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Studies of a Reluctant Ligand. An X-ray Crystallographic and NMR Spectroscopic Analysis of $(OC)_5W(\eta^1\text{-}PPh_2CH_2PPh_2)$ and Its $(OC)_5W(\mu\text{-}PPh_2CH_2PPh_2)W(CO)_5$ Derivative

John William Benson

Department of Chemistry, Rockford College, Rockford, Illinois 61108

Richard L. Keiter* and Ellen A. Keiter*

Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920

Arnold L. Rheingold* and Glenn P. A. Yap

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Vera V. Mainz

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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Tungsten pentacarbonyl complexes, $(OC)_5W(\eta^1\text{-}PPh_2CH_2PPh_2)$ (**1**) and $(OC)_5W(\mu\text{-}PPh_2CH_2PPh_2)W(CO)_5$ (**2**), have been synthesized from $(OC)_5WNH_2Ph$ and $Ph_2PCH_2PPh_2$ in toluene, and their solid-state structures have been determined by single-crystal X-ray diffraction. The lone pair of electrons on the dangling phosphine in **1** is oriented toward the $W(CO)_5$ unit in the solid state, and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data suggest that this conformation may also be dominant in solution. Phosphorus−phosphorus coupling in **1** ($^2J_{PP}$ = 106 Hz) is significantly larger than in any previously reported complex of $Ph_2PCH_2PPh_2$ and is highly dependent on changes in temperature and solvent. Also observed is an unprecedented long-range phosphorus−carbon coupling ($^4J_{PC}$ = 3.0 Hz) between the dangling phosphine and the equatorial carbonyl carbons of **1**, which is attributed to a conformational and/or "through-space" enhancement. On the basis of the structural and spectral data, the reluctance of **1** to react with $(OC)_5WNH_2Ph$ to give **2** is explained in terms of the substantial ligand conformation change required.

Introduction

Bis(diphenylphosphino)methane (dppm) is an important and widely used ligand in homogeneous catalysis and organometallic chemistry.[1] Enormously flexible, with P−C−P bond angles ranging from 92° to 133°, it is able to accommodate a wide variety of structural demands including those associated with chelation of a single metal center and bridging two metal atoms. In addition, a number of compounds exist in which dppm is bound as a monodentate ligand.[2] The first example to be reported was $(OC)_5W(\eta^1\text{-dppm})$, **1**,[3] and its appearance was followed by a number of others, including some that have been structurally characterized (Table 1).

Coordination of one end of dppm in **1** tends to reduce the reactivity of the unbound end but not sufficiently to prevent chelation,[4] protonation,[5] and quaternization.[3] Nonetheless, early attempts to coordinate a second $M(CO)_5$ fragment to the free end of $(OC)_5M(\eta^1\text{-dppm})$ (M = Cr, Mo, W) were unsuccessful,[3,6] even though the ethylene-bridged ligand, dppe (dppe = $Ph_2PCH_2CH_2PPh_2$) in $(OC)_5M(\eta^1\text{-dppe})$ readily forms bimetallic complexes at room temperature or below.[7] The analogous arsenic and antimony complexes, $(OC)_5M(\eta^1\text{-}Ph_2AsCH_2\text{-}$

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Table 1. Ligand Torsion Angles, P−C−P Angles, $^2J_{PP}$ Coupling Constants, and Configuration Type for Structurally Characterized Compounds Containing η^1-dppm

compound	torsion angle (deg)	P−C−P angle (deg)	$^2J_{PP}$ (Hz)	conf. type	ref
dppm	74.3	106.2	125 (CD_2Cl_2)	I	25
$W(CO)_5(\eta^1$-dppm)	26.5	111.5	106 ($CDCl_3$)	I	this work
$Fe(CO)_4(\eta^1$-dppm)	20.3	112.6	75.7 ($CDCl_3$)	I	11
$Mo_2(\eta^5$-Cp$)_2(\mu$-CNBu$^t)(\eta^1$-dppm)	88.8	116.3	73	I	29
$Fe_2(CO)_5$(u-PCy_2)(u-$PBu^t{}_2)(\eta^1$-dppm)	42.0	110.6	46 (CD_2Cl_2)	I	30
$Fe(\eta^5$-Cp$)(\eta^3$-$MeCS_2)(\eta^1$-dppm)	38	114.0	40.0 (THF)	I	2f
$Fe(\eta^5$-Cp$)(\eta^2$-$MeCS_2)(\eta^1$-dppm)	152.0	117.3	47.7 (THF)	II	2f
$Os_3(CO)_9(\mu$-dppm$)(\eta^1$-dppm)	167.3	117.2	54.7 (CD_2Cl_2)	II	2h
Ru(*trans*-quin$)_2(\eta^1$-dppm$)_2$ quin = 2-quinaldinate	170.3	118.9	21.5 ($CDCl_3$)	II	2d
Ru(TTP$)(\eta^1$-dppm$)_2$ TTP = tetraphenylphorphyrin	178.6	118.7	30.2 ($CDCl_3$)	II	2n
$RuCl(PPh_3)(\eta^5$-Cp$)(\eta^1$-dppm)	177	117	18.3 ($CDCl_3$)	II	28
$Ru(\eta^5$-Cp$)(\eta^2$-dppm$)(\eta^1$-dppm)	140.9	120.4	40.2 (CD_2Cl_2)	II	31
fac-$Mo(CO)_3(\eta^2$-phen$)(\eta^1$-dppm)	156.8	118.0	66.1	II	32
W(L)(OAr-2,6,6$Ph_2)(\eta^1$-dppm) L = (OC_6H_3Ph-η^6-C_6H_5)	158.9	116.4	65	II	33
$Pt_4(\mu$-H$)(\mu$-CO$)_2(\mu$-dppm$)_3(\eta^1$-dppm$)^+$	161.9	120.1	73	II	34
$(OC)_5W(\mu$-dppm$)W(CO)_5$	43.3	133.1	22.9 ($CDCl_3$)	III	this work

$AsPh_2)$[8] and $(OC)_5M(\eta^1$-$Ph_2SbCH_2SbPh_2)$[9] (M = Cr, Mo, W) were isolated long ago, but their bimetallic derivatives were also unknown until quite recently.[9b] The reluctance of these monodentate complexes to function as ligands toward a second $M(CO)_5$ group was attributed to unfavorable steric interactions between the four phenyl groups and the two metal carbonyl fragments that result because the methylene bridge provides a bite angle that is too small to allow the necessary space accommodations. This notion was supported by the fact that while **1** reacts with MeI at room temperature to give the quaternized product, $[(OC)_5W(\eta^1$-$PPh_2CH_2PPh_2$-Me]I, it does not react with the bulkier benzyl bromide.[3] Furthermore, substituting the sterically less demanding $Fe(CO)_4$ for $M(CO)_5$ allows formation of $(OC)_4Fe(\mu$-dppm$)Fe(CO)_4$,[10] and $(OC)_4Fe(\eta^1$-dppm)[11] has been shown to combine with $Mo(CO)_5$ to give $(OC)_5Mo(\mu$-dppm$)Fe(CO)_4$.[12]

Early unsuccessful efforts to synthesize $(OC)_5W(\mu$-dppm$)W(CO)_5$, **2**, were performed at near room temperature to minimize chelation of **1**.[3,6] More recently, it has been shown that **2** does in fact form from $(OC)_5W(NCMe)$ and dppm if reactions are carried out at higher temperatures.[13] Likewise, the dppm-bridged complex, $[\{(\eta^5$-$C_5H_5)Ru(1,10$-phen$)\}_2(\mu$-dppm$)](PF_6)_2$, forms in refluxing ethanol, while only the monodentate complex forms at room temperature.[14]

In this work we report an improved synthesis of **2**, X-ray structures of both **1** and **2**, and $^{31}P\{^1H\}$ and ^{13}C NMR spectral data suggesting that solution and solid-state conformations of dppm in complex **1** are very similar. This information is used to explain the reluctance of **1** to bind to a second $W(CO)_5$ unit to form **2.**

Experimental Section

General Comments. All reactions were performed in a nitrogen atmosphere using standard Schlenk apparatus. Toluene was dried over CaH_2 and distilled at ambient pressure. All other solvents were of reagent grade and used without further purification. Other materials were prepared as previously described: $(OC)_5W(NH_2Ph)$,[3,15] $(OC)_5W(\eta^1$-dppm),[3] and $(OC)_5W(\eta^1$-dppe).[3] Solution FT-IR spectra were obtained on a Nicolet 20-DBX spectrometer. Room-temperature $^{31}P\{^1H\}$ NMR (referenced to an external standard of 85% H_3PO_4) and $^{13}C\{^1H\}$ NMR (referenced to TMS) spectra were obtained on a General Electric QE-300 NMR spectrometer. Variable-temperature $^{31}P\{^1H\}$ NMR spectra were performed at Spectral Data Services, Champaign, IL, using a Nicolet NT-400 spectrometer. Phosphorus decoupled C-13 spectra were obtained with a Varian Unity Inova 500 MHz spectrometer.

Synthesis of $(OC)_5W(\mu$-dppm$)W(CO)_5$ (2). Method A. A toluene solution (25 mL) of $(OC)_5W(\eta^1$-dppm) (0.150 g, 0.212 mmol) and $(OC)_5W(NH_2Ph)$ (0.113 g, 0.271 mmol) was stirred at 60 °C for 16 h. The dark solution was cooled to room temperature and filtered to give a greenish yellow solution and a black precipitate. The solvent was removed from the filtrate under vacuum, and the resulting solid was chromatographed on neutral, deactivated[16] alumina using 3:1 hexanes/CH_2Cl_2 as the eluent. The first yellow band collected was identified as the product, **2,** by its $^{31}P\{^1H\}$ NMR spectrum.[13a] The solvent was removed under vacuum; the resulting solid was recrystallized from CH_2Cl_2/CH_3OH (1:10) to give 0.191 g (87%). ^1H

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Table 2. Crystal Data for $(OC)_5WPPh_2CH_2PPh_2$ (1) and $[(OC)_5WPPh_2]_2CH_2$(2)

	1	**2**
formula	$C_{30}H_{22}O_5P_2W$	$C_{35}H_{22}O_{10}P_2W_2$
fw	708.27	1032.17
temp, K	296(2)	296(2)
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	Pc	$P2_1/c$
a, Å	8.798(2)	17.494(8)
α, deg	90	90
b, Å	13.936(3)	10.332(4)
β, deg	96.54(3)	93.67(4)
c, Å	11.266(2)	19.796(9)
γ, deg	90	90
vol, Å^3; Z	1372.3(5); 2	3571(3); 4
density (calcd), Mg/m^3	1.714	1.920
abs coeff, mm^{-1}	4364	6583
F(000)	962	1960
cryst size, mm	0.40 × 0.30 × 0.20	0.40 × 0.12 × 0.10
cryst color	colorless	colorless
θ range for data collection, deg	2.33−30.07	2.06−27.57
limiting indices	$-12 \le h \le 12$, $0 \le k \le 19$, $-1 \le l \le 15$	$-22 \le h \le 22$, $0 \le k \le 13$, $0 \le l \le 25$
no. of rflns collected	4589	8437
no. of indep rflns	4589 ($R_{int} = 0.0000$)	8193 ($R_{int} = 0.0314$)
refinement meth	full-matrix least-squares on F^2	
no. of data/restraints/parameters	4585/15/409	8193/0/442
goodness-of-fit on F^2	1.034	1.152
final R indices [$I > 2\sigma(I)$]	R1 = 0.0589, wR2 = 0.1384	R1 = 0.0386, wR2 = 0.0646
R indices (all data)	R1 = 0.0637, wR2 = 0.1444	R1 = 0.0794, wR2 = 0.0672
absolute structure parameter	0.02(6)	
extinction coeff	8766(395)	
largest diff peak and hole, e Å^{-3}	4.865 and -1.882	1.075 and -1.672

NMR ($CDCl_3$): δ 7.4−7.1 (m, Ph), 4.05 (t, $^2J_{PH} = 5.0$ Hz, CH_2). $^{13}C\{^1H\}$ ($CDCl_3$): δ 199.2 (t, $|^2J_{CP} + {}^4J_{CP}| = 23.2$ Hz, trans CO), 197.0 (t, $|^2J_{CP} + {}^4J_{CP}| = 5.9$ Hz, $^1J_{CW} = 119.6$ Hz, cis CO), 133.2 (five-line pattern, $|^1J_{CP} + {}^3J_{CP}| = 41.9$ Hz, *ipso*), 132.1 (t, $|^2J_{CP} + {}^4J_{CP}| = 11.7$, *ortho*), 130.4 (s, *para*), 128.6 (t, $|^3J_{CP} + {}^5J_{CP}| = 9.7$ Hz, *meta*), 37.2 (t, $^1J_{CP} = 5.0$ Hz, CH_2). A second, bright yellow band eluted and was identified by its IR spectrum as unreacted $(OC)_5W(NH_2Ph)$.

Method B. A toluene solution (20 mL) of $(OC)_5W(NH_2Ph)$ (0.601 g, 1.44 mmol) and dppm (0.269 g, 0.700 mmol) was heated to 60 °C for 19 h. The resulting solution was worked up as above to give 0.428 g of **2** (58%).

$^{13}C\{^1H\}$ NMR of $(OC)_5W(\eta^1$-dppm) (1). (CD_2Cl_2): δ 200.1 (d, $^2J_{CP} = 22.0$ Hz, trans CO), 197.6 (dd, $^2J_{CP} = 6.9$ Hz, $^4J_{CP} = 3.0$ Hz, cis CO), 136.0 (d, $^1J_{CP} = 40.7$ Hz, *ipso*), 135.9 (d, $^1J_{CP} = 41.1$ Hz, *ipso*), 132.7 (d, $^2J_{CP} = 21.1$ Hz, *ortho*), 132.2 (d, $^2J_{CP} = 11.7$ Hz, *ortho*), 128.4 (d, $^3J_{CP} = 2.9$ Hz, *meta*), 128.3 (d, $^3J_{CP} = 5.3$ Hz, *meta*), 130.2 (d, $^4J_{CP} = 1.7$ Hz, *para*), 128.7 (s, *para*), 33.7 (dd, $^1J_{CP} = 30.3$, 22.1 Hz, CH_2).

$^{13}C\{^1H\}$ NMR of $(OC)_5W(\eta^1$-dppe) (3). ($CDCl_3$): δ 199.1 (d, $^2J_{CP} = 21.5$ Hz, trans CO), 196.7 (d, $^2J_{CP} = 7.1$ Hz, $^1J_{CW} = 126.4$ Hz, cis CO), 137.2 (d, $^1J_{CP} = 13.5$ Hz, *ipso*), 135.5 (d, $^1J_{CP} = 40.1$ Hz, *ipso*), 132.5 (d, $^2J_{CP} = 18.5$ Hz, *ortho*), 131.9 (d, $^2J_{CP} = 11.0$ Hz, *ortho*), 130.3 (s, *para*), 128.7 (m, Ph), 29.4 (dd, $^1J_{CP} = 23.2$, $^2J_{CP} = 18.9$ Hz, CH_2CH_2), 22.2 (d, $^1J_{CP} = 16.1$ Hz, CH_2CH_2).

Structure Determination of $(OC)_5W(\eta^1$-dppm) (1) and $(OC)_5W(\mu$-dppm)$W(CO)_5$ (2). Crystals of **1** and **2** were grown in a CH_2Cl_2/hexanes solution at −18 °C. Data collection and parameters are listed in Table 2. Preliminary photographic evidence showed that both **1** and **2** were monoclinic. Systematic absences in the diffraction data indicated that **1** belonged to either of the space groups *Pc* or *P*2/*c*. Since **1** does not possess 2-fold symmetry, the noncentrosymmetric alternative, *Pc*, was used for refinement. Empirical corrections for absorption were applied for both data sets. Initially, the refinement process for **1** for an all anisotropic model converged at $R(F) =$ 13.4% with several large (>10 e Å^{-3}) unassigned peaks near the W atom. In an exploration of the many factors that can contribute to poor refinement, we discovered the presence of a minor contribution (ca. 8%) from a racemic twin. With the inclusion of these contributions, $R(F)$ dropped to 5.9% and the largest peak on the difference map was now 2.5 e Å^{-3}. For **2**, all non-hydrogen atoms were also refined anisotropically. In both cases, hydrogen atoms were included in idealized contributions. All software, including routines for dealing with twinning, is contained in SHELXTL.[17]

Conformational Analysis of η^1-dppm Ligands. Torsion angles (M−P−P−lone pair) for complexes containing η^1-dppm ligands were determined using CS Chem 3D Pro, version 3.5 (CambridgeSoft Corporation). Literature values for atomic coordinates were used to reconstruct the dppm framework including the metal atom. The position of the lone pair on the unbound P atom was determined by placing a single atom (A) in an idealized position, such that all three lone pair−P−C angles were equal. Values for torsional angles are listed in Table 1.

Results and Discussion

Synthesis and Characterization of 2. Compound **2** was synthesized either from a 2:1 ratio of $(OC)_5W$-(NH_2Ph) and dppm or from a 1:1 ratio of **1** and $(OC)_5W$-(NH_2Ph) in toluene at 60 °C.

$$2(OC)_5W(NH_2Ph) + \text{dppm} \rightarrow \underset{\mathbf{2}}{(OC)_5W(\mu\text{-dppm})W(CO)_5} + 2PhNH_2 \quad (1)$$

$$(OC)_5W(NH_2Ph) + \underset{\mathbf{1}}{(OC)_5W(\eta^1\text{-dppm})} \rightarrow \underset{\mathbf{2}}{(OC)_5W(\mu\text{-dppm})W(CO)_5} + PhNH_2 \quad (2)$$

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[17] Sheldrick, G. SHELXTL, ver 5.01, Program Libraries, Siemans XRD: Madison, WI.

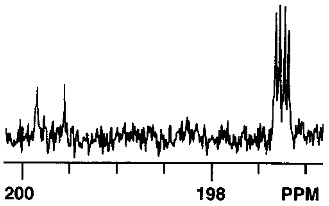

Figure 1. $^{13}C\{^{1}H\}$ NMR spectrum of the carbonyl region of $(OC)_5W(\eta^1\text{-dppm})$ (**1**).

The IR and $^{31}P\{^{1}H\}$ NMR spectra are in agreement with previous assignments,[13a] and characterization of **2** is now complete with the addition of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra and single-crystal X-ray diffraction. The preparation of **2** from $(OC)_5W(NCMe)$ as described previously[13a] is limited because $(OC)_4W(\eta^2\text{-dppm})$ forms in addition to **2** as a significant side product. Using aniline as a leaving group instead of acetonitrile, however, essentially eliminates the competing chelation reaction and increases the yield of **2** to 87%. The formation of $(OC)_4W(\eta^2\text{-dppm})$ from $(OC)_5W(NCMe)$ apparently occurs because the acetonitrile complex[18] disproportionates to give $W(CO)_6$ and $(OC)_4W(NCMe)_2$, which can then react with dppm and undergo chelation. The disproportionation reaction is not known to occur for $(OC)_5W(NH_2Ph)$.

The CO region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2** consists of a set of downfield peaks assigned to the ^{13}CO group trans to the coordinated phosphorus atom and a set of upfield signals arising from cis ^{13}CO groups. An AA'X pattern is apparent in these signals as well as for those in the phenyl region of the spectrum.[19,20] Both the trans and cis ^{13}CO signals should appear as five-line patterns, but the two outer lines of each are not sufficiently intense to be observed. For the former the separation of the two lines flanking the center line corresponds to $|^{2}J_{CP} + {}^{4}J_{CP}| = 23.2$ Hz, quite consistent with trans couplings observed in **1** ($^{2}J_{C-P} = 22.0$ Hz) and **3** ($^{2}J_{CP} = 21.5$ Hz); for the latter $|^{2}J_{C-P} + {}^{4}J_{C-P}| = 5.9$ Hz and is similar to the cis coupling in **3** ($^{2}J_{C-P} = 7.1$ Hz).

Complex **1** shows a cis carbonyl spectral pattern that is quite unexpected[21] (Figure 1). Here we see an apparent doublet of doublets ($^{2}J_{C-P} = 6.3$ Hz; $^{4}J_{C-P} = 3.0$ Hz) for which there is no precedent in the $LM(CO)_5$ literature. The possibility of endo and exo isomers was considered as an explanation for the four-line pattern but ruled out because other signals in the $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were entirely consistent with one conformation. The possibility of two sets of nonequivalent CO groups resulting from restricted rotation about the W−P bond (which would give rise to two doublets rather than a doublet of doublets) was also considered. The infrared spectrum of **1,** however, is consistent with C_{4v} symmetry (overlapping E and $A_1^{(1)}$ modes at 1938 cm^{-1}; $A_1^{(2)}$ mode at 2071 cm^{-1}, B_1 mode at 1981 cm^{-1}) and within experimental error identical to that of **3** in both $CHCl_3$ and CCl_4. The possibility of restricted rotation, which might cause only a slight perturbation in the IR spectrum, could not be completely eliminated on the basis of the IR data alone. Additional support was provided by $^{13}C\{^{31}P\}$ spectra in which the coordinated and dangling phosphorus nuclei were independently decoupled from carbon. The result for each was a doublet for the equatorial CO signal, proving that the dangling phosphorus is indeed coupled to the cis carbonyl carbons. In view of the general observation that coupling is more effective through a trans configuration than through a cis arrangement (e.g., $^{2}J_{PC}$ trans is greater than 3 times $^{2}J_{PC}$ cis), it is noteworthy that no long-range coupling is observed between the dangling phosphorus atom and the trans carbonyl carbon. These observations led us to speculate about the possibility of the uncoordinated phosphorus group interacting directly with the equatorial carbonyl group. The crystal structure of **1**, presented in the next section, shows that the dangling phosphorus is tilted toward the cis carbonyl plane, bisecting the C(3)−W−C(4) angle and giving a phosphorus−carbon separation [3.5 Å] equal to the approximate sum of the van der Waals radii for C (1.70 Å) and P (1.85 Å).[22] Evidence is presented suggesting that this molecular arrangement also exists in solution. However, neither $^{13}C\{^{1}H\}$ NMR nor IR spectra support a localized interaction between the dangling phosphorus group and an individual equatorial carbonyl carbon. A nonlocalized van der Waals interaction in which the dangling phosphorus group of **1** is precessing about the plane of the equatorial carbonyl groups is consistent with the spectral data. The observed long-range coupling may arise from a particularly favorable conformational arrangement of the dppm ligand or from a through-space interaction or a combination of both.[23]

Structures of 1 and 2. The structures of **1** and **2** are shown in Figures 2 and 3, respectively, and selected bond distances and angles for both compounds are given in Table 3. Each tungsten atom is coordinated to five carbonyl ligands and one phosphine in approximate C_{4v} symmetry; the P−W−C axis angles are 175.1(8)° in **1** and 179.4(2)° and 178.8(3)° in **2**. Slight tilting of this axis has been observed previously in $LM(CO)_5$ complexes and attributed to dissimilar orientations of substituents on phosphorus relative to the equatorial carbonyl groups; that is, one R group lies between while

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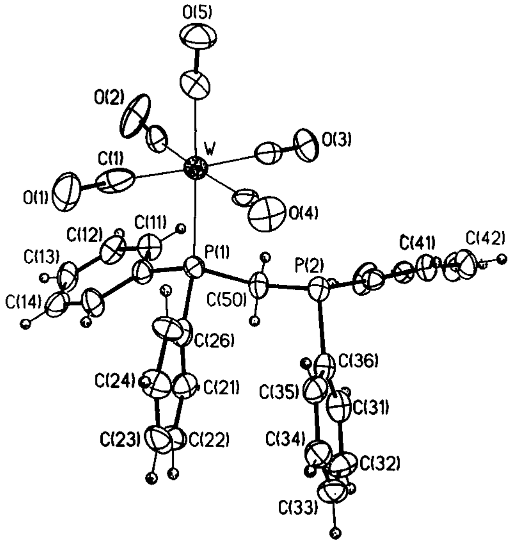


Figure 2. Molecular structure of $(OC)_5W(\eta^1\text{-dppm})$ (**1**).

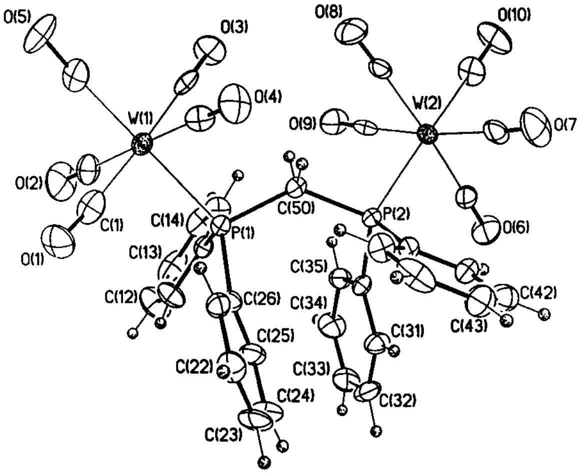


Figure 3. Molecular structure of $(OC)_5W(\mu\text{-dppm})W(CO)_5$ (**2**).

the other two nearly eclipse the carbonyls.[24] The W−P bond distance in **1** is 2.516(5) Å, identical to that found in $(OC)_5WPMe_3$, 2.516(2) Å,[24b] even though dppm is generally viewed as more sterically demanding than PMe_3. The W−P bond distances in **2** are 2.536(2) and 2.540(2) Å, very similar to the W−P bond distance in $(OC)_5WPPh_3$, 2.545(1) Å,[24c] and not unexpected.

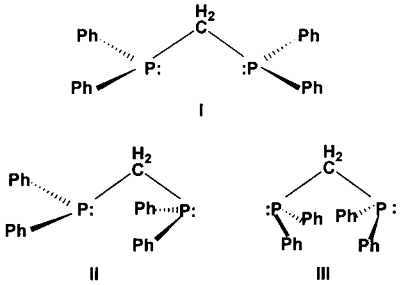
An unusual structural feature of **1** is the deviation from linearity in the equatorial O−C−W bond angles (166−170°). The torsional angle of dppm in **1** is 26.5°, which directs the dangling phosphorus lone pair toward C(4)−O(4). The W−C(4)−O(4) bond angle is 166(2)° with O(4) directed away from the phosphorus lone pair, which raises the possibility that the absence of linearity is due to some interaction between CO and the dangling phosphorus group.

The structure of the free dppm ligand is known,[25] allowing for comparison of conformational changes in the dppm ligand when one end (**1**) or both ends (**2**) are coordinated to $W(CO)_5$. Three possible conformations are shown in Chart 1. As a free ligand, dppm adopts conformation **I**, an orientation that minimizes steric interactions between the phenyl rings. The lone pairs of electrons are staggered, each on opposite sides of the plane formed by P(1), C(50), and P(2); the computed torsion angle between the two lone pairs is 74.3°.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $(OC)_5W(\eta^1\text{-dppm})$ (1) and $(OC)_5W(\mu\text{-dppm})W(CO)_5$ (2)

	1	**2**		**2**
		Distances		
W(1)−P(1)	2.516(5)	2.536(2)	W(2)−P(2)	2.540(2)
W(1)−C(1)	2.026(8)	2.029(11)	W(2)−C(6)	2.056(9)
W(1)−C(2)	2.025(8)	2.083(9)	W(2)−C(7)	2.078(9)
W(1)−C(3)	2.023(8)	2.084(10)	W(2)−C(8)	2.071(9)
W(1)−C(4)	2.028(9)	2.037(9)	W(2)−C(9)	2.043(9)
W(1)−C(5)	2.019(8)	2.031(10)	W(2)−C(10)	2.045(10)
C(1)−O(1)	1.152(9)	1.127(11)	C(6)−O(6)	1.138(9)
C(2)−O(2)	1.148(9)	1.104(10)	C(7)−O(7)	1.120(10)
C(3)−O(3)	1.147(8)	1.124(10)	C(8)−O(8)	1.125(8)
C(4)−C(4)	1.155(9)	1.123(9)	C(9)−O(9)	1.121(9)
C(5)−C(5)	1.142(8)	1.125(10)	C(10)−O(10)	1.119(10)
P(1)−C(26)	1.83(3)	1.829(8)		
P(1)−C(50)	1.85(2)	1.856(8)		
P(1)−C(16)	1.82(2)	1.830(9)		
P(2)−C(36)	1.86(3)	1.822(8)		
P(2)−C(46)	1.83(2)	1.846(8)		
P(2)−C(50)	1.84(2)	1.858(7)		
		Angles		
P(1)−C(50)−P(2)	111.5(11)	133.1(4)		
O(1)−C(1)−W(1)	170(4)	175.6(9)	O(6)−C(6)−W(2)	178.8(9)
O(2)−C(2)−W(1)	169(3)	179.1(9)	O(7)−C(7)−W(2)	176.4(9)
O(3)−C(3)−W(1)	177(2)	179.1(9)	O(8)−C(8)−W(2)	176.7(8)
O(4)−C(4)−W(1)	166(2)	179.1(8)	O(9)−C(9)−W(2)	176.9(8)
O(5)−C(5)−W(1)	170(4)	177.5(10)	O(10)−C(10)−W(2)	179.2(10)
C(1)−W(1)−C(2)	87.9(14)	88.6(4)	C(6)−W(2)−C(7)	93.1(4)
C(1)−W(1)−C(3)	174(2)	177.0(3)	C(6)−W(2)−C(8)	176.3(4)
C(1)−W(1)−C(4)	98.5(14)	90.8(4)	C(6)−W(2)−C(9)	90.8(3)
C(1)−W(1)−C(5)	86.1(14)	85.7(4)	C(6)−W(2)−C(10)	89.6(4)
C(2)−W(1)−C(3)	86.5(9)	89.2(4)	C(7)−W(2)−C(8)	89.9(4)
C(2)−W(1)−C(4)	173.5(9)	179.1(3)	C(7)−W(2)−C(9)	174.4(3)
C(2)−W(1)−C(5)	94.5(11)	89.7(4)	C(7)−W(2)−C(10)	87.3(4)
C(3)−W(1)−C(4)	87.1(9)	91.5(4)	C(8)−W(2)−C(9)	86.4(3)
C(3)−W(1)−C(5)	86.1(14)	92.3(3)	C(8)−W(2)−C(10)	92.7(3)
C(4)−W(1)−C(5)	87.1(12)	90.8(4)	C(9)−W(2)−C(10)	88.6(4)
C(1)−W(1)−P(1)	90.4(9)	94.7(3)	C(6)−W(2)−P(2)	88.9(3)
C(2)−W(1)−P(1)	88.9(7)	89.8(3)	C(7)−W(2)−P(2)	92.0(3)
C(3)−W(1)−P(1)	89.8(7)	87.3(2)	C(8)−W(2)−P(2)	88.8(2)
C(4)−W(1)−P(1)	90.0(9)	89.7(2)	C(9)−W(2)−P(2)	92.2(2)
C(5)−W(1)−P(1)	175.1(8)	179.4(2)	C(10)−W(2)−P(2)	178.8(3)
C(26)−P(1)−C(50)	102.4(11)	107.6(3)		
C(26)−P(1)−C(16)	104.2(10)	104.9(4)		
C(16)−P(1)−(C(50)	104.5(10)	104.5(4)		
C(46)−P(2)−C(50)	101.4(10)	106.6(3)		
C(46)−P(2)−C(36)	101.4(9)	102.9(4)		
C(36)−P(2)−C(50)	102.2(10)	108.7(4)		
C(26)−P(1)−W(1)	119.2(7)	119.3(3)	C(36)−P(2)−W(2)	116.2(3)
C(50)−P(1)−W(1)	113.2(8)	108.6(2)	C(50)−P(2)−W(2)	108.3(2)
C(16)−P(1)−W(1)	111.8(7)	110.9(3)	C(46)−P(2)−W(2)	113.7(3)

Chart 1



Coordination of one $W(CO)_5$ unit to dppm changes the conformation of the dppm ligand only slightly. The

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dppm ligand still adopts conformation **I** with the lone pair of electrons on the free phosphine end directed toward $W(CO)_5$. This seems to be a more stable arrangement than configuration **II**, which would direct the phenyl rings on the uncoordinated end toward the bulky $W(CO)_5$ group. The P(1)−C(50)−P(2) angle of 111.5(11)° is greater than the value of 106.2(3)° in the free ligand but is more acute than typically found in η^1-dppm complexes (see Table 1).

Addition of a second $W(CO)_5$ to give **2** results in a dramatic alteration of the dppm conformation. The ligand now adopts conformation **III** (Chart 1), giving a severely crowded arrangement for the four phenyl rings. The crowding is relieved in several ways. First, the P(1)−C(50)−P(2) bond angle increases to 133.1(4)°, an increase of over 21° from **1**. Extreme P−C−P angles have been observed previously in $[Ir_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-dppm})]$ (127.2°)[26] and $[Ru_2(\eta^5\text{-}C_5H_5)_2(1,10\text{-phenanthroline})_2(\mu\text{-dppm})]^{2+}$ (133.1°).[14] Second, the tungsten atoms are on opposite sides of the P−C−P plane; the torsion angle of 43.3° allows for staggering of the Ph groups. Third, the W−P bond lengths in **2** are somewhat longer than in **1**, which may provide some added steric benefit. (The P(1)−C(50) and P(2)−C(50) bond distances in **2** are not lengthened over those found in **1** or in the free ligand.) Fourth, the C−P−C bond angles in **2** are larger than those in the free ligand as well as those associated with the coordinated phosphorus in **1**.

Solution Conformation of dppm in 1 and Its Relationship to Reactivity. It has been observed that the magnitude of $^2J_{PP}$ depends on temperature, the electronegativities of substituents bound to phosphorus, the oxidation state of phosphorus, and the phosphorus coordination number. It is also affected by the conformation.[27] When lone pairs of electrons of uncoordinated diphosphines are separated by an amine or methylene group and oriented toward each other (conformation **I**, Chart 1), the value of $^2J_{PP}$ tends to be significantly higher than when they are oriented away from each other (conformations **II** and **III**, Chart 1). Compounds containing η^1-dppm for which X-ray structures have been determined and for which solution $^2J_{PP}$ values are known are found in Table 1, along with torsion and P−C−P angles. Although one would not expect structures in the solid state to necessarily correspond to those in solution, some correlations are apparent. Type **I** complexes tend to have smaller P−C−P bond angles (110.6−116.3°) than type **II** complexes (116.4−120.1°). At the same time the coupling constants for type **I** complexes (40−106 Hz) tend to be larger than for type **II** complexes (18.3−73 Hz). These observations lead us to conclude that there is a tendency for the conformation observed in the solid state to persist in solution. In particular, complex **1** has the largest $^2J_{PP}$ of all dppm complexes and one that is similar to that of the free ligand; both the free ligand and **1** have type **I** solid-state structures. Molecular models suggest that P(2) in **1** is tilted toward the equatorial plane as a forced consequence of the steric demands of the $W(CO)_5$ and four phenyl groups. The uncoordinated phosphine of $(OC)_4Fe(\eta^1\text{-dppm})$ also points toward the CO groups in the solid state, but the $Fe(CO)_4$ moiety is less sterically demanding than $W(CO)_5$ and the dppm conformation may not be as fixed, leading to a smaller phosphorus−phosphorus coupling[11b] in solution. A solution structure for **1** that is consistent with all evidence is one in which the dangling phosphine precesses around the equatorial carbonyl plane, delocalized with respect to the four carbonyl groups but experiencing a van der Waals interaction.

Table 4. Variation of $^2J_{PP}$ (Hz) with Temperature in $(OC)_5W(\eta^1\text{-dppm})$ (1)

$^2J_{PP}$ ($C_6D_5CD_3$)	temp (°C)	$^2J_{PP}$ ($C_6D_5CD_3$)	temp (°C)
122.4	−50	114.1	30
121.0	−30	111.7	50
119.0	−10	110.6	70
116.6	10		

Table 5. Variation of $^2J_{PP}$ (Hz) with Solvent in $(OC)_5W(\eta^1\text{-dppm})$ (1)

solvent	$^2J_{PP}$ (∼20 °C)	solvent	$^2J_{PP}$ (∼20 °C)
$(CD_3)_2CO$	119.1	C_6D_6	114.7
THF-d_8	116.0	CD_2Cl_2	109.4
$C_6D_5(CD_3)$	114.7	$CDCl_3$	106.2

Based on the solid-state structures of **1** and **2** and the evidence that these structures persist in solution, the dppm ligand must undergo a significant conformational change in order to coordinate to a second $W(CO)_5$ group. The failure of **1** to react with $(OC)_5W(NH_2Ph)$ at room temperature at measurable rates can be attributed to the substantial energy required to provide a sufficient population of structures with conformations favorable to reaction.

The sensitivity of $^2J_{PP}$ to conformational changes suggested that it might depend on temperature and solvent. Values of $^2J_{PP}$ for **1** in deuterated toluene were determined from −50 to 70 °C and found to decrease from 122.4 to 110.6 Hz as the temperature was increased (Table 4). This can be attributed to a steady decrease in the population of complexes having conformation **I** as the temperature increases. A significant solvent dependence is also observed with $^2J_{PP}$ varying over about 13 Hz (Table 5); higher values of $^2J_{PP}$ tend to occur in solvents with greater donor numbers.

Conclusions. The dppm-bridged complex, **2**, does not form from **1** at room temperature but does form at elevated temperatures. An explanation, derived from the crystal structures of the two complexes and their ^{31}P and ^{13}C spectra, is the dramatic conformational change in the dppm ligand that accompanies the reac-

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tion. Supporting evidence for the solution conformation of **1** includes phosphorus−phosphorus coupling that is the largest yet observed in a complex of dppm and long-range coupling between the uncoordinated phosphine and the equatorial carbonyl carbons, an unprecedented observation.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond distances and angles for complexes **1** and **2** (14 pages). Ordering information is given on any current masthead page.

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