

Phosphido bridged heterodinuclear (Mn/Fe, Mn/Cr, Mn/W) complexes

Giann T. Lin ^{a,*}, An C. Yeh ^b, Yung C. Chou ^a, Thomas Y.R. Tsai ^b, Yuh S. Wen ^a

^a Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan

^b Department of Chemistry, Chun-Yuan Christian University, Chung-Li, Taiwan

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Abstract

Treatment of (MeCp)Mn(CO)₂(Ph₂PLi), generated in situ, with M(CO)_n(THF) in THF at –60°C followed by cation exchange, provides [Et₄N][(MeCp)Mn(CO)₂(μ-PPh₂)M(CO)_n] (**3**, M = Fe, *n* = 4; **5**, M = Cr, *n* = 5; **6**, M = W, *n* = 5). Complex **3** reacts with NO⁺BF₄[–] to give (MeCp)MnFe(CO)₄(NO)(μ-PPh₂) (**7**) which contains a metal–metal (Mn–Fe) bond. Photolysis of **6** also results in formation of a metal–metal bond, and [Et₄N][(MeCp)MnW(CO)₆(μ-PPh₂)] (**8**) was isolated. Complex **8** reacts with CO and MeNC to afford **6** and [Et₄N][(MeCp)Mn(CO)₂(μ-PPh₂)W(CO)₄(MeNC)] (**9**), respectively. X-ray diffraction studies of [(MeCp)Mn(CO)₂(μ-Ph₂PPPh₂)] (**4**), **6**, and **9** were carried out to give data as follows. **4**: *P*2₁/*n*, *Z* = 4, *a* = 9.6875(9), *b* = 12.191(1), *c* = 15.382(2) Å, β = 107.20(1)°, *V* = 1735.4(4) Å³, *R* = 0.032, *R*_w = 0.036. **6**: *Pbca*, *Z* = 8, *a* = 13.197(2), *b* = 20.544(4), *c* = 24.953(4) Å, *V* = 6765(2) Å³, *R* = 0.031, *R*_w = 0.031. **9**: *P*2₁/*c*, *Z* = 4, *a* = 14.252(1), *b* = 12.816(3), *c* = 19.176(2) Å, β = 96.255(9)°, *V* = 3481.6(9) Å³, *R* = 0.035, *R*_w = 0.038.

Keywords: Iron; Manganese; Chromium; Phosphide; Heterobimetallics; Metal carbonyl anions

1. Introduction

The chemistry of heterobimetallic transition metal complexes has been of considerable interest for over a decade [1]. Owing to the intrinsic instability of the heteronuclear metal–metal bond, a bridge ligand is frequently introduced to prevent fragmentation of a heterodinuclear complex [2]. The phosphido ligand, PR₂, is one of the most favoured choices in this aspect because of its ability to bring two metal atoms into close proximity and because of the unique geometrical flexibility of the M–(μ-PR₂)–M linkage [3].

In view of the rich chemistry related to “CpMn(CO)₂” [4], it is somewhat surprising that phosphido bridged heterodinuclear complexes derived from this fragment and analogues are very rare [5]. Complex CpMn(CO)₂(PR₂H) which is available via the photochemical substitution of CpMn(CO)₃ [6] should be a good precursor for phosphido bridged dimers. In this

paper, we will describe several phosphido bridged heterodinuclear anions derived from (MeCp)Mn(CO)₂–(PPh₂H). Among many heterodinuclear complexes with a phosphido bridge in the literature, the anionic dimers appeared to be much less in quantity than their neutral analogues.

2. Experimental section

2.1. Materials and apparatus

The ¹H and ³¹P NMR spectra were recorded on Bruker AC200 or AC300 spectrometers. IR spectra were measured with a Perkin-Elmer 880 spectrometer. Electron impact (EI) mass spectra were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

All reactions and manipulations were carried out under N₂ with use of standard inert-atmosphere and Schlenk techniques. Solvents were dried by standard

* Corresponding author.

procedures. All column chromatography was performed with use of silica gel (230–400 mesh ASTM, Merck) as the stationary phase in a column 35 cm in length and 2.5 cm in diameter. (MeCp)Mn(CO)₃ was purchased from Strem. Fe₂(CO)₉ was prepared by the published procedure [7]. The synthesis of (MeCp)Mn(CO)₂(Ph₂PH) is described since no detail was provided in literature [8]. Complexes M(CO)₅(THF) (M = Cr, W) were prepared by irradiating a THF solution of M(CO)₆ [6], using a Hanovia medium pressure mercury lamp (450 W), at room temperature for 1–1.5 h. The photolysis was monitored by IR spectroscopy.

2.2. (MeCp)Mn(CO)₂(Ph₂PH) (1)

(MeCp)Mn(CO)₃ (12.8 g, 12.6 mmol) and Ph₂PH (3.21 g, 17.2 mmol) were dissolved in 200 ml of THF in a quartz Schlenk vessel. Under a continuous flow of nitrogen the solution was stirred magnetically and photolyzed for 2.5 h at 0°C with a 450 W Hanovia mercury vapour lamp. The solvent was removed and the crude reaction mixture was chromatographed. Elution with hexane recovered (MeCp)Mn(CO)₃ in 5% yield. Further elution with Et₂O/hexane (1:99) gave two removable bands. Complex 1 was isolated from the first band in 60% yield. The second band gave (MeCp)Mn(CO)(Ph₂PH)₂ (2) as orange oil in 10% yield.

2.3. [Et₄N][(MeCp)Mn(CO)₂(μ-PPh₂)Fe(CO)₄] (3)

A solution of 1 (1.01 g, 2.69 mmol) in THF (40 ml) was cooled to –60°C and n-BuLi (1.35 ml, 2.0 M) was added. The resulting dark red solution was stirred for 30 min and a solution of Fe₂(CO)₉ (1.10 g, 2.70 mmol) in THF (50 ml) was slowly added. After 12 h at –60°C the solvent was removed at room temperature. A solution of Et₄N⁺Br[–] (0.57 g, 2.70 mmol) in CH₃CN (40 ml) was added and the mixture was stirred at room temperature for 12 h. The red precipitates were filtered and the filtrate was pumped dry and washed with Et₂O (2 × 10 ml). Recrystallization of the residue from THF/Et₂O provided 3 as a yellow powder (941 mg, 52%). Anal. Found: C, 56.96; H, 5.45; N, 2.65. C₃₂H₃₇NO₆PF₆Mn calcd. C, 57.06; H, 5.50; N, 2.68%. The red precipitate was washed with CH₃CN and pumped dry to give [(MeCp)Mn(CO)₂]₂(μ-Ph₂PPH₂) (4) in 5% yield (101 mg). Anal. Found: C, 63.78; H, 4.52. C₄₀H₃₄O₄P₂Mn₂ calcd.: C, 63.98; H, 4.53%.

2.4. [Et₄N][(MeCp)Mn(CO)₂(μ-PPh₂)M(CO)₅] (5, M = Cr; 6, M = W)

The same procedure as that for the synthesis of 3 was followed except that M(CO)₅(THF) prepared *in situ* was used instead of Fe₂(CO)₉. Yellow powdery 5

Table 1
Crystal data for complexes 4, 6, and 9

	4	6	9
Formula	C ₂₀ H ₁₇ MnO ₂ P	C ₃₃ H ₃₇ MnNO ₇ PW	C ₃₄ H ₄₀ MnN ₂ O ₆ PW
Formula weight	375.26	829.42	842.45
<i>a</i> , Å	9.6875(9)	13.197(2)	14.252(1)
<i>b</i> , Å	12.191(1)	20.544(4)	12.816(3)
<i>c</i> , Å	15.382(2)	24.953(4)	19.176(2)
β, deg	107.20(1)		96.255(9)
Cryst. syst.	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4	8	4
<i>V</i> , Å ³	1735.4(4)	6765(2)	3481.6(9)
<i>D</i> _{calc} g/cm ³	1.436	1.629	1.607
Cryst. size, mm	0.34 × 0.24 × 0.28	0.39 × 0.16 × 0.14	0.20 × 0.20 × 0.20
Radiation	Mo Kα (λ = 0.7093 Å)	same	same
μ, cm ^{–1}	8.3	39.2	38.2
transmission factors (max; min)	1.00; 0.96	1.00; 0.86	1.00; 0.66
2θ range, deg	0–50	0–45	0–50
Octants	± h(–11 ~ 10), + k(0 ~ 14), + l(0 ~ 18)	+ h(0 ~ 14), + k(0 ~ 22), + l(0 ~ 26)	± h(–16 ~ 16), + k(0 ~ 15), + l(0 ~ 22)
No. of unique rflns.	3057	4406	6108
No. of rflns. with <i>I</i> > <i>nσ</i>	2186 (<i>n</i> = 2)	2244 (<i>n</i> = 2)	3799 (<i>n</i> = 2)
No. of variables	217	397	407
<i>R</i> , <i>R</i> _w	0.032; 0.036	0.031; 0.031	0.035; 0.038
GOF	1.50	1.15	1.47
max Δ/ <i>σ</i>	0.001	0.096	0.001

Table 2

Positional parameters and B_{iso} for the atoms in complexes **4**, **6**, and **9**

Atom	x	y	z	B_{iso}
Complex 4				
Mn	0.61034(5)	0.73914(4)	0.0648(3)	2.29(2)
P	0.47186(8)	0.59161(6)	0.01355(5)	1.88(3)
O1	0.4128(3)	0.8686(2)	0.0768(2)	5.9(2)
O2	0.8066(3)	0.7039(3)	0.1896(2)	5.2(1)
C1	0.4909(4)	0.8155(3)	0.0499(2)	3.5(2)
C2	0.7261(4)	0.7147(3)	0.1176(2)	3.1(2)
C3	0.7174(4)	0.7017(3)	−0.0961(2)	2.9(1)
C4	0.5786(4)	0.7450(3)	−0.1389(2)	3.1(1)
C5	0.5746(4)	0.8515(3)	−0.1062(2)	3.4(2)
C6	0.7094(4)	0.8747(3)	−0.0415(2)	3.4(2)
C7	0.7989(4)	0.7820(3)	−0.0357(2)	3.0(1)
C8	0.9570(4)	0.7752(3)	0.0179(3)	4.5(2)
C11	0.4484(3)	0.5725(2)	0.1274(2)	2.1(1)
C12	0.3278(4)	0.6134(3)	0.1477(2)	3.2(2)
C13	0.3132(4)	0.5999(3)	0.2346(3)	4.2(2)
C14	0.4167(5)	0.5458(3)	0.3005(3)	4.7(2)
C15	0.5389(5)	0.5078(3)	0.2826(2)	4.5(2)
C16	0.5558(4)	0.5226(3)	0.1965(2)	3.2(2)
C21	0.2827(3)	0.6007(3)	−0.0603(2)	2.1(1)
C22	0.1787(3)	0.5228(3)	−0.0589(2)	2.7(1)
C23	0.0420(4)	0.5278(3)	−0.1202(3)	3.6(2)
C24	0.0062(3)	0.6099(3)	−0.1846(2)	3.7(2)
C25	0.1055(4)	0.6903(3)	−0.1847(2)	3.6(2)
C26	0.2423(3)	0.6864(3)	−0.1231(2)	2.9(1)
Complex 6				
W	0.14545(4)	0.47184(2)	0.11830(2)	3.52(2)
Mn	0.14468(15)	0.67227(7)	0.07243(6)	3.55(8)
P	0.21918(20)	0.59027(13)	0.12239(12)	3.16(13)
N	0.6942(7)	0.3482(4)	0.1751(4)	4.3(5)
O1	0.0286(7)	0.4897(4)	0.2279(3)	6.8(5)
O2	−0.0503(7)	0.5241(4)	0.0583(3)	6.1(5)
O3	0.2440(8)	0.4429(5)	0.0050(4)	8.2(6)
O4	0.3410(7)	0.4300(4)	0.1834(4)	7.0(5)
O5	0.0581(7)	0.3301(4)	0.1227(4)	6.7(5)
O6	−0.0566(6)	0.6638(4)	0.1196(4)	6.2(5)
O7	0.2028(7)	0.7728(4)	0.1479(3)	6.3(5)
C1	0.0739(9)	0.4853(5)	0.1882(5)	4.4(6)
C2	0.0197(9)	0.5060(5)	0.0804(5)	4.3(6)
C3	0.2087(10)	0.4539(6)	0.0460(5)	5.2(7)
C4	0.2706(10)	0.4444(5)	0.1594(5)	4.6(6)
C5	0.0907(9)	0.3820(6)	0.1192(5)	4.7(6)
C6	0.0262(9)	0.6649(5)	0.1020(5)	4.2(6)
C7	0.1797(8)	0.7314(5)	0.1168(5)	4.5(6)
C8	0.2164(15)	0.7221(8)	0.0055(5)	6.0(9)
C9	0.1125(18)	0.7221(10)	−0.0010(7)	7.8(10)
C10	0.0760(15)	0.6598(16)	−0.0045(8)	10.9(17)
C11	0.1530(23)	0.6221(8)	−0.0019(6)	8.4(13)
C12	0.2426(12)	0.6559(11)	0.0061(5)	6.3(9)
C13	0.2774(18)	0.7788(11)	0.0085(6)	17.1(18)
C21	0.3577(8)	0.5951(5)	0.1070(3)	3.2(5)
C22	0.4111(9)	0.5445(5)	0.0816(4)	4.3(6)
C23	0.5093(9)	0.5549(6)	0.0651(5)	4.8(6)
C24	0.5572(9)	0.6141(7)	0.0737(5)	5.2(7)
C25	0.5053(9)	0.6624(6)	0.0999(4)	4.1(6)
C26	0.4079(8)	0.6530(5)	0.1156(4)	3.7(5)
C31	0.2250(8)	0.6066(4)	0.1954(4)	3.1(5)
C32	0.3072(9)	0.5881(5)	0.2257(5)	3.9(6)
C33	0.3069(10)	0.5956(5)	0.2810(5)	4.5(6)
C34	0.2211(11)	0.6188(6)	0.3067(5)	5.4(8)
C35	0.1396(12)	0.6364(6)	0.2765(5)	5.5(7)
C36	0.1407(10)	0.6317(5)	0.2213(4)	4.3(6)

Table 2 (continued)

Atom	x	y	z	B_{iso}
C41	0.6315(11)	0.3273(6)	0.1282(5)	5.6(7)
C42	0.5298(11)	0.3569(8)	0.1218(8)	9.9(11)
C43	0.7104(11)	0.4213(6)	0.1757(5)	6.4(7)
C44	0.7618(11)	0.4480(6)	0.1259(6)	7.8(8)
C45	0.6424(11)	0.3332(6)	0.2269(5)	6.2(7)
C46	0.6227(11)	0.2621(6)	0.2380(5)	7.0(8)
C47	0.7940(10)	0.3116(7)	0.1692(5)	5.9(7)
C48	0.8698(12)	0.3247(9)	0.2133(7)	10.4(13)
Complex 9				
W	0.27246(3)	0.03197(3)	0.17995(2)	3.21(2)
Mn	0.19267(11)	0.34797(11)	0.11704(7)	4.59(7)
P	0.22135(15)	0.22470(17)	0.20545(11)	3.29(10)
N1	0.4546(5)	0.0615(6)	0.2964(4)	4.4(4)
C1	0.3056(6)	−0.1149(8)	0.1629(4)	3.9(4)
C2	0.2026(6)	−0.0205(8)	0.2595(5)	4.4(4)
C3	0.1601(7)	0.0151(7)	0.1087(5)	4.1(5)
C4	0.3520(7)	0.0765(7)	0.1057(5)	4.7(5)
C5	0.3005(9)	0.3429(7)	0.0923(5)	5.5(6)
C6	0.2226(7)	0.4522(8)	0.1733(5)	4.7(5)
C7	0.3906(6)	0.0526(6)	0.2549(4)	3.8(4)
C8	0.5325(7)	0.0772(8)	0.3488(5)	5.8(5)
C9	0.1118(6)	0.2276(7)	0.2507(5)	4.1(4)
C10	0.0432(7)	0.1500(8)	0.2403(5)	5.2(5)
C11	−0.0397(8)	0.1565(11)	0.2696(7)	7.4(7)
C12	−0.0556(9)	0.2423(14)	0.3108(8)	8.8(9)
C13	0.0095(10)	0.3195(11)	0.3210(7)	8.2(8)
C14	0.0916(7)	0.3127(8)	0.2914(6)	5.5(5)
C15	0.3064(6)	0.2713(6)	0.2776(4)	3.2(4)
C16	0.2995(6)	0.2420(7)	0.3467(5)	4.3(5)
C17	0.3622(8)	0.2756(8)	0.4009(5)	5.1(5)
C18	0.4371(7)	0.3399(8)	0.3892(5)	4.9(5)
C19	0.4485(6)	0.3662(7)	0.3209(5)	4.5(5)
C20	0.3836(6)	0.3330(7)	0.2656(4)	4.0(4)
C21	0.1572(12)	0.4253(13)	−0.0372(10)	12.8(12)
C22	0.1185(9)	0.3877(13)	0.0195(6)	7.9(8)
C23	0.0743(9)	0.4335(10)	0.0674(7)	7.1(7)
C24	0.0377(8)	0.3621(12)	0.1093(6)	7.5(7)
C25	0.0663(9)	0.2608(10)	0.0817(8)	7.3(7)
C26	0.1161(9)	0.2735(9)	0.0256(7)	7.0(7)
O1	0.3192(5)	−0.2022(5)	0.1513(4)	6.1(4)
O2	0.1683(5)	−0.0533(6)	0.3062(4)	7.5(4)
O3	0.0972(5)	0.0026(6)	0.0671(4)	6.9(4)
O4	0.4004(5)	0.0940(6)	0.0622(3)	6.5(4)
O5	0.3797(6)	0.3459(6)	0.0729(4)	7.1(4)
O6	0.2408(5)	0.5248(6)	0.2088(4)	6.3(4)
N2	0.7070(5)	0.2075(6)	0.0798(4)	4.7(4)
C27	0.6943(8)	0.2176(9)	0.1567(5)	6.3(6)
C28	0.6031(9)	0.1782(11)	0.1784(6)	8.6(8)
C29	0.7020(9)	0.0943(9)	0.0564(6)	7.4(7)
C30	0.07772(13)	0.0246(10)	0.0937(8)	11.0(11)
C31	0.8016(7)	0.2548(7)	0.0695(5)	5.1(5)
C32	0.8294(8)	0.2522(9)	−0.0032(6)	7.1(7)
C33	0.6285(8)	0.2650(11)	0.0355(5)	6.7(7)
C34	0.6212(10)	0.3808(12)	0.0504(7)	9.8(9)

was isolated in a yield of 35%. Anal. Found: C, 57.02; H, 5.39; N, 1.96. $\text{C}_{33}\text{H}_{37}\text{NO}_7\text{PCrMn}$ calcd.: C, 56.81; H, 5.31; N, 2.01%. Complex **6** was isolated as yellow powders in 45% yield. Anal. Found: C, 47.98; H, 3.25; N, 1.67. $\text{C}_{33}\text{H}_{37}\text{NO}_7\text{PMnW}$ calcd.: C, 47.77; H, 3.26; N, 1.69%.

2.5. (MeCp)MnFe(CO)₄(NO)(μ-PPh₂) (7)

One equivalent of NO⁺BF₄[−] (90 mg, 0.75 mmol) was added all at once via a Schlenk tube into a vigorously stirring CH₂Cl₂ solution (40 ml) of **3** (500 mg, 0.75 mmol) prechilled to −60°C. After 12 h at −60°C the solvent was removed and the residue was chromatographed. Elution with hexane gave a red band, from which reddish brown **7** was isolated in 53% yield (204 mg) after removal of solvent. Anal. Found: C, 51.12; H, 3.24; N, 2.86. C₂₂H₁₇NO₅PF₆Mn calcd.: C, 51.06; H, 3.38; N, 2.92%.

2.6. [Et₄N][(MeCp)MnW(CO)₆(μ-PPh₂)] (8)

Nitrogen was continuously bubbled through a solution of **6** (2.50 g, 3.02 mmol) in THF (200 ml) prechilled to 0°C and the solution was irradiated with a 550 W Hanovia mercury vapour lamp for 30 minutes. The solution was concentrated to 5 ml and 200 ml of Et₂O was added. The supernatant was removed and the precipitates were washed with Et₂O and pumped dry to give **8** as a yellow-orange powder (82% yield). Anal. Found: C, 48.03; H, 4.69; N, 1.78. C₃₂H₃₇NO₆PMnW calcd.: C, 47.94; H, 4.62; N, 1.75%.

2.7. [Et₄N][(MeCp)Mn(CO)₂(μ-PPh₂)W(CO)₄(MeNC)] (9)

0.5 ml of MeNC was added to a flask containing 500 mg (0.655 mmol) of **8** in THF (30 ml) prechilled to 0°C. After 30 min at 0°C the solvent was removed and the residue was washed with Et₂O to provide yellow-orange, powdery **9** (274 mg, 52% yield). Anal. Found: C, 47.44; H, 4.72; N, 3.28. C₃₄H₄₀N₂O₆PMnW calcd.: C, 48.47; H, 4.79; N, 3.32%.

2.8. Crystallographic studies

Crystals of **4** and **6** were grown by slow diffusion of hexane into a concentrated solution of the corresponding complex in CH₂Cl₂, and **9** was grown by slow diffusion of Et₂O into a concentrated solution of **9** in CH₂Cl₂. Crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated Mo K_α radiation (λ = 0.7093 Å) with the θ – 2θ scan mode. Unit cells were determined by centring 25 reflections in the suitable 2θ range. Other relevant experimental details are listed in Table 1. Absorption corrections (empirical method) according to ψ scans of three reflections were applied. All data processing was carried out on a Micro Vax 3600 computer by the NRCC SDP program [9]. The coordinates of the transition-metal atoms were obtained from Patterson syntheses. The coordinates of all remaining

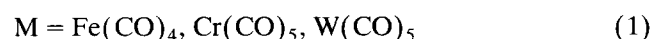
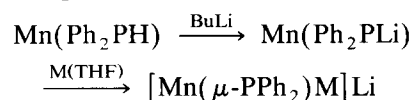
atoms except hydrogen were obtained from a series of structure factor calculations and Fourier syntheses. The structure were refined by minimizing Σw(|F_o| – |F_c|)², where w = 1/σ(F_o)² was calculated from the counting statistics. The atomic scattering factors and anomalous dispersion terms f' and f'' were taken from Ref. [10]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the structure factor calculation in idealized positions with d_{C–H} = 0.98 Å. The final positional parameters are listed in Table 2, and selected interatomic distances and bond angles are given in Table 3.

Supplementary material available

Comprehensive listings of bond lengths and angles for **4** (Table S1A, 2 pages), **6** (Table S1B, 3 pages) and **9** (Table S1C, 3 pages); anisotropic (non-hydrogen atoms) and isotropic (hydrogen atoms) thermal parameters for **4** (Table S2A, 1 page), **6** (Table S2B, 2 pages) and **9** (Table S2C, 2 pages); positional parameters for calculated hydrogen atoms for **4** (Table S3A, 1 page), **6** (Table S3B, 1 page) and **9** (Table S3C, 1 page); observed and calculated structure factors for **4** (Table S4A, 11 pages), **6** (Table S4B, 15 pages) and **9** (Table S4C, 21 pages), are available from the authors.

3. Results and discussion

Conversion of organometallic complexes to intermediates containing ligated solvents has been found useful in ligand substitution [11]. We successfully applied this strategy for the syntheses of several phosphido bridged heterodinuclear anions (Eqn. (1)).



Air sensitive complexes [Et₄N][(MeCp)Mn(CO)₂(μ-PPh₂)Fe(CO)₄] (**3**) and [Et₄N][(MeCp)Mn(CO)₂(μ-PPh₂)M(CO)₅] (**5**, M = Cr; **6**, M = W) could be isolated from the reaction of the lithiated phosphine complex [(MeCp)Mn(CO)₂(Ph₂PLi)], generated in situ, with Fe(CO)₄(THF) and M(CO)₅(THF) (M = Cr, W), respectively, in THF at −60°C followed by metathesis with Et₄N⁺Br[−]. A side product, [(MeCp)Mn(CO)₂](μ-PPh₂PPPh₂) (**4**) was also isolated in 5% yield during the synthesis of **3**. Complex **4** is probably derived from the dimerization of “(MeCp)Mn(CO)₂(PPh₂)”, the radical which forms from the oxidation of (MeCp)Mn(CO)₂(PPh₂Li). Dinuclear complexes with μ-R₂PPR₂ are

Table 3
Selected bond distances (Å) and angles (°) for complexes **4**, **6**, and **9**^a

	4	6	9
Mn–W		4.274(2)	4.342(2)
Mn–C(1)	1.763(4)		
Mn–C(2)	1.770(4)		
Mn–C(5)			1.66(1)
Mn–C(6)		1.74(1)	1.74(1)
Mn–C(7)		1.71(1)	
W–C(1)		2.00(1)	1.98(1)
W–C(2)		2.04(1)	2.025(9)
W–C(3)		2.02(1)	2.00(1)
W–C(4)		2.02(1)	2.00(1)
W–C(5)		1.98(1)	
W–C(7)			2.109(9)
Mn–P	2.2655(9)	2.315(3)	2.321(3)
W–P		2.622(3)	2.636(2)
P–Pa	2.365(2)		
C(1)–O(1)	1.161(4)	1.16(2)	1.16(1)
C(2)–O(2)	1.158(4)	1.14(2)	1.15(1)
C(3)–O(3)		1.15(2)	1.14(1)
C(4)–O(4)		1.14(2)	1.16(1)
C(5)–O(5)		1.15(1)	1.23(2)
C(6)–O(6)		1.18(2)	1.17(1)
C(7)–O(7)		1.19(2)	
C(7)–N(1)			1.15(1)
Mn–P–Pa	124.79(4)		
Mn–P–W		119.8(1)	122.2(1)
Mn–C(1)–O(1)	177.8(3)		
Mn–C(2)–O(2)	176.0(3)		
Mn–C(5)–O(5)			175.9(9)
Mn–C(6)–O(6)		175(2)	177.1(8)
Mn–C(7)–O(7)		179(1)	
W–C(1)–O(1)		176(1)	175.7(7)
W–C(2)–O(2)		178(1)	175.6(8)
W–C(3)–O(3)	179(1)	177.7(8)	
W–C(4)–O(4)		178(1)	174.5(8)
W–C(5)–O(5)		176(1)	
W–C(7)–N(1)			178.4(7)
P–Mn–C(1)	86.4(1)		
P–Mn–C(2)	92.0(1)		
P–Mn–C(5)			95.0(3)
P–Mn–C(6)		95.2(4)	93.3(3)
P–Mn–C(7)		93.1(4)	
C(1)–Mn–C(2)	91.3(2)		
C(5)–Mn–C(6)			92.0(5)
C(6)–Mn–C(7)		91.7(5)	
P–W–C(1)		90.7(3)	177.3(3)
P–W–C(2)		90.0(3)	90.2(3)
P–W–C(3)		92.9(3)	90.6(3)
P–W–C(4)		86.3(3)	93.1(3)
P–W–C(5)		177.1(4)	
P–W–C(7)			88.4(2)
C(1)–W–C(2)		88.4(5)	87.4(4)
C(1)–W–C(3)		175.6(5)	88.4(4)
C(1)–W–C(4)		88.9(5)	89.4(4)
C(1)–W–C(5)		87.0(5)	
C(1)–W–C(7)			92.6(3)
C(2)–W–C(3)		89.1(5)	93.2(3)
C(2)–W–C(4)		175.5(4)	174.6(4)
C(2)–W–C(5)		91.7(5)	
C(2)–W–C(7)			87.1(3)
C(3)–W–C(4)		93.7(5)	91.1(4)
C(3)–W–C(5)		89.5(5)	
C(3)–W–C(7)			179.0(3)

Table 3 (continued)

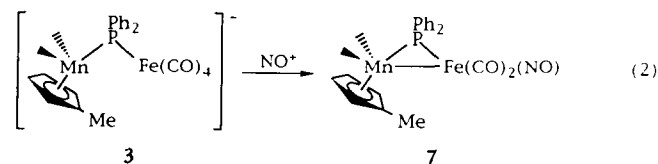
	4	6	9
C(4)–W–C(5)		91.8(5)	
C(4)–W–C(7)			88.7(3)

^a Atoms P and Pa are symmetry equivalent.

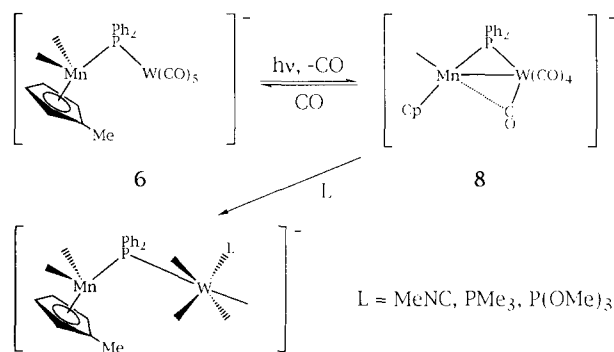
generally synthesized by use of R_2PPR_2 [12], and to our knowledge, there was no example for the formation of $M(\mu-R_2PPR_2)M$ complexes via the coupling of $M(PR_2)$. On the contrary, cleavage of R_2PPR_2 to form phosphides is more common [13].

The $\nu(CO)$ stretchings of **3**, **5** and **6** in the IR spectra (Table 4) appear to be lower than those of $M(CO)_n(Ph_2PH)$ ($M = Fe$, $n = 4$; $M = Cr$, W , $n = 5$) [14] and are consistent with the anionic nature of the dimers. The crystal structural determination of **6** (vide infra) indicates the absence of the metal–metal bond in these new complexes. The chemical shift (δ) of $\mu-PPh_2$ for the three (**3**, 88.6 ppm; **5**, 60.3 ppm; **6**, 26.0 ppm) appears to be higher than those (–50 to –150 ppm) normally observed for phosphido bridged dimers without a metal–metal bond [15]. This could possibly be a result of the high δ_P value (76 ppm) for (MeCp) $Mn(CO)_2(Ph_2PH)$.

Reaction of phosphine-substituted metal carbonyls with NO^+ salts was found to be an effective way for the incorporation of NO ligands [16]. Treatment of **3** with $NO^+BF_4^-$ affords the complex (MeCp) $MnFe(CO)_4(NO)(\mu-PPh_2)$ (**7**) (eqn. 2) which has a very prominent $\nu(NO)$ absorption at 1720 cm^{-1} . The higher $\nu(CO)$ stretchings in **7** than in **3** agrees well with the decreasing electron density in **7** and the better π -accepting ability of NO than CO. The NO ligand is most probably coordinated to the iron atom since only the fragments, “(MeCp) $Mn(CO)_2(\mu-PPh_2)$ ” ($m/e = 375$) and “ $Fe(CO)_2(NO)(\mu-PPh_2)$ ” ($m/e = 327$), but not “(MeCp) $Mn(NO)$ ”, “(MeCp) $Mn(NO)(PPh_2)$ ”, and “ $Fe(CO)_4(PPh_2)$ ”, were observed in the mass spectra. Nitrosylation of **3** seemed to also promote the formation of Mn–Fe metal–metal bond on the basis of the following reasons: (1) the electron-counting rule would require the presence of Mn–Fe bond for (MeCp) $Mn(CO)_2(\mu-PPh_2)Fe(CO)_2(NO)$; (2) the chemical shift of $\mu-PPh_2$ (255 ppm) for the complex **7** appears at an unusually lower field than those of **7** and $Fe(CO)_4(\mu-PPh_2)Fe(CO)_2(NO)$ (194 ppm) [17] in the $^{31}P\{H\}$ NMR spectra.



Reactions of **5** or **6** with $NO^+BF_4^-$ did not result in formation of a metal–metal bond and only intractable



Scheme 1.

products were obtained. It was well recognized that photolytic extrusion of a carbonyl ligand could lead to formation of a metal–metal bond [18]. Not unexpectedly, **6** readily loses a CO ligand upon photolysis and affords the complex [Et₄N][(MeCp)MnW(CO)₆(μ -PPh₂)] (**8**) (Scheme 1). The ³¹P{H} chemical shift of μ -PPh₂ (152 ppm) for complex **8** appears at much lower field than that of **6** (26.0 ppm) and suggests the presence of the metal–metal (Mn–W) bond in **8**. Photolytic extrusion of a CO from CpFe(CO)₂(μ -PPh₂)W(CO)₅, an isoelectronic analogue of **6**, gave CpFe(CO)(μ -CO)(μ -PPh₂)W(CO)₄ which contains a metal–metal bond and a semibridging CO [19]. Complex **8** probably has a structure similar to that of CpFe(CO)(μ -CO)(μ -PPh₂)W(CO)₄ both in solution

and in solid state on the basis of the similarity of the IR spectra between the two. The absence of bridging CO absorption in solution IR may be due to the existence of another structural isomer which does not contain a bridging carbonyl. This feature is similar to that reported for CpFe(CO)(μ -CO)(μ -PPh₂)W(CO)₄ [19] and CpW(CO)₂(μ -CO)(μ -PPh₂)Cr(CO)₄ [20]. The latter was obtained from the thermal extrusion of a CO ligand from complex CpW(CO)₃(μ -PPh₂)Cr(CO)₅.

The complex **8** is extremely air-sensitive and has to be stored at temperature below 0°C. Under an atmospheric pressure of CO, the complex **8** was converted to **6** instantaneously. Reactions of **8** with MeNC was also complete within seconds, and a new complex [Et₄N][(MeCp)Mn(CO)₂(μ -PPh₂)W(CO)₄(MeNC)] (**9**) was isolated and characterized by a single crystal structural determination (vide infra). The reaction of **8** with MeNC bears close resemblance to that of CpW(CO)₂(μ -CO)(μ -PPh₂)Mo(CO)₄ [21]. Our preliminary results indicated that **8** also reacted with PMe₃ and P(OMe)₃ instantaneously to afford extremely air-sensitive complexes [Et₄N][(MeCp)Mn(CO)₂(μ -PPh₂)W(CO)₄(*L*)] (**10**, *L* = PMe₃; **11**, *L* = P(OMe)₃). The ν (CO) stretchings of **10** and **11** are similar to those of **9**, suggesting that **9**, **10** and **11** have a similar structure. The chemical shifts of μ -PPh₂ (**10**, δ = 30.0 ppm; **11**, δ = 24.0 ppm) and the presence of the tungsten satellites for *L* (**10**, δ = –34.0 ppm, *J*_{W–P} = 234

Table 4
IR spectra and ¹H and ³¹P{H} NMR spectra for complexes 1–9

Compound	ν (CO), ν (NO) ^a (cm ^{–1})	δ (ppm) ^{b,c} , J(Hz)	δ (ppm) ^{b,d} , J(Hz)
1	1930s, 1863s, 2272m	<i>Ph</i> (7.90–7.25, m, 10H); <i>H</i> PPh ₂ (7.00, d, ¹ <i>J</i> (P–H) = 312, 1H); C ₅ H ₄ (4.36, br, 4H); <i>Me</i> (1.67, s, 3H)	<i>P</i> Ph ₂ (76.2, s, br, ¹ <i>J</i> (P–H) = 312 for power-off)
2	(ν (P–H)) 1828m, 2305m (ν (P–H))	<i>Ph</i> (7.60–7.30, m, 20H); <i>H</i> PPh ₂ (6.80, d, ¹ <i>J</i> (P–H) = 328, 2H); C ₅ H ₄ (4.30, br, 4H); <i>Me</i> (1.62, s, 3H)	<i>P</i> Ph ₂ (80.2, s, br, ¹ <i>J</i> (P–H) = 328 for power-off)
3 ^e	2011m, 1926sh, 1904s 1839m	<i>Ph</i> (7.90–7.10, m, 10H); C ₅ H ₄ (4.40, br, 2H), (4.11, br, 2H); <i>Me</i> (1.86, s, 3H)	<i>P</i> Ph ₂ (88.6, s, br)
4	1926s, 1883s	<i>Ph</i> (7.80–7.15, m, 10H); C ₅ H ₄ (3.98, br, 4H); <i>Me</i> (1.89, s, 3H)	<i>P</i> Ph ₂ (103, s)
5 ^e	2038w, 1956sh, 1916vs, 1907sh, 1877m, 1828w	<i>Ph</i> (7.83–7.07, m, 10H); C ₅ H ₄ (3.96, br, 2H), (3.91, br, 2H); <i>Me</i> (1.66, s, 3H)	<i>P</i> Ph ₂ (60.3, s, br)
6 ^e	2050w, 1958sh, 1916vs, 1875m, 1828w	<i>Ph</i> (7.76–7.04, m, 10H); C ₅ H ₄ (3.85, m 4H); <i>Me</i> (1.63, s, 3H)	<i>P</i> Ph ₂ (26.0, s, br, ¹ <i>J</i> (W–P) = 248)
7	2016s, 1958s, 1940sh, 1916sh, 1712s	<i>Ph</i> (7.35–7.16, m, 10H); C ₅ H ₄ (4.64, br, 2H), (4.10, br, 2H); <i>Me</i> (2.09, s, 3H)	<i>P</i> Ph ₂ (255, s)
8 ^e	1990m, 1915sh, 1891s, 1859s, 1839sh ^f 1986m, 1880s, 1850s, 1813s, 1740m	<i>Ph</i> (7.90–7.10, m, 10H); C ₅ H ₄ (4.21, br, 2H), (3.77, br, 2H); <i>Me</i> (1.60, s, 3H)	<i>P</i> Ph ₂ (152, s, ¹ <i>J</i> (W–P) = 230)
9 ^e	1995s, 1888vs, 1857sh, 1830s, 1825s, 2162m	<i>Ph</i> (7.88–6.95, m, 10H); C ₅ H ₄ (3.93, br, 2H), (3.83, br, 2H); MeNC (3.06, s, 3H); <i>Me</i> (1.60, s, 3H)	<i>P</i> Ph ₂ (32.3, s, ¹ <i>J</i> (W–P) = 167)

^a Measured in CH₂Cl₂ (**1**, **2**, **4**, **7**) or THF (**3**, **5**, **6**, **8**, **9**). ^b Measured in CDCl₃ (**1**, **2**, **4**, **7**) or CD₃CN (**3**, **5**, **6**, **8**, **9**). ^c Reported in ppm relative to δ (Me₄Si) = 0 ppm. ^d Reported in ppm relative to δ (85% H₃PO₄) = 0 ppm. ^e The ¹H NMR signals of Et₄N⁺ are very similar. CH₂ protons appear as quartet (³*J*(H–H) = 7.2 Hz) or broad peaks in δ 3.15–3.35 region, and CH₃ protons appear as triplet of triplet (³*J*(N–H) = 2.0 Hz) or broad peaks. ^f Nujol mull.

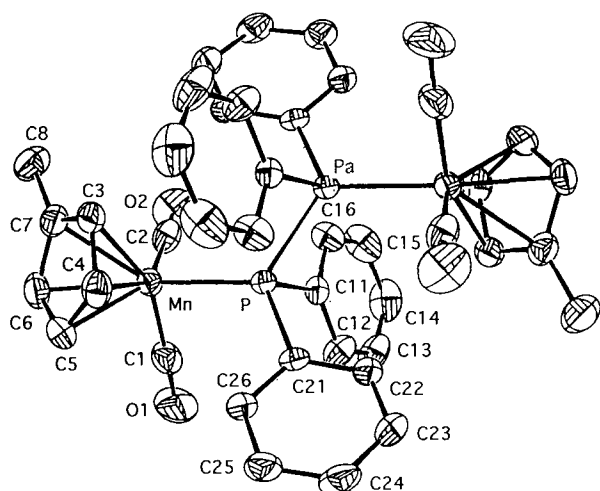


Fig. 1. ORTEP drawing of $[(\text{MeCp})\text{Mn}(\text{CO})_2]_2(\mu\text{-Ph}_2\text{PPPh}_2)$. Only one half of the molecule is labelled because of the presence of an inversion centre. The Pa and P atoms are related by the inversion centre. Thermal ellipsoids are drawn with 30% probability boundaries.

Hz; **11**, $\delta = 150$ ppm, $J_{\text{W-P}} = 353$ Hz) in the $^{31}\text{P}\{\text{H}\}$ NMR are consistent with the absence of a metal–metal bond [14] and ligation of L at the tungsten atom. The coupling constants, $^2J_{(\mu\text{-P})\text{-L}}$, for **10** (22 Hz) and **11** (24 Hz) agree with those of mutually *cis* phosphorus atoms reported by Schenk on $\text{W}(\text{CO})_4(\text{P}(\text{P}'))$ [22]. Further

investigation as well as parallel reactions for **5** will be pursued in future.

3.1. Crystal Structure of $[(\text{MeCp})\text{Mn}(\text{CO})_2](\mu\text{-Ph}_2\text{PPPh}_2)$ (**4**), $[\text{Et}_4\text{N}][(\text{MeCp})\text{Mn}(\text{CO})_2(\mu\text{-PPh}_2)\text{W}(\text{CO})_5]$ (**6**), and $[\text{Et}_4\text{N}][(\text{MeCp})\text{Mn}(\text{CO})_2(\mu\text{-PPh}_2)\text{W}(\text{CO})_4(\text{MeNC})]$ (**9**)

The ORTEP drawings of **4** and the anions of **6** (**6⁻**) and **9** (**9⁻**) are shown in Figs. 1–3, respectively. Important interatomic distances and angles are listed in Table 3. The structure of **4** is similar to those of $[\text{Ni}(\text{CO})_3]_2(\mu\text{-Ph}_2\text{PPPh}_2)$ [23] and $[\text{Fe}(\text{CO})_4]_2(\mu\text{-Me}_2\text{PPMe}_2)$ [24] in having a centrosymmetric μ -catenary form and a staggered conformation of substituents about the Mn–P and P–P bonds. The rather long P–Pa distance (2.365(2) Å) [25] and the large Mn–P–Pa angle (124.79(4) Å) reflect the steric crowding of the molecule. Other relevant crystal data appear to be normal.

The anions, **6⁻** and **9⁻**, have a very similar structure. The long distance between Mn and W atoms (**6**, 4.274(2); **9**, 4.342(2) Å) preclude the existence of a metal–metal bond. The obtuse Mn–P–W angle (**6**, 119.8(1)°; **9**, 122.18(9)°) is also consistent with this argument. The MeCp ring stays away from the phenyl ring so as to avoid steric congestion. The tungsten atom resides in roughly octahedron environment. The

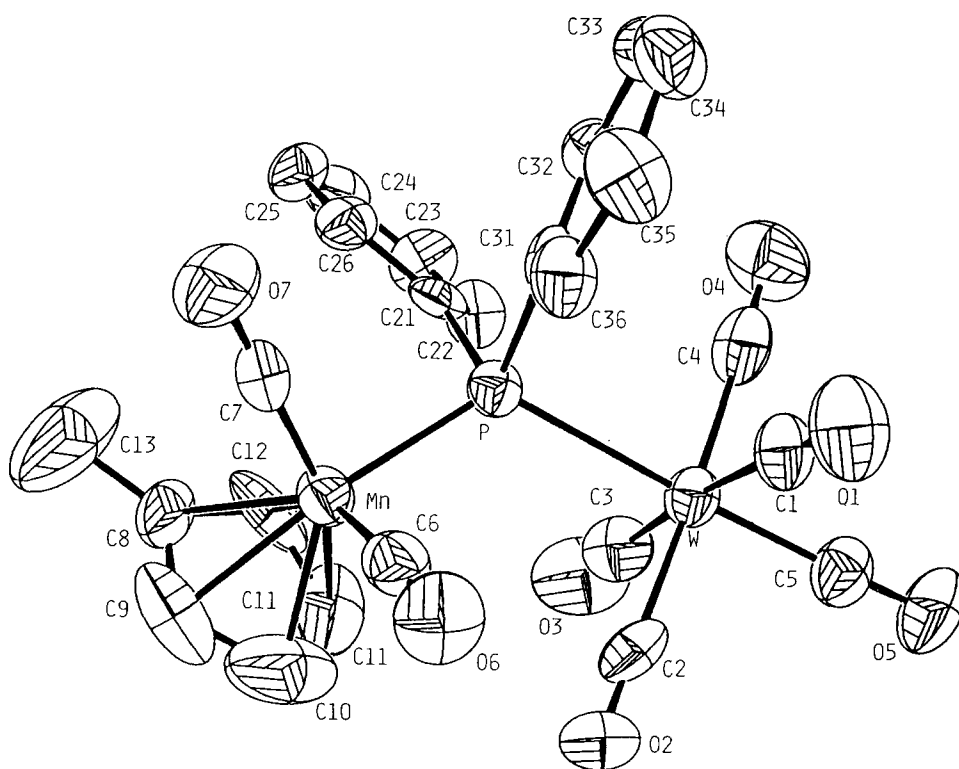


Fig. 2. ORTEP drawing of $[(\text{MeCp})\text{Mn}(\text{CO})_2(\mu\text{-PPh}_2)\text{W}(\text{CO})_5]^-$. Thermal ellipsoids are drawn with 30% probability boundaries.

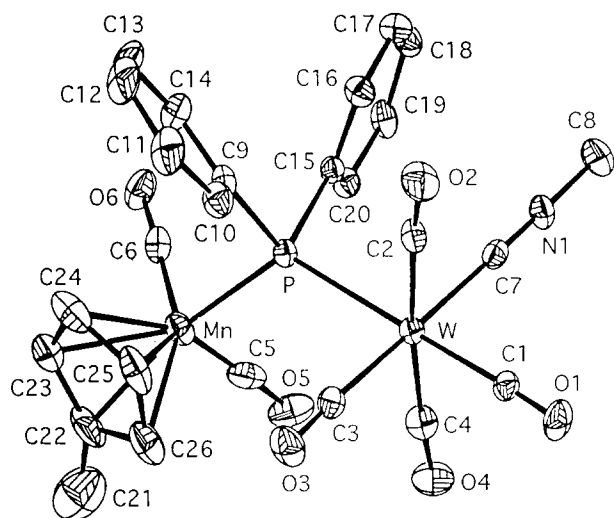


Fig. 3. ORTEP drawing of $[(\text{MeCp})\text{Mn}(\text{CO})_2(\mu\text{-PPh}_2)\text{W}(\text{CO})_4(\text{MeNC})]^-$. Thermal ellipsoids are drawn with 30% probability boundaries.

MeNC ligand in **9** is linearly coordinated to the W atom ($\text{W}-\text{C}7-\text{N}1 = 178.4(7)^\circ$) and is *cis* to the phosphido bridge. All carbonyls are in a linear fashion (**6**, ave. $\text{M}-\text{C}-\text{O} = 177(2)^\circ$; **9**, ave. $\text{M}-\text{C}-\text{O} = 176(1)^\circ$). The carbonyl ligand which is *trans* to $\mu\text{-PPh}_2$ has a shorter metal–carbon distance (**6**, 1.98(1); **9**, 1.98(1) Å) than the average of the remaining carbonyls on the tungsten atom (**6**, 2.02(2); **9**, 2.01(1) Å) since CO and MeNC are better π -electron-acceptor than phosphine. The W–P bond length for **6**[−] (2.622(3) Å) and **9**[−] (2.636(2) Å) is more elongated than Mn–P bond (**6**, 2.315(3); **9**, 2.321(3) Å) compared to their corresponding sum of covalent radii (W, 1.30; Mn, 1.17; P, 1.10 Å).

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