm, 1H, ^2J(P–H) = 24.0, 13.7, 12.0; ^1J(W–H) = 41.4, isomer (1(2))	
12	2012s, 2000m, 1952s 1907sh, 1884s, 1870sh, *1632m*, 1702s (ν(C=O))	*Ph* (7.46–7.14, m, 50H, isomers 1 & 2); P*H* (5.10, dm, 2H, ^1J(P–H) = 360, isomers 1 & 2); PCH_aH$_b$P (4.78, m, 1H, isomer 1(2)); PCH_aH$_b$P (4.52, m, 1H, isomer 1(2)); PCH$_a$$H_b$P (3.62, m, 2H, isomers 1 & 2); CH_2 (2.40, m, 4H, isomers 1 & 2); CH_2 (2.22, m, 4H, isomers 1 & 2); *Me* (1.86, s, 6H, isomers 1 & 2), W–*H* (−10.0, dddm, 1H, ^2J(P–H) = 22.0, 14.0, 8.0; ^1J(W–H) = 44.0, isomer 1); W–*H* (−10.3, dddm, 1H, ^2J(P–H) = 22.0, 12.0, 10.0; ^1J(W–H) = 44.0, isomer 2)	*P*Ph$_2$ (21.4, two overlapping doublets, 2P, ^2J(P–P) = 64.8; ^1J(W–P) = 229, isomers, 1 & 2); *P*Ph$_2$ (12.0, dd, 1P, ^2J(P–P) = 64.8, 17.8; ^1J(W–P) = 243, isomers, 1(2)); *P*Ph$_2$ (10.7, dd, 1P, ^2J(P–P) = 64.0, 17.0; ^1J(W–P) = 243, isomer 1(2)); Ph*P*H(Y) (−11.8, d, 2P, ^2J(P–P) = 17.8; ^1J(W–P) = 218. isomers 1 & 2)

---

[a] Measured in CH_2Cl_2 solution. [b] Measured in acetone-d_6. [c] Reported in ppm relative to $\delta(Me_4Si) = 0$ ppm. [d] Reported in ppm relative to δ (85% H_3PO_4) = 0 ppm. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. These abbreviations do not include the satellites.

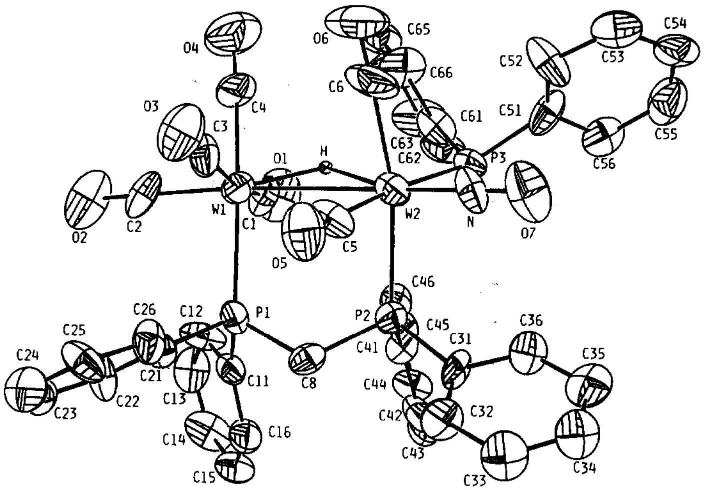

Fig. 1. Molecular structure of **13**. The ellipsoids are drawn with 30% probability boundaries.

the synthesis of optically pure chiral phosphines via chirality transfer through the use of chiral bidentate phosphine bridge.

Molecular structure of $(\mu\text{-}H)(\mu\text{-}dppm)W_2(CO)_6(Ph_2PH)(NO)$ *(13) and* $(\mu\text{-}H)(\mu\text{-}dppm)W_2(CO)_6(PhPH(CH_2CH_2CN))(NO)$ *(10)*

The ORTEP drawings of **13** and **10** are shown in Figs. 1 and 2, respectively. Two crystallographically independent molecules are found in **10** [20] and they differ only slightly in corresponding bond distances and angles. In both of the complexes the tungsten atoms reside in roughly octahedral environments. They are of the bent, staggered configuration, similar to $(\mu\text{-H})(\mu\text{-Ph}_2\text{P} \sim \text{PPh}_2)\text{W}_2(\text{CO})_7(\text{NO})$ [7]. The NO ligand in **13** or **10** is found to occupy the axial site (*i.e.*, *trans* to the bridging hydride) [21*]. As expected, the monodentate phosphine and NO ligands are coordinated to the same tungsten atom. In both complexes **13** and **10**, the **H** atom in **PhPH(Y)** lies closer to the bidentate phosphines so as to reduce the steric repulsion between phosphine ligands.

The position of μ-H was located in the final difference Fourier maps for **13**. The observed W–H distances (1.8/2.0 Å) and the W–H–W angle (126°) are in agreement with the reported values (W–H, 1.8–1.9 Å; W–H–W, 115–135°) [22].

The W–W distances in **13** (3.401(1) Å) and **10** (3.405(1); 3.387(1) Å) are longer than those in **1** (3.349(1); 3.350(1) Å), apparently due to the steric demanding of the phosphine ligands. Nevertheless, they are still shorter than that of the unsupported μ-H dimer, $(\text{CO})_5\text{W}(\mu\text{-H})\text{W}(\text{CO})_2(\text{Ph}_2\text{PH})_2(\text{NO})$ (3.418(1) Å) [3a].

Other relevant crystal data appear to be normal. The W–C–O and W–N–O linkages do not deviate significantly from linearity. The W–N distances in **13** (1.82 Å) and **10** (1.74(1)/1.85(1) Å) are shorter than those of W–C, ranging from 1.90–2.02 Å.

Supplementary material available: All bond distances and angles (Table S1: **13**, 3 pages; **10**, 4 pages), anisotropic thermal parameters and isotropic thermal

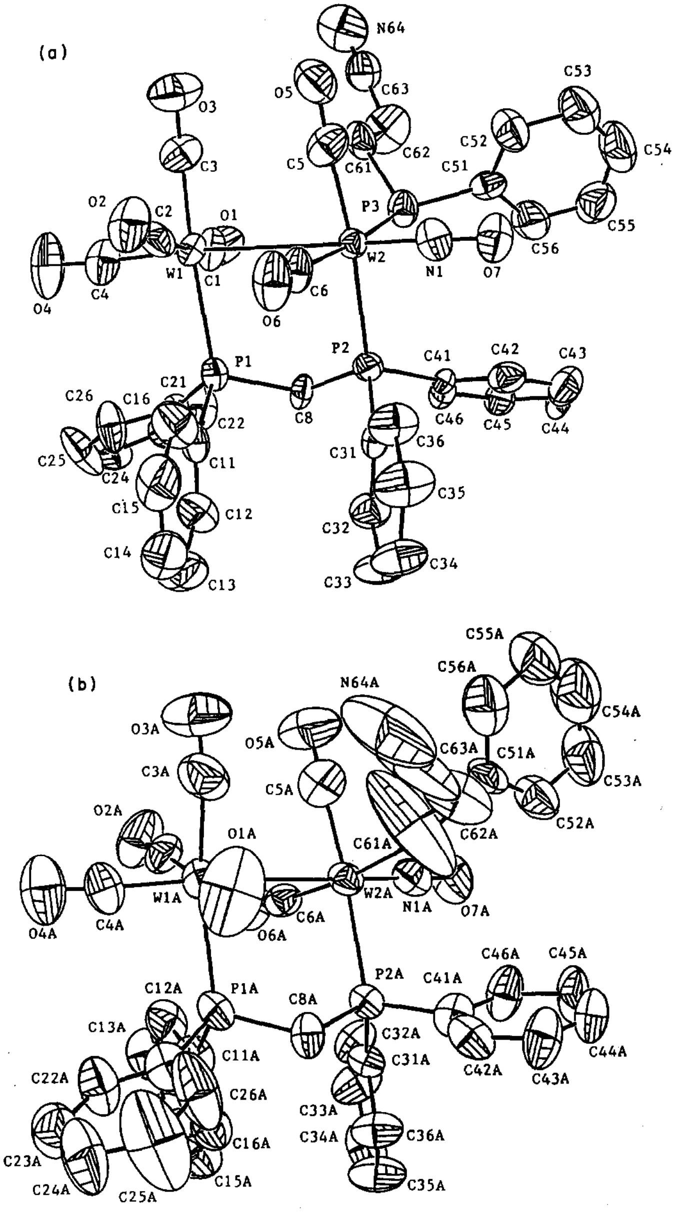

Fig. 2. Molecular structure of **10**. The ellipsoids of the two independent molecules are drawn with 30% probability boundaries.

parameters (Table S2: **13**, 2 pages; **10**, 3 pages), positional parameters for calculated hydrogen atoms (Table S3: **13**, 1 page; **10**, 1 page), and structure factors (Table S4: **13**, 21 pages; **10**, 34 pages), are all available from the authors.

Acknowledgment

We wish to thank the National Science Council of Republic of China for the support (Grant no. NSC80-0208-M001-38).

References

1 L.M. Venanzi, Coord. Chem. Rev., 43 (1982) 251.

2 B. Jezowska-Trzebiatowska and B. Nissen-Sobocinska, J. Organomet. Chem., 322 (1987) 331.

3 (a) J.T. Lin, S.Y. Wang, P.S. Huang, Y.M. Hsiao, Y.S. Wen and S.K. Yeh, J. Organomet. Chem., 388 (1990) 151; (b) M.K. Lee, P.S. Huang, Y.S. Wen and J.T. Lin, Organometallics, 9 (1990) 2181.

4 (a) M.Y. Darensbourg, J.L. Atwood, R.R. Burch Jr., W.E. Hunter and N. Walker, J. Am. Chem. Soc., 102 (1979) 2631; (b) M.Y. Darensbourg, J.L. Atwood, W.E. Hunter and N. Walker, J. Am. Chem. Soc., 102 (1980) 3290; (c) J.L. Petersen, R.K. Brown and J.M. Williams, Inorg. Chem., 20 (1981) 158; (d) J.L. Petersen, A. Masino and R.P. Stewart Jr., J. Organomet. Chem., 208 (1981) 55; (e) J. Roziere, P. Teulon and M.D. Grillone, Inorg. Chem., 22 (1983) 557.

5 (a) A. Blagg, R. Robson, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1987) 2171; (b) G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1987) 1509; (c) ibid., 1489.

6 (a) M.J. Mays and D.W. Prest, J. Chem. Soc., Chem. Commun., (1980) 171; (b) D.W. Prest, M.J. Mays and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1982) 737; (c) H.C. Aspinall and A.J. Deeming, J. Chem. Soc., Chem. Commun., (1983) 838; (d) F.J.G. Alonso, M.G. Sanz, V. Riera, M.A. Ruiz, A. Tiripicchio and M. Tiripicchio Camellini, Angew. Chem., Int. Ed. Engl., 27 (1988) 1167.

7 J.T. Lin, K.Y. Chang, S.Y. Wang, Y.S. Wen, C.C. Chang, S.M. Peng, Y. Wang and G.H. Lee, Organometallics, 10 (1991) 2377.

8 H. Zimmer and G. Singh, J. Org. Chem., 28 (1963) 483.

9 (a) E.J. Gabe and F.L. Lee, Acta. Crystallogr., 37 (1981) S339; (b) E.J. Gabe, Y. LePage, P.S. White and F.L. Lee, ibid., 43 (1987) C294.

10 International Tables for X-ray Crystallography: Kynoch, Birmingham, England, 1974, Vol. IV and Vol. III, p. 276.

11 It is generally recognized that nucleophilic attack at a coordinated CO is favorable if the metal carbonyl complex has at least one IR active CO stretching frequency approximately at or above 2000 cm^{-1}. (a) D.J. Darensbourg and M.Y. Darensbourg, Inorg. Chem., 9 (1970) 1691; (b) R.J. Angelici, Acc. Chem. Res., 5 (1972) 335.

12 M.Y. Darensbourg, R. El. Mehdawi, T.J. Delord, F.R. Fronczek and S.F. Watkins, J. Am. Chem. Soc., 106 (1984) 2583.

13 Compound $(\mu\text{-H})(\mu\text{-dppm})W_2(CO)_6({}^tBuNC)(NO)$ was isolated in a yield of 55%. IR (CH_2Cl_2, cm^{-1}): $\nu(CO)$ 2028ms, 2003m, 1963ms, 1883s, br; $\nu(NO)$ 1639m; $\nu(CN)$ 2174w–m). ^1H NMR(acetone-d_6. δ): *Ph* (7.50–7.38 m, 20H); CH_aH_b (4.5 m, 1H); CH_aH_b (3.7 m, 1H); ${}^tBu$ (1.4, s, 9H); W–*H* (−10.8, ddd, ^2J(P–H) 16.5, 13.9; ^4J(H–H) 2.04; ^1J(W–H) 41.4, 32.2 Hz). $^{31}P\{H\}$ NMR (acetone-d_6 δ): PPh_2 (22.0, d, 1P, ^2J(P–P) 56.8; ^1J(W–P) 221 Hz); PPh_2 (13.8, d, 1P, ^1J(W–P) 245 Hz). Anal. Found: C, 42.31; H, 3.03; N, 2.66. $C_{36}H_{32}N_2O_7P_2W_2$ calc.: C, 41.81; H, 3.12; N, 2.71%.

14 (a) G.L. Geoffroy, C.A. Mirkin, K.L. Lu, A.L. Rheingold and D.L. Staley, J. Am. Chem. Soc., 111 (1989) 7279; (b) H. Schmidbauer, Angew. Chem., Int. Ed. Engl., 22 (1983) 907; (c) H. Alper and R.A. Partis, J. Organomet. Chem., 35 (1972) C40.

15 G.B. Richter-Addo and P. Legzdins, Chem. Rev., 88 (1988) 1010 and references therein.

16 J. Powell, C. Couture, M.R. Gregg and J.F. Sawyer, Inorg. Chem., 28 (1989) 3437 and references therein.

17 J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, McGraw-Hill, New York, 1977.

18 C.A. Tolman, Chem. Rev., 77 (1977) 313.

19 G.M. Kosolapoff and L. Maier, Organic Phosphorus Compounds, Wiley, 1972, Vol. 1, p. 61.

20 The atomic coordinates were checked through with MISSYM program (Y. Le Page, J. Appl. Crystallogr., 20 (1987) 264), no extra symmetry element was found. The lattice parameters were also tried with several transformations, no monoclinic cell resulted.

21 The locations of the NO ligand was distinguished from the CO ligands by conspicuous discrepancies in the thermal parameters for the N and C atoms when incorrectly assigned.

22 R. Bau, R.G. Teller and T.F. Koetzle, Acc. Chem. Res., 12 (1979) 176.