Inorg. Chem. 1993, 32, 233-236

A New Water-Soluble Phosphine for Use in Aqueous Organometallic Systems. Products from the Reactions of 2,3-Bis(diphenylphosphino)maleic Anhydride with Water and Oxygen

Alfred Avey, David M. Schut, Timothy J. R. Weakley, and David R. Tyler*

Department of Chemistry, University of Oregon,
Eugene, Oregon 97403

Received May 6, 1992

We report the synthesis of a new water-soluble phosphine for use in the study of aqueous organometallic systems. Aqueous organometallic chemistry is receiving increased attention,[1] but a severe limitation is the small number of appropriate water-soluble ligands, chelating phosphines in particular. Commonly used water-soluble phosphines include I ((diphenylphosphino)-benzenesulfonate, "triphenylphosphinemonosulfonate", TPPMS),[1,2] II (phosphinetriyltris(benzenesulfonate), "triphenylphosphine-trisulfonate", TPPTS),[1,3] and various sulfonated-derivatives of dppe (1,2-bis(diphenylphosphino)ethane) and related chelating ligands (e.g., complex III).[1,4] Unfortunately, the use of these ligands can be problematic. For example, TPPMS is not soluble in aqueous solution at room temperature, and TPPTS and the sulfonated diphosphines[4,5] are difficult to purify.

$P(C_6H_5)_2(C_6H_4SO_3^-)$

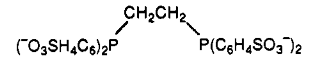
I

TPPMS

$P(C_6H_4SO_3^-)_3$

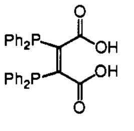
II

TPPTS

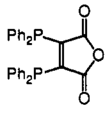


III

For our work with water-soluble 19-electron complexes,[6] we needed a ligand that was readily soluble in aqueous solution at room temperature, that could be synthesized without complication in a pure state, and that was bidentate. In this note, we report the synthesis of L_2, a new ligand that meets these requirements.



L_2



IV

Our starting point in the synthesis of L_2 was the known ligand 2,3-bis(diphenylphosphino)maleic anhydride (IV).[7] In our synthesis of L_2 from IV, we discovered several unexpected reactions of L_2 with water and oxygen that yielded interesting products. In this paper we also describe those reactions and products.

Results and Discussion

Synthesis and Reactions of L_2. L_2 was synthesized by the route in Scheme I and was easily purified by extraction followed by crystallization from diethyl ether. The structure of L_2 was confirmed by X-ray crystallography (Figure 1; Table I). Ligand L_2 is readily soluble in aqueous solution at pH 5 or greater. For example, the solubility is >1 M at pH 7. (The ligand is, of course, deprotonated at this pH.)

To demonstrate the utility of L_2 in aqueous organometallic chemistry, we irradiated ($\lambda > 500$ nm) solutions of the water-soluble complexes $(CpCOOH)_2W_2(CO)_6$ and $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in the presence of L_2. The disproportionation reactions (eqs 1 and 2; Table II) proceeded analogously to the reaction of $Cp_2M_2(CO)_6$ (M = Mo or W) and dppe (1,2-bis(diphenylphosphino)ethane) in benzene solution (eq 3; Table II).[6,8,9]

$$[(CpCOO^-)_2W^I_2(CO)_6]^{2-} + L_2^{2-} \xrightarrow[H_2O,\ pH\ 10]{h\nu} [(CpCOO^-)W^{II}(CO)_2(L_2^{2-})]^{2-} + [(CpCOO^-)W^0(CO)_3]^{2-} + CO \quad (1)$$

$$[(CpCH_2CH_2NH_3^+)_2Mo^I_2(CO)_6][NO_3^-]_2 + L_2^{2-} \xrightarrow[H_2O,\ pH\ 7]{h\nu} [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(L_2^{2-})]^0 + [(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]^0 + 2NO_3^- + CO \quad (2)$$

$$L_2^{2-} = \text{deprotonated } L_2$$

$$Cp_2Mo_2(CO)_6 + dppe \xrightarrow{h\nu} CpMo^{II}(CO)_2dppe^+ + CpMo^0(CO)_3^- + CO \quad (3)$$

Our previous work[8] in nonaqueous solvents also showed that, in the presence of reducible substrates, disproportionation of the metal-metal-bonded dimers did not occur. Rather, reduction of the substrate occurred as exemplified by the following reaction in which methyl viologen (MV^{2+}) is reduced:[6]

$$Cp_2W_2(CO)_6 + 2dppe + 2MV^{2+} \rightarrow 2CpW(CO)_2dppe^+ + 2MV^{\bullet+} + 2CO \quad (4)$$

An analogous reaction occurred with the L_2 ligand and $[(CpCOO^-)_2W_2(CO)_6]^{2-}$ in aqueous solution:[10]

$$[(CpCOO^-)_2W_2(CO)_6]^{2-} + 2L_2^{2-} + 2MV^{2+} \xrightarrow[H_2O,\ pH\ 10]{h\nu} 2[(CpCOO^-)W^{II}(CO)_2(L_2^{2-})]^{2-} + 2MV^{\bullet+} + 2CO \quad (5)$$

In summary, L_2 is an aqueous-soluble ligand that is easily synthesized and purified. In aqueous solution, L_2^{2-} reacts

---

[1] Barton, M.; Atwood, J. D. *J. Coord. Chem.* **1991**, *24*, 43-67.

[2] Ahland, S.; Chatt, J.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1958**, 276-288.

[3] (a) Escaffre, P.; Thorez, A.; Kalck, P. *J. Chem. Soc., Chem. Commun.* **1987**, 146-147. (b) Kalck, P. *Pure Appl. Chem.* **1989**, *61*, 967-971. (c) Kalck, P.; Escaffre, P.; Serein-Spirau, F.; Thorez, A. *New. J. Chem.* **1988**, *12*, 687-690. (d) Larpent, C.; Dabard, R.; Patin, H. *Inorg. Chem.* **1987**, *26*, 2922-2924. (e) Larpent, C.; Dabard, R.; Patin, H. *Tetrahedron Lett.* **1987**, *28*, 2507-2510. (f) Larpent, C.; Patin, H. *J. Organomet. Chem.* **1987**, *335*, C13-C16. (g) Larpent, C.; Patin, H. *J. Mol. Catal.* **1988**, *44*, 191-195. (h) Larpent, C.; Dabard, R.; Patin, H. *New J. Chem.* **1988**, *12*, 907-913. (i) Hermann, W.; Kulpe, J.; Kellner, J.; Ripel, H.; Bahrmann, H.; Konkol, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 391-393.

[4] (a) Bartik, T.; Bartik, B.; Hanson, B. E.; Glass, T.; Bebout, W. *Inorg. Chem.* **1992**, *31*, 2667-2670. (b) Nuzzo, R.; Haynie, S.; Wilson, M.; Whitesides, G. *J. Org. Chem.* **1981**, *46*, 2861-2867. (c) Alorio, F.; Amrani, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 202-203. (d) Lecomte, L.; Sinou, D. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1990**, *53*, 2391. (e) Amrani, Y.; Lecomte, L.; Sinou, D.; Bakos, J.; Toth, I.; Heil, B. *Organometallics* **1989**, *8*, 542.

[5] Larpent, C.; Patin, H.; Thilmont, N.; Valdor, J. F. *Synth. Commun.* **1991**, *21*, 495-503.

[6] Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607-3613.

[7] (a) Fenske, D. *Chem. Ber.* **1979**, *112*, 363. (b) For an improved synthesis of IV, see Mao, F.; Sur, S. K.; Tyler, D. R. *Organometallics* **1991**, *10*, 419.

[8] (a) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217. (b) Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253. (c) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032.

[9] Our previous studies showed that "19-electron" complexes are key intermediates in the nonaqueous metal-metal bond disproportionation reactions[8] such as that shown in eq 3. It is likely therefore that 19-electron species are also intermediates in the aqueous disproportionation reactions.[6]

[10] Our previous work showed that 19-electron adducts are the reductants in the nonaqueous reactions such as that shown in eq 4.[6,8] It is likely, but by no means certain, that 19-electron adducts are also forming in the aqueous reaction shown in eq 5.

0020-1669/93/1332-0233$04.00/0

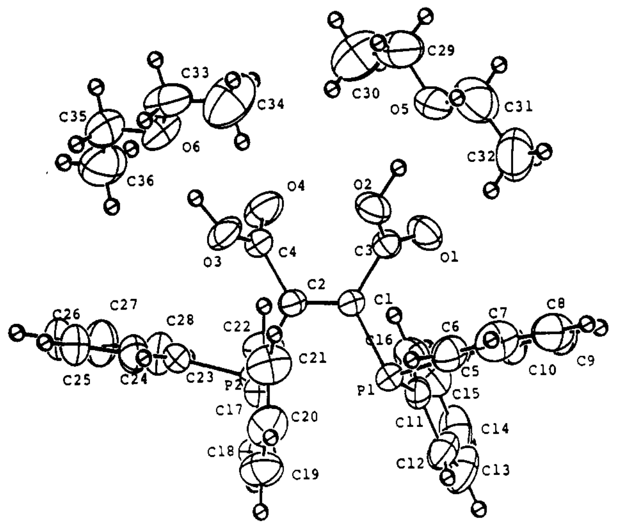
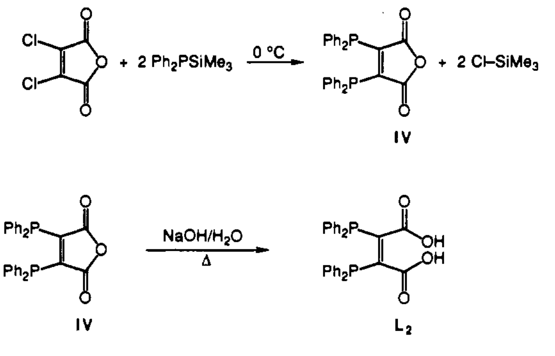


Figure 1. Molecular structure of $L_2 \cdot 2Et_2O$.

Scheme I. Synthesis of L_2

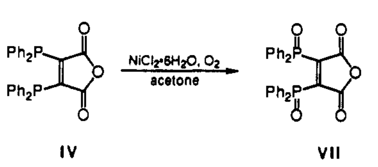


analogously to the dppe ligand in nonaqueous solvents; it should find a wide range of uses in the emerging area of aqueous organometallic chemistry.[11]

Other Hydrolysis Reactions of Compound IV. As indicated in Scheme I, compound IV is synthesized by the reaction of dichloromaleic anhydride with $Ph_2P-SiMe_3$.[7] The final step of the preparation is the separation of crystalline IV from the ether mother liquor. Compound IV is the product of this reaction as long as the filtration step is carried out under nitrogen. However, when the filtration is carried out in air and an aspirator is used as the source of the vacuum, the product obtained by filtration is compound V (see Scheme II). Spectroscopic data for V are reported in the Experimental Section. An X-ray crystal structure confirmed the identity of complex V (Figure 2; Table I). For comparison, the crystal structure of IV was also obtained (Figure 3; Table I).

Reaction of L_2 with oxygen and HCl (5%) in THF gave compound VI (Scheme II). Spectroscopic data are reported in the Experimental Section, and an X-ray analysis again confirmed the identity of the compound (Figure 4; Table I).

Although complex V formally results from the reaction of IV with a stoichiometric amount of H_2O, repeated attempts to synthesize V directly by reacting IV with stoichiometric amounts of water led only to decomposition and small amounts of VI.[12] An alternative synthesis of V (but hardly more rational than the one involving filtration of IV in air with an aspirator) is based on the literature report that IV reacts with oxygen in the presence of $NiCl_2 \cdot 6H_2O$ to give complex VII:[13]



(6)

In our hands, the product of this reaction is compound V (Scheme II). The "aspirator" synthetic route to V gives a better yield, so reaction 6 is therefore not recommended as a preparation of V.

Complex VI formally results from the addition of two water molecules and one oxygen atom to IV. It is reasonable to propose that V is an intermediate in the formation of VI from IV, but reaction of small amounts of water with V led only to decomposition. Note the two hydrogen atoms formally add trans to the double bond in IV to form V, while VI results from cis addition. In each case, the molecular geometry is the one which minimizes intramolecular steric interactions (Figures 2 and 4).

The molecular structures of complexes IV–VI (Figures 3, 2, and 4, respectively) exhibit no surprising features; bond lengths and bond angles are those expected for the atoms and structures involved. One noteworthy structural feature concerns the flexibility of the C–C–P angles in IV. Note that the C–C–P bond angles in IV (131.1 (3) and 130.2 (3)°) are similar to the H–C–C bond angles in maleic anhydride (≈130°).[14] This angle can change, however, when IV is coordinated. For example, the C–C–P angles are 123 and 118° in the $Co(CO)_3(IV)$[15] and $Co(CO)_2(PPh_3)(IV)$[16] complexes, respectively. The flexibility of the C–C–P angles is also reflected in the P(1)···P(2) (nonbonded) distances. In IV, this distance is 3.718 (2) Å. Upon coordination, however, this distance can shorten considerably: e.g., 3.07 Å, $Co(CO)_3(IV)$;[15] 3.07 Å, $Fe(CO)_3(IV)$;[15] 3.11 Å, $Co(CO)_2PPh_3(IV)$;[16] 3.07 Å, $(\eta^5-C_5Ph_4H)Mo(CO)_2(IV)$.[17] A second noteworthy structural point is the crystal packing of molecule VI: A figure provided in the supplementary material shows that chains of molecules are formed by hydrogen bonding between the oxygen atoms on the phosphorus atoms and hydrogen atoms on the carboxylic acid groups.

Experimental Section

Materials and Reagents. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere with use of standard Schlenk or vacuum line techniques or a Vacuum Atmospheres Co. glovebox.

2,3-Bis(diphenylphosphino)maleic anhydride (IV) was synthesized as previously described.[7] $(CpCOOH)_2W_2(CO)_6$[4] and $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$[6] were synthesized as previously reported. The pH 7 buffer (VWR) was deoxygenated by an N_2 purge. Methyl viologen (Aldrich) was used as received. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled under nitrogen from potassium benzophenone ketyl. Methylene chloride and chlorotrimethylsilane were distilled under nitrogen from calcium hydride. Hexanes were distilled under nitrogen from sodium. Dichloromaleic anhydride was recrystallized from Et_2O. $NiCl_2 \cdot 6H_2O$ was recrystallized from ethanol. Butyllithium (1.6 M in hexanes) and diphenylphosphine were obtained from Aldrich Chemical Co. and purged with nitrogen immediately before use.

Equipment. Photochemical reactions and wavelength selection were carried out as previously described.[8] Infrared spectra were obtained with a Nicolet 5 DXB FT-IR spectrometer. ^1H NMR spectra were obtained on a GE QE-300 spectrometer at 300.15 MHz. ^{31}P NMR spectra were obtained using a modified Nicolet NTC-360 spectrometer operating at

---

(11) L_2 is also useful in nonaqueous solvents: reactions 1, 2, and 5 also occurred in THF.

(12) Oxidation of phosphine complexes can be accomplished under mild conditions with I_2 and H_2O. (a) Bentrude, W. G.; Sopchik, A. E.; Gajda, T. *J. Am. Chem. Soc.* **1989**, *111*, 3981–3987. (b) Letsinger, R. L.; Lunsford, W. B. *J. Am. Chem. Soc.* **1976**, *98*, 3655–3661.

(13) Several rhodium complexes also oxidize the water-soluble phosphine $Ph_2P(CH_2)_2NMe_3^+$. See: Smith, R. T.; Ungar, K.; Sanderson, L. J.; Baird, M. C. *Organometallics* **1983**, *2*, 1138–1144.

(14) (a) Marsh, R. E.; Ubell, E.; Wilcox, H. E. *Acta Crystallogr.* **1962**, *15*, 35–41. (b) Hilderbrandt, R. L.; Peixoto, E. M. A. *J. Mol. Struct.* **1972**, *12*, 31–37.

(15) Fenske, D. *Chem. Ber.* **1979**, *112*, 363–375.

(16) Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, *111*, 130–134.

(17) Mao, F.; Philbin, C. E.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1990**, *9*, 1510–1516.

Table I. Crystallographic Data

	$L_2 \cdot 2Et_2O$	IV	V	VI
formula	$C_{28}H_{22}O_4P_2 \cdot 2C_4H_{10}O$	$C_{28}H_{20}O_3P_2$	$C_{28}H_{22}O_4P_2 \cdot 0.5C_6H_{14}$	$C_{28}H_{24}O_6P_2$
fw	632.7	466.41	527.5	518.4
space group	$P2_1/c$	$P2/n$	$P2_1/c$	$C2/c$
a, Å	9.193 (2)	13.253 (4)	10.654 (3)	20.560 (5)
b, Å	11.008 (2)	7.501 (4)	24.049 (4)	6.966 (6)
c, Å	34.778 (5)	24.087 (5)	11.500 (4)	17.935 (8)
β, deg	91.94 (2)	93.28 (2)	110.15 (2)	103.27 (3)
V	3517 (2)	2390 (3)	2766 (1)	2500 (4)
Z	4	4	4	4
d_{calc}, g cm^{-3}	1.195	1.296	1.267	1.377
T, °C	20	20	21	20
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
μ, cm^{-1}	1.59	2.03	1.85	2.09
rel trans coeff	0.96–1.00	0.94–1.00	0.96–1.00	0.95–1.00
no. of indep rflns with $I \geq 3\sigma(I)$	6507	2655	1800	1259
$R(F)^a$	0.048	0.052	0.058	0.057
$R_w(F)^b$	0.052	0.059	0.069	0.067

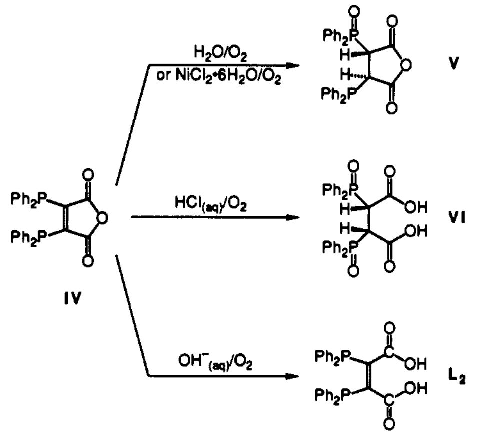
[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

Table II. Infrared Data

complex	$\nu(C{\equiv}O)$, cm^{-1}	ref
$(MeCp)_2Mo_2(CO)_6$[a,b]	2012 (m), 1956 (s), 1912 (s)	20
$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]$[c]	2009 (m), 1958 (s), 1908 (s)	21
$[(MeCp)Mo^{II}(CO)_2dppe^+]X^-$[a,d,e,f]	1980 (s), 1915 (s)	22
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(L_2^{2-})]^0$[c,g]	1956 (s), 1916 (s)	this work
$K^+[CpMo^0(CO)_3^-]$[h]	1898 (s), 1790 (s), 1750 (s)	23
$[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]^0$[c]	1905 (s), 1780 (s)	21
$Cp_2W_2(CO)_6$[i]	2012 (w), 1952 (s), 1905 (s)	6
$[(CpCOO^-)_2W_2(CO)_6]^{2-}$[j]	2011 (w), 1961 (s), 1910 (m)	6
$(CpCOOH)_2W_2(CO)_6$[h]	2015 (m), 1965 (s), 1914 (s), 1727 (w)[k]	6
$[CpW^{II}(CO)_2dppe^+]PF_6^-$[f,l]	1980 (s), 1905 (s)	24
$[(CpCOO^-)W^{II}(CO)_2(L_2^{2-})]^{2-}$[j]	1966 (s), 1902 (s)	this work
$[CpCOOH)W^{II}(CO)_2(L_2)]^+$[h,m]	1957 (s), 1900 (s)	this work
$Na^+[CpW^0(CO)_3^-]$[h]	1894 (s), 1790 (s), 1740 (s)	6
$[(CpCOO^-)W^0(CO)_3]^{2-}$[j]	1897 (s), 1791 (s, br)	6
$CpW(CO)_3H$[n]	2020 (vs), 1929 (vs), 1880 (w)	6
$(CpCOOH)W(CO)_3H$[h]	2023 (m), 1933 (s), 1884 (m)	this work

[a] MeCp = $(\eta^5\text{-}C_5H_4CH_3)$. [b] CCl_4. [c] H_2O, pH 7 buffer. [d] $X^- = (MeCp)Mo(CO)_3^-$. [e] CH_2Cl_2. [f] dppe = 1,2-bis(diphenylphosphino)ethane. [g] L_2^{2-} = deprotonated complex II. [h] THF. [i] Benzene. [j] H_2O, pH 10 buffer. [k] $\nu(C{=}O)$ in COOH. [l] $CHCl_3$. [m] L_2 = species II. [n] CS_2.

Scheme II. Reactions of L_2 with H_2O and O_2



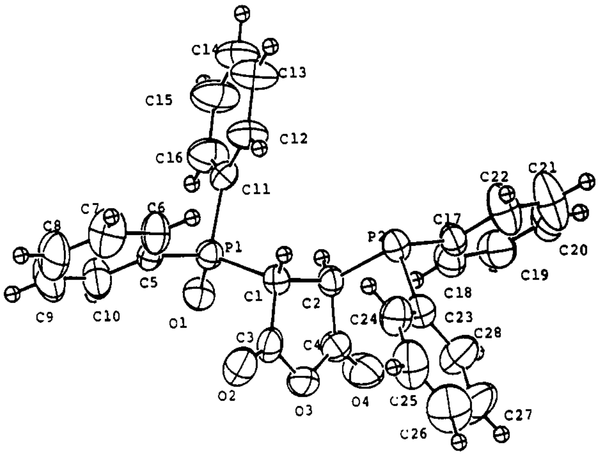


Figure 2. Molecular structure of compound V.

146.1763 MHz. Data were acquired with a modified Hare Research FELIX acquisition program.[18] Resolution for ^1H NMR was 8K for a sweep width of 6024 Hz, and for ^{31}P NMR, it was 8K for a sweep width of 10 000 Hz. Electron ionization mass spectra were obtained with a VG ZAB-2FHF mass spectrometer. Complete details of the X-ray crystallographic analyses are provided in the supplementary material.

Synthesis of L_2. 2,3-Bis(diphenylphosphino)maleic anhydride[7] (complex IV in Scheme I; 400 mg, 0.86 mmol) and NaOH (100 mg, 2.5 mmol) were placed in 25 mL of distilled H_2O. The heterogeneous mixture was refluxed until no yellow solid remained (approximately 15 min). The straw-colored solution was cooled to room temperature and extracted with ether (3 × 25 mL). Upon acidification of the aqueous solution with 5% H_2SO_4, the solution became cloudy yellow. The acidified aqueous layer was extracted with ether (3 × 25 mL). The bright yellow ether layers were combined, dried with $MgSO_4$, and filtered. Crystalline L_2 was obtained by concentration of the ether solution (yield: 330 mg; 60%). The compound is stable for at least several months in the solid state in the freezer. Likewise, there is no indication of decomposition in deoxygenated, basic (pH 10) aqueous solution over several days. Crystals for X-ray analysis were grown by dissolving 100 mg of the phosphine in 10 mL of ether in an 8-in. test tube. Slow evaporation of the ether over several days yielded large yellow blocks. Mp: 135–140 °C dec. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ = 8.5 (s(br), 2 H, acid protons; this resonance disappears upon treatment of the sample with D_2O), 7.2 (m,

---

[18] The program was modified by Dr. M. Strain, Institute of Molecular Biology, University of Oregon.

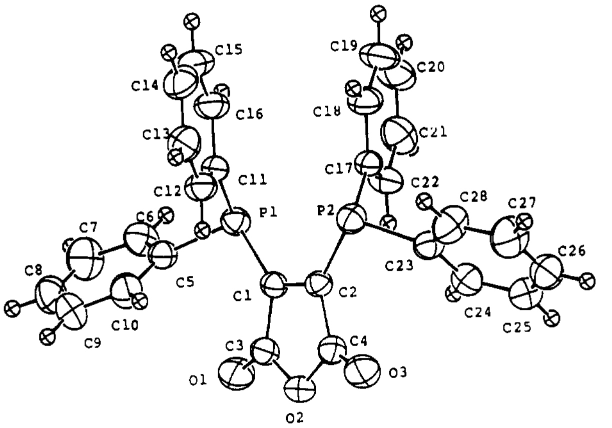


Figure 3. Molecular structure of compound IV.

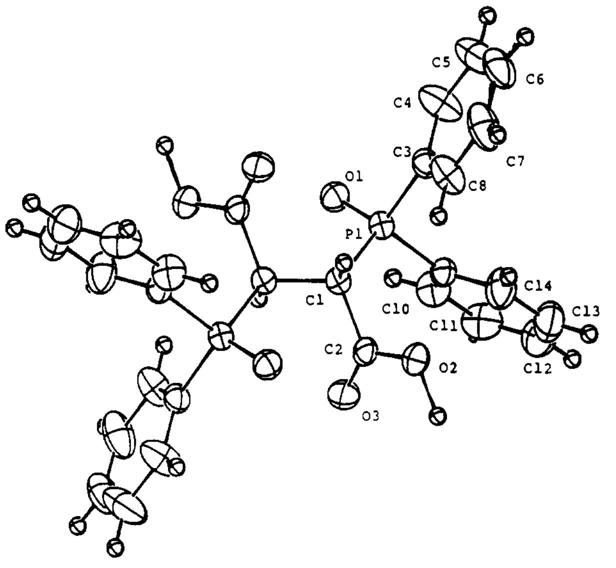


Figure 4. Molecular structure of compound VI.

20 H, phenyl protons). IR (KBr), $\bar{\nu}$ (cm^{-1}): 3000 (m, br) ν(OH); 1721 (s) ν(C=O); 1553 (w), 1482 (w), 1433 (m), 1215 (s), 1145 (m), 1089 (s), 1032 (m), 934 (w), 850 (m), 751 (s), 695 (s), 625 (w), 491 (m). Anal. Calcd for $C_{28}H_{22}O_4P_2\cdot 2C_4H_{10}O$: C, 69.42; H, 4.58. Found: C, 69.42; H, 4.45.

2-(Diphenylphosphino)-3-(diphenyloxophosphoranyl)succinic Anhydride (V), $(Ph_2P)(Ph_2PO)C_4H_2O_3$. The synthesis of this compound was identical to that of IV[7b] except for the isolation step. Instead of filtering the precipitate under N_2, the product was filtered in air with an aspirator, giving a white precipitate with yellow crystals of IV as an impurity. The IV impurity was removed by extracting the impure product with hot hexanes and then filtering the remaining undissolved white material. The white product was recrystallized by dissolving it in methylene chloride and layering hexanes over the solution. Yield: 0.0959 g; 57%.

A second synthesis[19] of this compound was conducted by dissolving 2,3-bis(diphenylphosphino)maleic anhydride (0.6818 g, 1.462×10^{-3} mol) and $NiCl_2\cdot 6H_2O$ (0.3470 g, 1.460×10^{-3} mol) in 10 mL of acetone. This solution was stirred vigorously in air for 12 h before filtering through a medium pore glass frit to remove the orange precipitate that formed during the reaction. The filtrate was collected and put into a test tube, and then hexanes were layered on top of the solution to precipitate the product. The precipitate was collected and recrystallized from acetone/hexanes. Yield: ≈0.07 g; <10%. Mp: 148–151 °C. ^{1}H NMR (δ, CD_2Cl_2): 7.60 (m, 20H), 4.41 (s, 1H), 4.39 (s, 1H); (δ, acetone-d_6): 7.51 (m, 20H), 5.59 (s, 1H), 5.55 (s, 1H). ^{31}P NMR (δ, $CDCl_3$): 30.30 (s), 7.59 (s). Mass spectrometry (*m/e*): C_6H_5, 77; $(C_6H_5)_2P$, 185; $(C_6H_5)_2P{=}O$, 201. Anal. Calcd: C, 69.42; H, 4.58. Found: C, 69.21; H, 4.37. IR (KBr): 1856, 1787, 1766 cm^{-1} ν(C=O); 1191 cm^{-1} ν(P=O); 3052 cm^{-1} ν(C—H, aromatic); 2915 cm^{-1} ν(C—H, aliphatic).

2,3-Bis(diphenylphosphoranyl)succinic Acid (VI), $(Ph_2PO)_2C_2H_2(CO_2H)_2$. 2,3-Bis(diphenylphosphino)maleic anhydride (0.50 g, 1.1×10^{-3} mol) was dissolved in 10 mL THF to which 10 mL of 5% HCl in H_2O had been added. The reaction mixture was covered with parafilm and allowed to sit for 3 days exposed to air. During this time, white crystals formed. The crystals were isolated by filtration and dried under reduced pressure. Yield: 0.0233 g; 14%. No other purification was necessary. Mp: 256–257 °C. IR (KBr): 1813, 1724 cm^{-1} ν(C=O); 1149 cm^{-1} ν(P=O). Mass spectrometry (*m/e*): C_6H_5, 77; $(C_6H_5)_2P{=}O$, 201. Anal. Calcd: C, 64.87; H, 4.67. Found: C, 64.36, 64.36; H, 4.76, 4.68.

Disproportionation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in Aqueous Solution with L_2. A solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (2.8 mM) and L_2 (115 mM) in pH 7 buffer was prepared and transferred to an IR cell via syringe. An initial spectrum and a spectrum taken after 5 min in the dark were identical. The solution was then irradiated (λ > 525 nm) for 2 min after which the reaction had gone to completion. The products were $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(L_2^{2-})]^{\bullet+}$ and $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]^0$ as identified by their IR spectra (Table II).

Disproportionation of $(CpCOOH)_2W_2(CO)_6$ in Aqueous Solution with L_2. A solution of L_2 (82 mM) and $(CpCOOH)_2W_2(CO)_6$ (2.8 mM) in pH 10 buffer was prepared and transferred to an IR cell via syringe. An initial spectrum and a spectrum taken after 5 min in the dark were identical. The solution was then irradiated (λ > 525 nm) for 1 min after which time the reaction had gone to completion. The products were $[(CpCOO^-)W^{II}(CO)_2(L_2^{2-})]^{2-}$, and $[(CpCOO^-)W^0(CO)_3]^{2-}$ as identified by their IR spectra (Table II).

Disproportionation of $(CpCOOH)_2W_2(CO)_6$ in Nonaqueous Solution with L_2. A solution of L_2 (78 mM) and $(CpCOOH)_2W_2(CO)_6$ (6.6 mM) in THF was prepared and transferred to an IR cell via syringe. An initial spectrum and a spectrum taken after 5 min in the dark were identical. The solution was then irradiated (λ > 525 nm) for 1 min after which time the reaction had gone to completion. The products were $[(CpCOOH)W^{II}(CO)_2(L_2)]^+$ and $(CpCOOH)W(CO)_3H$ as identified by their IR spectra, (Table II).

Reduction of Methyl Viologen. A solution of L_2 (3.3 mM), $(CpCOOH)_2W_2(CO)_6$ (0.033 mM), and methyl viologen (3.3 mM) in 4 mL of pH 10 buffer was prepared in a quartz cuvette with a freeze–pump–thaw side arm. The solution was freeze–pump–thaw degassed four times. No reaction was observed after 5 min in the dark. However, after 5 min of irradiation (λ > 525 nm), the electronic spectrum of the solution showed the characteristic spectrum[6] of the methyl viologen cation radical [λ_{max} = 396 nm (ϵ = 42 100); 606 (13 700)] with loss of the low-energy absorption (λ_{max} = 485 nm) due to the W dimer starting material. The reaction was complete after 30 min.

Acknowledgement is made to the National Science Foundation for financial support. A.A. and D.M.S. acknowledge the Department of Education National Needs Program for partial support.

Supplementary Material Available: Text detailing the crystal structure analysis and tables of crystallographic information, bond lengths and bond angles, nonbonded contact distances, calculated coordinates and thermal parameters for hydrogen atoms, anisotropic thermal parameters, torsion angles, and least-squares planes for L_2, compound V, compound IV, and compound VI and an ORTEP drawing of L_2 (67 pages). Ordering information is given on any current masthead page.

---

(19) Becher, H. J.; Bensmann, W.; Fenske, D. *Chem. Ber.* **1977**, *100*, 315–321.
(20) Goldman, A. S.; Tyler, D. R. *Organometallics* **1984**, *3*, 449.
(21) Avey, A.; Tyler, D. R. *Organometallics*, in press.
(22) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43.
(23) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263.
(24) Treichel, P. M.; Barnett, K. W.; Shubkin, R. L. *J. Organomet. Chem.* **1967**, *7*, 449.