δ 0.45 (s, 12 H, $Si(CH_3)_2$), 1.04 (s, 4 H, $SiCH_2$), 6.07 (t, *J*(H-H) = 2.7 Hz, 4 H, C_5H_4), 6.62 (t, *J*(C-H) = 2.7 Hz, 4 H, C_5H_4). FD mass spectrum (10 mA, CH_2Cl_2): molecular ion at *m/e* 1044. Molecular weight determination (in benzene, cryoscopic): calcd 521.9; found, 512. Anal. Calcd for $C_{16}H_{24}Cl_2HfSi_2$: C, 36.82; H, 4.64. Found: C, 37.37; H, 4.71.

Acknowledgment. We are grateful to the U.S. Air Force Office of Scientific Research (Grant AF-AFOSR-85-0265) for support of this work. H.L. is indebted to the Deutsche Forschungsgenienschaft (DFG) for a postdoctoral fellowship.

Registry No. 1, 130904-26-6; **3a**, 130904-27-7; **3b**, 130904-28-8; **3c**, 130904-29-9; cyclopentadiene, 542-92-7; 1,4-dichloro-1,1,4,4-tetramethyl-1,4-disilabutane, 13528-93-3; titanium tetrachloride, 7550-45-0; zirconium tetrachloride, 10026-11-6; halfnium tetrachloride, 13499-05-3.

Tungsten(0) Complexes of Bis(dialkoxyphosphino)methylamines. Crystal and Molecular Structure of the Novel Cycloheptatriene-Bridged Dimer $[(mer\text{-}W(CO)_3(CH_3N(P(OCH_3)_2)_2))_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_7H_8)]$

Joel T. Mague* and M. Pontier Johnson

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Received March 21, 1990

Summary: The cycloheptatriene-bridged ditungsten complexes $[(mer\text{-}W(CO)_3(CH_3N(P(OR)_2)_2))_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_7H_8)]$ (R = CH_3 (**1**), $CH(CH_3)_2$ (**2**), CH_2 (**3**)) have been identified as minor products of the reaction of $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ with $CH_3N(P(OR)_2)_2$. Slow reaction of **1** with carbon monoxide occurs to form *cis*-$[W(CO)_4(CH_3N(P(OCH_3)_2)_2)]$. The crystal structure of **1** (triclinic $P\bar{1}$, *a* = 14.256 (4) Å, *b* = 14.629 (4) Å, *c* = 9.737 (4) Å, α = 97.51 (3)°, β = 96.89°, γ = 64.25 (2)°, *Z* = 2, 3106 data ($I \geq 3\sigma(I)$), *R* = 0.034, R_w = 0.045) shows the two $[mer\text{-}W(CO)_3(CH_3N(P(OCH_3)_2)_2)]$ moieties to be bonded to the same face of the cycloheptatriene ring, which adopts a tub conformation, via the two nonadjacent carbon–carbon double bonds. Metal–metal bonding is absent.

Few tungsten complexes containing simple η^2-olefin ligands are known[1-11] and even fewer have been structurally characterized.[1,7,10,11] The number of bimetallic complexes bridged solely by a cyclic polyolfin where metal–metal bonding is absent is also small, and to the best of our knowledge, the only examples previously reported are $[(Fe(CO)_4)_2(\mu\text{-}\eta^2{:}\eta^2\text{-ol})]$ (ol = cycloocta-1,3,6-triene,[12] cycloocta-1,5-diene,[13] 1,1′-diphenylfulvalene[14]), $[(cpFe(CO)_2)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_4H_4)]$,[15] and $[(ML_n)_2(\mu$-hexafluorobicyclo[2.2.0]hexa-1,4-diene)] (ML_n = $Pd(PPh_3)_2$, $Pt(PPh_3)_2$, $Rh(acac)(C_2H_4)$).[16] Of these, only two are structurally characterized.[13,14] We report here the synthesis and structural characterization of what appears to be the first example of a ditungsten complex, $[(mer\text{-}W(CO)_3(CH_3N(P(OCH_3)_2)_2))_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_7H_8)]$, containing a bridging cyclic polyolefin and the first fully characterized example of this mode of coordination for cycloheptatriene.

Experimental Section

All manipulations were preformed under an atmosphere of purified nitrogen by using standard Schlenk techniques. Solvents were appropriately dried and distilled in an inert atmosphere prior to use. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on an IBM/Bruker AF200 spectrometer at 200.132 and 81.015 MHz, respectively, and referred to tetramethylsilane (δ 0.0) and 85% H_3PO_4 (δ 0.0) as external standards. Positive chemical shifts are downfield of the standard. Literature methods were used to prepare $[W(CO)_3(\eta^6\text{-}C_7H_8)]$[17] and $CH_3N(P(OR)_2)_2$ (R = $CH_3(L_2)$,[18] $CH(CH_3)_2(L'_2)$,[19] $CH_2(L''_2)$[19]).

$[(mer\text{-}W(CO)_3(CH_3N(P(OCH_3)_2)_2))_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_7H_8)]$ (1). A toluene solution (10 mL) of $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ (0.300 g, 0.833 mmol) and $CH_3N(P(OCH_3)_2)_2$ (0.269 g, 1.250 mmol) was stirred for 6 h at room temperature. The solvent was removed in vacuo (25 °C) to give a yellow oil that was taken up in a few drops of toluene and chromatographed on a 1.5 × 20 cm column of Brockman I alumina. Development with hexane followed by elution with hexane/diethyl ether (4:1, v:v) removed a yellow band that was shown by ^{31}P NMR to be a mixture of 1 and *cis*-$[W(CO)_4(L_2)]$.[19] Futher elution with hexane/diethyl ether (1:1, v:v) afforded a second fraction containing more 1 together with a large quantity of *mer*-$[W_2(CO)_6(L_2)_2(\mu\text{-}L_2)]$[19] and a small amount of *mer*-$[W(CO)_3(\eta^2\text{-}L_2)(\eta^1\text{-}L_2)]$.[19] Yellow, air-sensitive crystals of 1 could be obtained by slow evaporation of both fractions followed by cooling, but those from the second fraction proved to be more satisfactory for the crystallographic study. Total yield estimated to be ca. 30% by NMR. Anal. Calcd for $C_{23}H_{38}O_{14}P_4N_2W_2$: C,

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Table I. Crystallographic Data for 1

formula	$C_{23}H_{38}O_{14}P_4N_2W_2$
fw	1058.21
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	14.256 (4)
b, Å	14.629 (4)
c, Å	9.737 (4)
α, deg	97.51 (3)
β, deg	96.89 (3)
γ, deg	64.25 (2)
V, Å^3	1809 (2)
Z	2
ρ(calcd), g cm^{-3}	1.94
radiation	Mo Kα, graphite monochromated; λ = 0.71073 Å
linear abs coeff, cm^{-1}	66.4
range of trans factors	0.51–1.27
θ range, deg	0.5–23.0
scan type	ω–2θ
scan width, deg	0.80 + 0.20 tan θ
scan rate, deg min^{-1}	16.5–1.5
atten factor	11.87
p factor in weight[a]	0.04
unique data	4532
data, $I \geq 3\sigma(I)$	3106
no. of variables	366
largest shift/esd in final cycle	0.02
R[b]	0.034
R[c]	0.045
GOF[d]	1.55

[a] The weighting scheme used in the final refinement was $w = 1/\sigma_F^2$ where $\sigma_F = \sigma_{F^2}/2F$ and $\sigma_{F^2} = [\sigma_I^2 + (pF^2)^2]^{1/2}$. [b] $R = \sum||F_o| - |F_c||/\sum F_o$. [c] $R_w = [\sum w(F_o - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [d] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ (N_o and N_v are the number of observations and variables, respectively).

Table II. Positional Parameters (Esd's in Parentheses) for $[W_2(CO)_6(CH_3N(P(OCH_3)_2)_2)_2(C_7H_8)]$[a]

atom	X	Y	Z	B, Å^2
W(1)	0.38297 (3)	0.31132 (3)	0.90042 (5)	4.58 (1)
W(2)	0.03952 (3)	0.76126 (3)	0.81260 (5)	4.25 (1)
P(1)	0.4491 (2)	0.3116 (2)	0.6803 (4)	6.05 (8)
P(2)	0.4544 (2)	0.1515 (2)	0.7651 (4)	6.25 (9)
P(3)	0.1137 (2)	0.7293 (2)	0.5863 (3)	5.28 (7)
P(4)	−0.0768 (2)	0.8508 (3)	0.6290 (4)	6.31 (9)
O(1)	0.3269 (8)	0.2273 (7)	1.140 (1)	11.1 (3)
O(2)	0.1596 (6)	0.3539 (6)	0.754 (1)	8.5 (3)
O(3)	0.5866 (7)	0.2738 (9)	1.086 (1)	14.0 (4)
O(4)	−0.0248 (6)	0.5786 (5)	0.764 (1)	8.2 (3)
O(5)	−0.1309 (6)	0.8470 (7)	1.0276 (9)	8.3 (3)
O(6)	0.8996 (7)	0.0583 (6)	0.087 (1)	10.3 (3)
O(11)	0.3660 (7)	0.3769 (6)	0.5613 (9)	8.8 (3)
O(12)	0.5457 (7)	0.3308 (8)	0.654 (1)	12.2 (3)
O(21)	0.3873 (7)	0.0939 (6)	0.689 (1)	11.5 (3)
C(11)	0.386 (1)	0.391 (1)	0.437 (2)	13.1 (6)*
C(12)	0.617 (1)	0.343 (1)	0.737 (2)	12.0 (6)*
C(21)	0.316 (1)	0.076 (1)	0.743 (2)	8.2 (4)*
C(22)	0.614 (1)	0.037 (1)	0.911 (2)	13.2 (6)*
C(31)	0.759 (2)	0.188 (2)	0.377 (2)	14.8 (7)*
C(32)	0.101 (1)	0.565 (1)	0.465 (2)	8.8 (4)*
C(41)	0.224 (1)	0.212 (1)	0.403 (2)	10.4 (5)*
C(42)	0.161 (1)	−0.041 (1)	0.282 (2)	12.5 (6)*
C(51)	0.3418 (7)	0.4865 (7)	0.935 (1)	5.2 (3)
C(52)	0.3067 (8)	0.4660 (7)	1.052 (1)	5.4 (3)
C(53)	0.1969 (8)	0.5027 (7)	1.078 (1)	5.6 (3)
C(54)	0.1253 (8)	0.5983 (8)	1.062 (1)	5.8 (3)
C(55)	0.1441 (8)	0.6791 (8)	1.011 (1)	5.5 (3)
C(56)	0.2094 (7)	0.6609 (7)	0.905 (1)	4.8 (3)
C(57)	0.2612 (8)	0.5545 (7)	0.837 (1)	4.9 (3)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

26.11; H, 3.63. Found: C, 26.5; H, 3.8. ^{1}H NMR (toluene-d_8): δ 6.63 (s, 2 H), 4.60 (m, 2 H), 4.12 (m, 2 H, C_7H_8), 3.46 (d, J = 13.0 Hz), 3.44 (d, J = 13.3 Hz), 3.41 (d, J = 14.0 Hz), 3.40 (d, J = 14.1 Hz, OCH_3), 2.30 (t, J = 9.34 Hz, NCH_3). $^{31}P\{^1H\}$ NMR (toluene-d_8): AB, δ (P_A) 126.3, (P_B) 117.5, J_{AB} = 66.6, $^1J_{W-P_A}$ = 364.7, $^1J_{W-P_B}$ = 292.8 Hz. The resonances for the methylene protons of the C_7H_8 ring could not be conclusively identified. They may be obscured by the methyl resonances of the phosphorus ligand.

X-ray Crystallography. An irregular yellow crystal of 1, obtained as described above, was cemented in a nitrogen-filled capillary with epoxy cement and mounted on an Enraf-Nonius CAD-4 diffractometer. General procedures for data collection and refinement have been published previously[20] while those specific to the present study are given in Table I. The choice of a triclinic cell was confirmed by a Delaunay reduction, which indicated the absence of higher symmetry, and the successful refinement confirms the choice of space group. The final unit cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections ($8.28 \leq \theta \leq 13.56$), which had been accurately centered on the diffractometer. The data were corrected for a 15% linear decay in the intensity monitors, and an empirical absorption correction[25] was applied. Equivalent reflections were averaged, resulting in an agreement factor of 0.02 on F_o. The refinement proceeded uneventfully, and near the end, nearly all the hydrogen atoms could be seen in a different map. These were placed in calculated positions (C–H = 0.95 Å) with isotropic thermal parameters 1.3 times that of the attached carbon atom and included as fixed contributions riding on the carbon atoms. The final difference map showed features ranging from 1.12 to −0.86 e/Å^3, which were primarily associated with the tungsten atoms and are most likely the result of the crystal decomposition. Final atomic positions are presented in Table II while additional crystallograhic data appear as supplementary material (Tables S1–S6).

Results and Discussion

In a recent paper[19] on the chemistry of the bis(dialkoxyphosphino)methylamines $CH_3N(P(OR)_2)_2$ (R = CH_3 (L_2), $CH(CH_3)_2$(L'_2), CH_2(L''_2)), we reported that $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ forms $[W_2(CO)_6(PNP)_2(\mu\text{-}PNP)]$ (PNP = L_2, L'_2, L''_2) as the major product together with lesser amounts of *mer*-$[W(CO)_3(\eta^2\text{-}PNP)(\eta^1\text{-}PNP)]$ (PNP = L_2, L'_2) and *cis*-$[W(CO)_4(L_2)]$ (4). Consistently, the crude reaction mixture obtained from $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ and L_2 showed ^{31}P NMR resonances consisting of a pair of overlapping AB patterns in addition to those assigned to the species listed above. Although we have been unable to chromatographically separate the material responsible for these resonances from all of the other products, we have now with some difficulty obtained crystals suitable for an X-ray structure determination by repeated fractional crystallization of the fraction containing this species and *mer*-$[W_2(CO)_6(L_2)_2(\mu\text{-}L_2)]$ and show it to be the cycloheptatriene-bridged ditungsten complex $[(mer\text{-}W(CO)_3(L_2))_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_7H_8)]$ (1; Figure 1).

The ^{31}P NMR spectrum of the sample of 1 used for the structural study showed only a single AB pattern that is invariant over the range 298–218 K as expected for the structure found in the solid state. As noted above, however, the crude material showed a second AB pattern with δ (P_A) 126.0, δ (P_B) 116.4, J_{AB} = 65.8, $^1J_{W-P_A}$ = 365.0, $^1J_{W-P_B}$

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(22) $^{31}P\{^1H\}$ NMR: **2** (C_6D_6) AB, δ (P_A) 117.7 (P_B) 110.2, J_{AB} = 77.2, $^1J_{W-P_A}$ = 362.0, $^1J_{W-P_B}$ = 289.0 Hz; **3** (acetone-d_6) AB, δ (P_A) 129.5, (P_B) 121.7, J_{AB} = 62.1 Hz.

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(24) Atoms C(51), C(52), C(55), and C(56) are planar to within 0.01 Å (equation of plane: $-0.736X - 0.316Y - 0.599Z - 12.216 = 0$). Atoms C(53), C(54), and C(57) lie ca. 0.7 Å below this plane toward W(1) and W(2).

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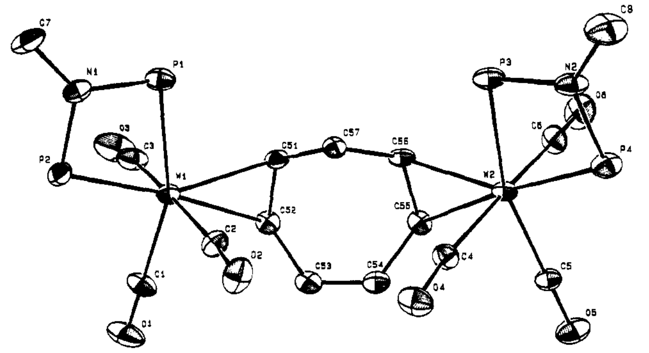

Figure 1. Inner coordination sphere of [(*mer*-W(CO)$_3$(CH$_3$N-(P(OCH$_3$)$_2$)$_2$))$_2$(μ-η^2:η^2-C$_7$H$_8$)] (1). Thermal ellipsoids are drawn at the 30% level.

= 295.7 Hz. On the basis of the similarity of these data with those for 1, we suggest that the crude material contains either a second conformer of 1 or perhaps an isomer. This is supported by the observation that when a C$_6$D$_6$ solution containing these two species is treated with carbon monoxide, *cis*-[W(CO)$_4$L$_2$] slowly forms as the sole product and the *relative* intensities of the two AB patterns do not change during the course of the reaction.

In previous studies of the reaction of [W(CO)$_3$(η^2-C$_7$H$_8$)] with Lewis base ligands (L), the formation of [W(CO)-(L)$_2$(η^2-C$_7$H$_8$)] has been proposed based on kinetic evidence.[21] We suggest that the formation of 1 can be considered a trapping of this intermediate.

With the identity of 1 established, we reexamined the ^{31}P NMR spectra of the crude product mixtures obtained from the reactions of L'$_2$ and L''$_2$ with [W(CO)$_3$(η^6-C$_7$H$_8$)].[19] Both of these contained AB patterns having very similar chemical shifts and coupling contants[22] to those observed for 1, suggesting the presence of the analogues [(*mer*-W-(CO)$_3$(PNP))$_2$(μ-η^2:η^2-C$_7$H$_8$)] (PNP = L'$_2$ (2), L''$_2$ (3)). Both of these are minor products, are not particularly stable, and could not be isolated in pure form. Thus chromatography of the crude product from the reaction involving L'$_2$ (Brockman III alumina, hexane eluant) gave an initial yellow fraction shown by ^{31}P NMR to contain 2 and a second species showing a single ^{31}P NMR resonance with tungsten satellites (δ (P) 113.4, $^1J_{W-P}$ = 305.1 Hz), which we suggest is *cis*-[W(CO)$_4$(L'$_2$)] by analogy with the spectroscopic data obtained for 4. However, on further workup of this fraction, decomposition to ill-defined solids occurred. Although 3 was observed in the ^{31}P NMR spectrum of the crude material obtained in the reaction involving L''$_2$, it could not be detected in the mother liquor remaining following isolation of the major product, [W$_2$-(CO)$_6$(L''$_2$)$_2$(μ-L''$_2$)], indicating it too has only limited stability.

The crystal structure of 1 consists of well-separated bimetallic molecules in which metal–metal interaction is clearly absent. A perspective view of the inner coordination spheres is given in Figure 1 while pertinent bond distances and interbond angles are listed in Table III. A view of the entire molecule is included as supplementary material (Figure S1). The localized nature of the W–C$_7$H$_8$ bonding is evident from inspection of the carbon–carbon distance in the ring and from the fact that C(53) and C(54) are > 3.0 Å, respectively, from W(1) and W(2). This contrasts with the metal–metal *bonded* complex [Fe$_2$-(CO)$_6$(μ-η^3:η^3-C$_7$H$_8$)][23] where each metal binds to *three* adjacent carbon atoms. Also, in contrast to the diiron complex where the cycloheptatriene ring is in a chair conformation (exo methylene carbon), 1 has the ring in a tub conformation with all three uncoordinated carbon atoms (C(53), C(54), C(57)) on the same side of the plane defined by the other four carbon atoms as the metal atoms.[24] At first sight, the binding of both [W(CO)$_3$(L$_2$)] moities to the same face of the cycloheptatriene ring might seem unusual since the other structurally characterized examples of bimetallic complexes bridged by cyclic polyolefins and lacking metal–metal bonding have the metals on opposite face of the ring.[13,14] However, inspection of models shows that for cycloheptatriene only the tub conformation permits the independent attachment of two ML$_n$ moieties to the nonadjacent double bonds without creating severe steric congestion and this in turn requires them to be attached to the same face. An interesting feature of the observed structure is the interposition of the endo methylene hydrogen (H(57A) on C(57)) between the two metals. An agostic interaction, which could serve to stabilize the observed conformation, is thus an attractive possibility, but the distances involved (W(1)--H(57A) = 3.35 Å, W(2)--H(57A) = 3.04 Å) are too long to support this proposal.

Table III. Selected Bond Distances (Å) and Interbond Angles (deg) for [W$_2$(CO)$_6$(CH$_3$N(P(OCH$_3$)$_2$)$_2$)$_2$(C$_7$H$_8$)]

Bond Distances			
W(1)–P(1)	2.443 (3)	W(2)–C(6)	2.00 (1)
W(1)–P(2)	2.384 (3)	W(2)–C(55)	2.40 (1)
W(1)–C(1)	1.98 (1)	W(2)–C(56)	2.358 (9)
W(1)–C(2)	2.00 (1)	C(51)–C(52)	1.42 (1)
W(1)–C(3)	1.93 (1)	C(52)–C(53)	1.46 (1)
W(1)–C(51)	2.353 (9)	C(53)–C(54)	1.34 (1)
W(1)–C(52)	2.422 (9)	C(54)–C(55)	1.48 (1)
W(2)–P(3)	2.460 (3)	C(55)–C(56)	1.40 (1)
W(2)–P(4)	2.382 (3)	C(56)–C(57)	1.50 (1)
W(2)–C(4)	2.03 (1)	C(57)–C(51)	1.49 (1)
W(2)–C(5)	1.99 (1)		
Interbond Angles			
P(1)–W(1)–P(2)	63.8 (1)	P(3)–W(2)–P(4)	64.0 (1)
P(1)–W(1)–C(1)	159.0 (3)	P(3)–W(2)–C(5)	159.0 (3)
P(1)–W(1)–C(2)	91.3 (3)	P(3)–W(2)–C(4)	92.9 (3)
P(1)–W(1)–C(3)	93.9 (4)	P(3)–W(2)–C(6)	93.0 (3)
P(1)–W(1)–C(51)	86.9 (2)	P(3)–W(2)–C(56)	87.4 (2)
P(1)–W(1)–C(52)	121.3 (3)	P(3)–W(2)–C(55)	121.1 (2)
P(2)–W(1)–C(1)	95.2 (3)	P(4)–W(2)–C(5)	95.0 (3)
P(2)–W(1)–C(2)	91.2 (3)	P(4)–W(2)–C(4)	94.2 (3)
P(2)–W(1)–C(3)	91.9 (5)	P(4)–W(2)–C(6)	91.5 (3)
P(2)–W(1)–C(51)	150.6 (2)	P(4)–W(2)–C(56)	150.9 (2)
P(2)–W(1)–C(52)	174.9 (3)	P(4)–W(2)–C(55)	174.8 (2)
C(1)–W(1)–C(2)	88.6 (5)	C(5)–W(2)–C(4)	86.9 (4)
C(1)–W(1)–C(3)	87.9 (5)	C(5)–W(2)–C(6)	88.8 (4)
C(1)–W(1)–C(51)	114.2 (4)	C(5)–W(2)–C(56)	113.6 (4)
C(1)–W(1)–C(52)	79.7 (4)	C(5)–W(2)–C(55)	79.9 (4)
C(2)–W(1)–C(3)	175.5 (5)	C(4)–W(2)–C(6)	173.1 (4)
C(2)–W(1)–C(51)	90.2 (4)	C(4)–W(2)–C(56)	92.7 (4)
C(2)–W(1)–C(52)	88.5 (4)	C(4)–W(2)–C(55)	85.9 (4)
C(3)–W(1)–C(51)	88.7 (4)	C(6)–W(2)–C(56)	84.1 (4)
C(3)–W(1)–C(52)	88.2 (5)	C(6)–W(2)–C(55)	88.0 (4)

The coordinated carbon–carbon bonds are at best marginally shorter than those found in *trans*-[W(C$_2$H$_4$)$_2$-(P(CH$_3$)$_4$],[10] but the W–C distances are significantly longer, implying a weaker binding of the cycloheptatriene. This is likely due to both steric congestion and to a significant trans influence of the phosphorus ligand. The W(1)–P(1) and W(2)–P(3) distances (trans to carbonyl) are essentially the same as the corresponding distance found in [W$_2$-(CO)$_6$(L$_2$)$_2$(μ-L$_2$)],[19] while W(1)–P(2) and W(2)–P(4) distances (trans to olefin) are significantly shorter. This probably reflects a low π-acceptor character for the olefin ligand, which in turn enhances the W → P π-backbonding. Other metrical parameters appear unexceptional.

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Registry No. 1, 126295-57-6; 2, 130698-84-9; 3, 130698-85-0; 4, 126327-44-4; $[W(CO)_3(\eta^6\text{-}C_7H_8)]$, 12128-81-3; *mer*-$[W_2(CO)_6(L_2)_2(\mu\text{-}L_2)]$, 126295-42-9; *mer*-$[W(CO)_3(\eta^2\text{-}L_2)(\eta^1\text{-}L_2)]$, 126295-43-0; *cis*-$[W(CO)_4(L'_2)]$, 130698-86-1.

Supplementary Material Available: A view of the complete molecule and tables of calculated hydrogen atom positions, bond distances, interbond angles, anisotropic thermal parameters, and root-mean-square amplitudes of anisotropic displacement (13 pages); a listing of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

Preparation and Structure of $[Cl_2W(\mu\text{-}Cl)(\mu\text{-dmpm})_2(\mu_2\text{-}PMe_2)WCl(\eta^2\text{-}CH_2PMe_2)]Cl$, a Product of an Unusual Cleavage of the dmpm Ligand

F. Albert Cotton,* Jo Ann M. Canich, Rudy L. Luck, and K. Vidyasagar

Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

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Summary: The title compound $[Cl_2W(\mu\text{-}Cl)(\mu\text{-dmpm})_2(\mu_2\text{-}PMe_2)WCl(\eta^2\text{-}CH_2PMe_2)]Cl$, **1**, is obtained when $W_2Cl_4(PBu_3)_4$ is treated with $Me_2PCH_2PMe_2$, dmpm, in a toluene–hexane mixture at reflux for 4 h. The compound has been characterized on the basis of ^1H and $^{31}P\{^1H\}$ NMR and IR spectra and electrochemical and electronic absorption properties and by analysis. A magnetic susceptibility measurement confirms that the complex contains one unpaired electron. The EPR spectrum exhibits hyperfine coupling, $g = 1.963$, $a_p = 30$ G (2.75×10^{-3} cm^{-1}). Hyperfine coupling to ^{183}W was not resolved. Red platelike crystals of composition $\mathbf{1}\cdot CH_2Cl_2$ grown by layering a dichloromethane solution of **1** with *n*-hexanes have been studied by X-ray crystallography: space group $P2_1/n$, $a = 8.852$ (2) Å, $b = 12.512$ (2) Å, $c = 31.341$ (6) Å, $\beta = 93.65$ (2)°, $V = 3464$ (2) Å^3, $Z = 4$. The $[Cl_2W(\mu\text{-}Cl)(\mu\text{-dmpm})_2(\mu_2\text{-}PMe_2)WCl(\eta^2\text{-}CH_2PMe_2)]^+$ ion is an edge-sharing bioctahedron with bridging dmpm molecules above and below a central plane consisting of $Cl_2W(\mu\text{-}Cl)(\mu\text{-}PMe_2)W'Cl(CH_2PMe_2)$. The W–W′ distance is 2.7331 (6) Å, and the μ-PMe_2 ligand is slightly unsymmetrical (W–P = 2.341 (3) Å; W′–P = 2.414 (3) Å). The η^2-Me_2PCH_2 ligand has W′–P = 2.448 (3) Å, W′–C = 2.28 (1) Å, P–C = 1.74 (1) Å, and P–W′–C = 43.0 (3)°.

The ligands $Ph_2PCH_2PPh_2$ (dppm) and $Me_2PCH_2PMe_2$ (dmpm) are well-known, are widely used, and display a variety of coordination modes.[1,2] In general they are preferred as bridging ligands to stabilize binuclear and cluster species, and they are assumed to be chemically inert. The work described here provides an example of where the dmpm ligand, far from being inert, undergoes P–C bond cleavage under mild conditions.

Our interest in the title compound began several years ago when we sought to prepare $W_2Cl_4(dmpm)_2$ by reaction of $W_2Cl_4(PBu_3)_4$ with dmpm.[3] Together with this green compound, we obtained some red crystals, which were not at the time characterized. In an effort to identify and characterize the red product, the mixture of green and red crystals was dissolved in CH_2Cl_2, and the solution was filtered and then layered with *n*-hexanes. At first some green crystals formed, and these were removed by filtration. The solution was then reduced to about one-third of its initial volume and again layered with *n*-hexanes. This led to the deposition of yellow and red crystalline material. The smallest crystals looked yellow, and the larger red crystals when crushed gave a yellow powder.

The red platelike crystals obtained in the way just described were shown by X-ray crystallography[4] to contain the title molecule. In addition, these crystals contain interstitial molecules of CH_2Cl_2 and possibly *n*-hexanes, and because of the difficulty of modeling these, the structure never refined as well as we desired. However, in the course of developing the improved preparative procedure reported here, we also obtained a different crystalline form in which only interstitial CH_2Cl_2 molecules were present, and this did refine to reasonable figures of merit. We thus report the latter structure in detail here together with the usual spectroscopic measurements.

Experimental Section

Reactions and manipulations were performed under dry nitrogen by using Schlenk techniques. Solvents were freshly distilled prior to use. Bis(dimethylphosphino)methane was purchased from Strem Chemicals, Inc. $W_2Cl_4(PBu_3)_4$ (Bu = *n*-C_4H_9) was prepared by a literature method.[6] The IR spectrum was recorded as a Nujol mull by using a Perkin-Elmer 783 infrared spectrophotometer. The ^1H NMR spectrum was recorded on a Varian XL200 spectrometer in acetone-d_6 and CD_2Cl_2, and a Varian EM390 spectrometer was used to do the measurement of the magnetic susceptibility with the Evans method.[5] This consisted of a 0.016 M solution of complex 1 in CD_2Cl_2 with C_6H_6 as the indicator placed inside a glass capillary, under Ar, sealed, and placed inside a 5-mm NMR tube contained CD_2Cl_2 and C_6H_6. The difference between the two proton resonances for the different C_6H_6 environments was 5.43 Hz. Attempts to record the $^{31}P\{^1H\}$ NMR spectrum were carried out on a Varian XL400 spectrometer. Electrochemical measurements were carried out with a Bioanalytical Systems Inc. Model 100 electrochemical analyzer in a dichloromethane solution that contained ca. 0.2 M tetra-*n*-butylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature

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[4] Space group $P2_1/n$ with $a = 13.476$ (3) Å, $b = 14.080$ (3) Å, $c = 21.735$ (6) Å, and $\beta = 107.25$ (2)°.

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