but appears as two separate pseudoquartet (doublets of triplets) patterns (δ = 3.21 and 3.64 ppm) in the meso system (Figure 4). For the racemic system, assuming an averaged symmetric structure in solution, the central methylene bridge protons are expected to be equivalent and only have coupling to the two equivalent P$_{\text{int}}$ phosphorus atoms. The P–CH$_2$–P protons in the meso complex, on the other hand, are inequivalent and should give rise to two separate resonances that will show both ^{1}H–^{1}H and ^{1}H–^{31}P coupling constants, and this is exactly what is observed.

Isolation of Pure *meso*- and *rac*-eLTTP Ligands. The ability to easily separate the meso and racemic forms of Ni$_2$Cl$_4$(eLTTP) suggested that the nickel complex could provide a vehicle for isolating each diastereomer if the ligand could be displaced from the nickel centers. Fortunately, cyanide anion has been successfully used in the past to displace phosphine ligands from Ni(II) complexes.[15] Refluxing *rac*- or *meso*-Ni$_2$Cl$_4$(eLTTP) in an aqueous solution of NaCN displaces eLTTP from the nickel atoms to produce Ni(CN)$_4^{2-}$. eLTTP is readily extracted from the aqueous solution with benzene, which, after column chromatography and evaporation, gives the pure eLTTP ligand in 45% isolated yield.

The ability to separate the racemic and meso diastereomers of eLTTP will considerably simplify our work in preparing, characterizing, and studying the reactivity of M$_2$(eLTTP) complexes, particularly since *rac*- and *meso*-M$_2$(eLTTP) complexes of other metals (e.g., Rh, Co) are not always as easy to separate as Ni$_2$Cl$_4$(eLTTP). Although we are still working on a direct chromatographic separation of the two diastereomers of eLTTP, the nickel route is currently satisfactory and several grams of each pure eLTTP diastereomer has been isolated.

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Supplementary Material Available: Figure S-1 (^{31}P NMR spectra for *rac*- and *meso*-Ni$_2$Cl$_4$(eLTTP)) and Tables S-I–S-VII (crystal and data collection parameters, all bond distances and angles, and anisotropic thermal parameters) (11 pages); Tables S-VIII and S-IX (observed and calculated structure factors) (28 pages). Ordering information is given on any current masthead page.

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Thermal and Photochemical Reactivity of Group VI Open-Mode Bimetallic Complexes Based on a Binucleating Hexaphosphine Ligand System. Crystallographic Characterization of a Novel Ditungsten Heptacarbonyl Pentaphosphine Compound

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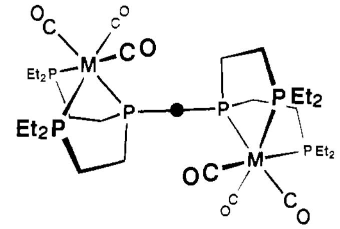
The thermal and photochemical reactivities of an isomorphous series of group VI bimetallic complexes, M$_2$(CO)$_6$(eHTP) (M = Cr, Mo, W; eHTP = (Et$_2$PCH$_2$CH$_2$)$_2$PCH$_2$P(CH$_2$CH$_2$PEt$_2$)$_2$), are reported. Thermally, the pure complexes are stable to refluxing xylene for extended periods of time. In the synthesis of W$_2$(CO)$_6$(eHTP), however, the occasional in situ formation of tungsten metal causes a partial fragmentation of the eHTP ligand. Single-crystal X-ray data for the isolated yellow complex from this fragmentation shows that it crystallizes in the acentric monoclinic space group *Pc* with a = 15.072 (4) Å, b = 8.007 (2) Å, c = 15.104 (7) Å, β = 102.8 (1)°, V = 1778 (2) Å^3, and Z = 2. The structure was refined to R = 0.029 and R_w = 0.039 by using 2281 unique data with $F_o^2 > 3\sigma(F_o^2)$. The structure reveals a ditungsten heptacarbonyl compound with an unusual pentaphosphine ligand derived from eHTP with the formula W$_2$(CO)$_7$(C$_{19}$H$_{43}$P$_5$). The original eHTP ligand has lost one of the four Et$_2$PCH$_2$CH$_2$– arms, and the resulting unsaturated phosphorus atom has formed a new P–C bond (with loss of H) to the starred carbon atom on a Et$_2$PC*H$_2$CH$_2$– arm from the other half of eHTP. This generates a multicycle pentaphosphine ligand that forms four- and five-membered chelate rings with one W(CO)$_3$ moiety and a single standard five-membered bis(phosphine) chelate with the other W(CO)$_4$ unit. The photolysis of the binuclear M$_2$(CO)$_6$(eHTP) (M = Cr, Mo, W) compounds in CH$_2$Cl$_2$ proceeds to give two distinct types of products: *mer,mer*-Cr$_2$Cl$_6$(eHTP) and M$_2$Cl$_4$(CO)$_4$(eHTP) (M = Mo, W). Cr$_2$(CO)$_6$(eHTP) is extremely photoreactive toward CH$_2$Cl$_2$, with the chlorination reaction forming Cr$_2$Cl$_6$(eHTP) proceeding in good yield and driven by even ambient laboratory fluorescent lighting. The Mo and W systems are considerably less photoreactive, with mercury lamp irradiation taking 4–6 days to produce two isomeric forms of the open-mode 7-coordinate M$_2$Cl$_4$(CO)$_4$(eHTP) (M = Mo, W) species.

Introduction

The hexatertiary phosphine ligand (Et$_2$PCH$_2$CH$_2$)$_2$PCH$_2$P(CH$_2$CH$_2$PEt$_2$)$_2$, eHTP, was designed to be a powerful binucleating ligand for lower valent transition-metal centers, and so far, every time we have reacted it with 2 equiv of a simple mononuclear metal halide, we have obtained a binuclear system. Our efforts have been directed at understanding the coordination chemistry of this polyphosphine ligand and its dynamic properties.[2-5] Recently we reported the synthesis and characterization of a homoleptic series of binuclear group VI systems based on eHTP, M$_2$(CO)$_6$(eHTP) (M = Cr, Mo, W).[6] These bimetallic compounds have an open-mode type eHTP conformation with M–M separations of ca. 6.3–6.5 Å. A schematic representation of these complexes is as follows:



It is somewhat difficult to come up with a proper nomenclature for identifying the various rotamers for the eHTP ligand, but we have used the syn and anti notations in describing our nickel system[3] and will continue with this nomenclature. Syn will, therefore, refer to the case where a metal atom is on the same side of the eHTP ligand as the central methylene group hydrogen atoms, while anti will indicate that the metal atom is on the opposite side. Although the solid-state structures of the M$_2$(CO)$_6$(eHTP) complexes have an anti–anti orientation of the metal

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centers with respect to the central methylene bridge, IR and NMR data, in conjunction with van der Waals energy calculations, point clearly to the presence of a syn–anti, "up–down", conformation in CH_2Cl_2 solution.[6]

Now that we have gained a more complete picture of the coordinating properties of eHTP, our studies are directed toward the reactivities of M_2(eHTP) species and the utilization of the structural and dynamic data for M_2(eHTP) systems to design new and improved binucleating polyphosphine ligands. We would, therefore, like to report our initial studies of the thermal and photochemical reactivity of the $M_2(CO)_6$(eHTP) (M = Cr, Mo, W) dimers and the transformation of our eHTP ligand to a *penta*phosphine system with tungsten to give the binuclear system $W_2(CO)_7(C_{19}H_{43}P_5)$.

Experimental Section

All manipulations were carried out under an inert atmosphere (N_2 or Ar) by using standard Schlenk or glovebox techniques unless stated otherwise. Solvents were distilled under an inert atmosphere from the following drying agents: diethyl ether, hexane, and THF (sodium/benzophenone); toluene (sodium); CH_2Cl_2 and acetonitrile (CaH_2); methanol and ethanol (magnesium). $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ (Strem Chemicals), sodium and potassium (Alfa Division of Morton Thiokol), and xylene and cycloheptatriene (Aldrich) were used as received without further purification. eHTP and the $M_2(CO)_6$(eHTP) dimers were prepared according to published procedures.[2,6] ^{31}P NMR spectra were run on Varian XL-300 or VXR-500 spectrometers, IR spectra were run on a Perkin-Elmer 283B spectrometer, NMR simulations were done on a Bruker Aspect 2000 stand-alone data station using the simulation program PANIC, and elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The ^{31}P COSY spectrum was obtained by the method of Bax[7] from a 128 × 1024 data matrix with zero filling to a 1024 × 1024 matrix. The spectral width was 16335 Hz with acquisition times of 8 and 31 ms for t_1 and t_2, respectively. Absolute-value processing was employed with pseudoecho weighting in both dimensions.

Photolysis of $Cr_2(CO)_6$(eHTP). $Cr_2(CO)_6$(eHTP) (0.100 g, 0.125 mmol) was dissolved in 50 mL of CH_2Cl_2, and the solution was stirred in a 20 °C circulating water bath and irradiated by a mercury lamp. Within 10 min the solution began to turn green, and within 1 h the solution darkened to purple with a small amount of solid dropping out of the solution. After 24 h the solid was removed by filtration and the purple solution evaporated to dryness. This sample showed no carbonyl stretches in the IR spectrum. The sample was purified by column chromatography on alumina using CH_2Cl_2 as the eluent. The major burgundy-colored fraction was collected and recrystallized to give X-ray-quality crystals (50–70% yield) by evaporation of CH_2Cl_2 and toluene. The elemental analysis, IR spectrum, and unit cell parameters for these burgundy-colored crystals are identical with those previously observed for *mer,mer*-Cr_2Cl_6(eHTP).[5]

Photolysis of $Mo_2(CO)_6$(eHTP). $Mo_2(CO)_6$(eHTP) (0.075 g, 0.083 mmol) was dissolved in 50 mL of CH_2Cl_2, and the solution was irradiated at 20 °C for 5 days. This produced a diamagnetic yellow solution and occasionally a yellow precipitate that was insoluble in all common solvents (very slightly soluble in DMSO). The IR spectrum (KBr) of this insoluble yellow solid showed strong ν_{CO} bands at 1970 and 1930 cm^{-1} and bands characteristic of eHTP. The soluble yellow species was isolated by vacuum evaporation and recrystallization from CH_2Cl_2/toluene to give 55–67% isolated yields of the Mo(II) species $Mo_2Cl_4(CO)_4$(eHTP).

Anal. Calcd for $C_{29}H_{58}Mo_2Cl_4O_4P_6$: C, 35.17; H, 5.90. Found: C, 35.63; H, 6.25. IR (KBr) (cm^{-1}): 2980, 2950, 2920, 2880 (m, C–H); 1970 (m), 1920 (s), 1830 (s), 1810 (s, sh, CO); 1460, 1420, 1380 (m-w, C–C); 1248, 1163, 1100 (w); 1035 (m, P–Et); 990 (w), 890 (m), 825 (w), 808, 770, 745, 735, 710 (m); 670, 625, 580 (w); 550 (m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, ppm, H_3PO_4 reference): 54.1 (s, 2 P), 66.3 (m, 1 P), 71.3 (m, 1 P), 75.5 (d, 2 P, J_{P-P} = 22.5 Hz).

Photolysis of $W_2(CO)_6$(eHTP). $W_2(CO)_6$(eHTP) was irradiated for 5 days by using the same conditions as for the Cr and Mo analogues. A diamagnetic yellow solution formed over the course of the photolysis. A diamagnetic insoluble yellow precipitate similar to that seen in the molybdenum reaction was generally produced during the reaction. The yellow precipitate had two strong ν_{CO} bands in the IR spectrum at 1950 and 1830 cm^{-1}. On two occasions both an intense purple-blue and a dirty green precipitate formed on the walls of the glass container where the light was shining through the solution. The purple-blue material was soluble in MeOH, while the green solid was insoluble in all common solvents. The soluble yellow species was isolated by vacuum evaporation and recrystallization from CH_2Cl_2/toluene to give 46–62% isolated yields of the W(II) species $W_2Cl_4(CO)_4$(eHTP).

Table I. Crystallographic Data for $W_2(CO)_7(C_{19}H_{43}P_5)$

formula: $W_2P_5O_7C_{26}H_{43}$	fw = 990.20
space group: *Pc* (No. 7)	λ = 0.71069 Å
a = 15.072 (4) Å	α = 90.00°
b = 8.007 (2) Å	β = 102.82 (1)°
c = 15.104 (7) Å	γ = 90.00°
V = 1778 (2) $Å^3$	Z = 2
d_{calc} = 1.85 g/mL	μ(Mo Kα) = 68.65 cm^{-1}
T = 22 °C	min transmissn coeff = 0.9270
$R(F_o)$ = 0.029	$R_w(F_o)$ = 0.039

Anal. Calcd for $C_{29}H_{58}W_2Cl_4O_4P_6$: C, 29.87; H, 5.01. Found: C, 30.53; H, 5.84. IR (KBr) (cm^{-1}): 2970, 2950, 2880 (m, C–H); 1955 (m, sh), 1920 (s), 1830 (s), 1810 (s, sh, CO); 1460, 1425, 1380 (m, C–C); 1260 (w), 1040, 1030 (m, P–Et); 890 (w); 820, 805, 790 (m); 770, 745, 730, 710 (m). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, ppm, H_3PO_4 reference): 37.75 (s, 2 P, J_{W-P} = 207.3 Hz), 50.0 (d, 2 P, J_{P-P} = 2 Hz), 51.0 (m, 1 P), 59.1 (d, 1 P, J_{P-P} = 17.9 Hz, J_{W-P} = 217.2 Hz).

Preparation of $W_2(CO)_7(C_{19}H_{43}P_5)$. eHTP (0.600 g, 1.1 mmol) and $W(CO)_6$ (0.775 g, 2.2 mmol) were added to 30 mL of xylene, and the mixture was refluxed for 5 days, during which time the solution turned yellow and a white precipitate of $W_2(CO)_6$(eHTP) formed. In half of the eight reactions we ran, a fine black precipitate of tungsten metal formed along with a light yellow precipitate of $W_2(CO)_6$(eHTP) (white) and $W_2(CO)_7(C_{19}H_{43}P_5)$ (yellow). The solution was allowed to cool and the volume reduced by vacuum evaporation to 10 mL. In the reactions where the black precipitate formed, the light yellow solid was collected by filtration and dissolved in CH_2Cl_2, and the mixture was filtered to remove the metallic tungsten. The light yellow solid was recrystallized from CH_2Cl_2/toluene to yield X-ray-quality crystals in ca. 40% yield. The crystals were a mixture of colorless square-prismatic $W_2(CO)_6$(eHTP) and yellow needlelike $W_2(CO)_7(C_{19}H_{43}P_5)$. The yellow $W_2(CO)_7(C_{19}H_{43}P_5)$ crystals were manually separated from those of $W_2(CO)_6$(eHTP).

Spectroscopic data for $W_2(CO)_7(C_{19}H_{43}P_5)$ are as follows. IR (KBr) (cm^{-1}): 2970, 2940, 2920, 2880 (m, C–H); 2010 (m), 1918, 1870, 1825, 1800 (s, CO); 1460, 1430, 1420, 1380 (mw, C–H); 1250 (w, br); 1040, 1030 (m, P–Et). $^{31}P\{^1H\}$ NMR (phosphorus atoms labeled as in the crystal structure, CD_2Cl_2, ppm, H_3PO_4 reference): −24.78 (dt, P1, J_{P1-P2} = 15 Hz, J_{P1-P4} = 16 Hz, J_{P1-P6} = 15 Hz, 1 P), 29.12 (dd, P6, J_{P6-P1} = 15 Hz, J_{P6-P2} = 23 Hz, 1 P), 33.73 (s, P5, 1 P), 36.65 (dd, P4, J_{P4-P1} = 16 Hz, J_{P4-P6} = 2 Hz, 1 P), 60.99 (dd, P2, J_{P2-P1} = 15 Hz, J_{P2-P6} = 23 Hz, 1 P). Each resonance is flanked by tungsten satellites with the following coupling constants: J_{W-P1} = 94 Hz, J_{W-P2} = 112 Hz, J_{W-P4} = 108 Hz, J_{W-P5} = 112 Hz, and J_{W-P6} = 87 Hz.

X-ray Crystallographic Procedure. Data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature using Mo Kα radiation and a graphite-crystal monochromator by the $\theta/2\theta$ scan technique using variable-speed scanning rates. Crystal data and experimental details are listed in Table I. Structure solving was done by using the Enraf-Nonius Structure Determination Package program set on a microVAX II computer system. Data reduction included corrections for background, Lorentz, and polarization effects, as well as an empirical absorption correction based on ψ scans of reflections near χ = 90°.

The tungsten atom positions were located from a Patterson map and the other non-hydrogen atoms located from subsequent difference Fourier maps after least-squares refinement of the W atom positions. A particularly good data set was not obtained due to the small size of the crystal, and this resulted in higher esd's for the bond distances and angles than those seen for the structure of the parent $W_2(CO)_6$(eHTP) compound.[6] Crystal and data collection parameters are listed in Table I, while positional parameters are given in Table II. Hydrogen atom positions were calculated by using the program HYDRO and were included in the final structure factor calculation. Tables of anisotropic thermal parameters and observed and calculated structure factors are included in the supplementary material.

Results and Discussion

The reactions of 2 equiv of $M(CO)_6$ (M = Cr, Mo, W) with eHTP produces the bimetallic species $Cr_2(CO)_6$(eHTP), $Mo_2(CO)_6$(eHTP), and $W_2(CO)_6$(eHTP).[6] An occasional side product isolated from the reactions of $W(CO)_6$ and eHTP in refluxing xylene consisted of yellow needlelike crystals that differed quite substantially in both shape and color from the squarish, nearly colorless $W_2(CO)_6$(eHTP) crystals. Both the IR and ^{31}P NMR

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Table II. Positional Parameters for $W_2(CO)_7(C_{19}H_{43}P_5)$

atom	x	y	z	B, Å$^{2\,a}$
W1	0.06200 (5)	0.05823 (6)	0.79762 (5)	2.848 (9)
W2	0.500	−0.02652 (8)	1.00	4.10 (1)
P1	0.1504 (2)	−0.1166 (5)	0.9184 (2)	2.93 (7)
P2	−0.0609 (3)	−0.0692 (5)	0.8620 (3)	3.60 (8)
P4	0.3520 (2)	−0.1700 (5)	0.9646 (3)	3.39 (8)
P5	0.5344 (3)	−0.2705 (6)	1.1042 (3)	4.7 (1)
P6	0.1086 (3)	−0.2138 (4)	0.7389 (2)	3.08 (8)
O1	−0.0863 (8)	0.191 (2)	0.6353 (8)	6.2 (3)
O2	0.2190 (9)	0.224 (2)	0.7232 (9)	6.5 (3)
O3	0.074 (1)	0.378 (1)	0.9186 (7)	5.8 (3)
O4	0.698 (1)	0.125 (2)	1.058 (1)	9.5 (5)
O5	0.420 (1)	0.272 (2)	0.872 (1)	11.0 (5)
O6	0.433 (1)	0.169 (2)	1.153 (1)	9.2 (5)
O7	0.554 (1)	−0.229 (3)	0. 839 (1)	10.2 (5)
C′	0.258 (1)	−0.067 (2)	1.001 (1)	4.1 (3)
C1	−0.032 (1)	0.148 (2)	0.695 (1)	4.4 (4)
C2	0.160 (1)	0.154 (2)	0.751 (1)	3.7 (3)
C3	0.067 (1)	0.261 (2)	0.8718 (9)	3.7 (3)
C4	0.627 (1)	0.063 (3)	1.038 (2)	6.8 (5)
C5	0.451 (1)	0.160 (2)	0.921 (1)	6.6 (5)
C6	0.460 (2)	0.096 (2)	1.097 (2)	6.7 (6)
C7	0.536 (1)	−0.151 (3)	0.898 (1)	6.1 (5)
C11	0.081 (1)	−0.222 (2)	0.9891 (9)	3.8 (3)
C12	−0.017 (1)	−0.249 (2)	0.936 (1)	3.9 (3)
C21	−0.109 (1)	0.063 (2)	0.939 (1)	5.3 (4)
C22	−0.157 (1)	0.213 (3)	0.892 (1)	7.4 (5)
C23	−0.163 (1)	−0.152 (3)	0.784 (1)	6.1 (5)
C24	−0.235 (2)	−0.222 (4)	0.827 (2)	11.9 (9)
C41	0.359 (1)	−0.372 (2)	1.020 (1)	5.3 (4)
C42	0.428 (1)	−0.365 (2)	1.117 (1)	5.6 (4)
C43	0.292 (1)	−0.218 (2)	0.848 (1)	4.0 (3)
C44	0.1920 (9)	−0.272 (2)	0.8450 (9)	3.1 (3)
C51	0.589 (1)	−0.216 (3)	1.227 (2)	7.2 (6)
C52	0.603 (2)	−0.366 (3)	1.291 (1)	7.9 (6)
C53	0.594 (2)	−0.452 (2)	1.073 (2)	7.8 (6)
C54	0.694 (2)	−0.404 (4)	1.069 (2)	10.6 (9)
C61	0.170 (1)	−0.205 (2)	0.646 (1)	3.9 (3)
C62	0.217 (1)	−0.366 (2)	0.626 (1)	5.3 (4)
C63	0.040 (1)	−0.404 (2)	0.712 (1)	3.8 (3)
C64	−0.033 (1)	−0.386 (2)	0.621 (1)	5.5 (5)

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

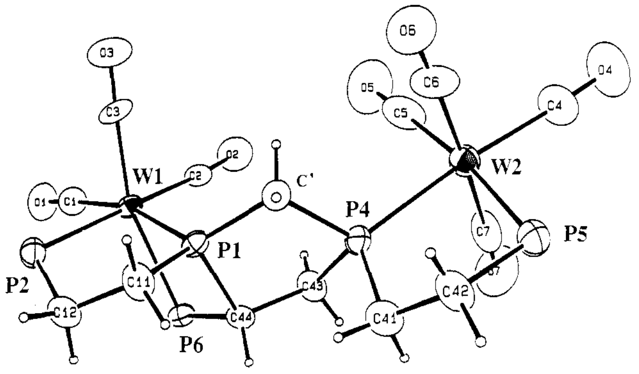

Figure 1. ORTEP plot of $W_2(CO)_7(C_{19}H_{43}P_5)$ (**1**). The ethyl groups on the terminal phosphorus atoms (P2, P5, and P6) have been omitted for clarity. The labeling scheme used is the same as that for the parent $W_2(CO)_6$(eHTP) complex, with the C13–C14–P3 group having been fragmented off P1. Thermal ellipsoids are shown at 50% probability level.

spectra clearly indicated that this material was *not* $W_2(CO)_6$(eHTP). A single-crystal X-ray structure revealed a binuclear tungsten heptacarbonyl complex $W_2(CO)_7(C_{19}H_{43}P_5)$ (**1**) in which the eHTP ligand has lost one (diethylphosphino)ethyl arm to form a rather novel pentaphosphine ligand. An ORTEP plot of this complex is shown in Figure 1, with selected bond distances and angles listed in Table III. The labeling scheme used in Figure 1 is the same utilized for our previously characterized complexes.[2-6]

Table III. Selected Bond Distances (Å) and Angles (deg) for $W_2(CO)_7(C_{19}H_{43}P_5)$

W1–W2	6.666 (1)	W2–C6	1.97 (3)
W1–P1	2.446 (5)	W2–C7	2.00 (2)
W1–P2	2.494 (5)	P1–C′	1.86 (2)
W1–P6	2.511 (4)	P4–C′	1.82 (2)
W1–C1	1.99 (2)	O1–C1	1.13 (2)
W1–C2	1.94 (2)	O2–C2	1.20 (2)
W1–C3	1.97 (2)	O3–C3	1.16 (2)
W2–P4	2.460 (5)	O4–C4	1.15 (3)
W2–P5	2.490 (6)	O5–C5	1.20 (3)
W2–C4	2.01 (3)	O6–C6	1.17 (3)
W2–C5	1.95 (3)	O7–C7	1.17 (3)
P1–W1–P2	78.7 (2)	C1–W1–C3	94.4 (8)
P1–W1–P6	67.5 (1)	C2–W1–C3	86.9 (8)
P1–W1–C1	164.7 (6)	P4–W2–P5	79.8 (2)
P1–W1–C2	99.4 (6)	P4–W2–C4	172.4 (9)
P1–W1–C3	96.0 (6)	P4–W2–C5	91.2 (7)
P2–W1–P6	94.2 (2)	P4–W2–C6	88.9 (9)
P2–W1–C1	89.6 (7)	P4–W2–C7	89.2 (7)
P2–W1–C2	178.0 (6)	P5–W2–C4	92.7 (9)
P2–W1–C3	92.9 (6)	P5–W2–C5	169.8 (7)
P6–W1–C1	104.0 (6)	P5–W2–C6	88.6 (8)
P6–W1–C2	85.4 (5)	P5–W2–C7	92.5 (9)
P6–W1–C3	160.3 (7)	C4–W2–C5	96 (1)
C1–W1–C2	92.4 (9)	P1–C′–P4	109 (1)
C4–W2–C6	93 (1)	W1–C1–O1	177 (2)
C4–W2–C7	89 (1)	W1–C2–O2	176 (2)
C5–W2–C6	86 (1)	W1–C3–O3	176 (2)
C5–W2–C7	92 (1)	W2–C4–O4	175 (3)
C6–W2–C7	178 (1)	W2–C5–O5	179 (3)
W1–P1–C′	128.8 (7)	W2–C6–O6	178 (3)
		W2–C7–O7	177 (3)

The structure shows that the internal phosphorus atom P1 has lost one of its (diethylphosphino)ethylene linkages (what would have normally been labeled P3), and to make up for the open valence, P1 has formed a new P–C bond to C44, which is part of the ethylene bridge between P4 and P6. C44, therefore, acts as a substituted methylene bridge between P1 and P6, which chelate to W1. This makes a strained four-membered chelate with W1 and results in a substantial distortion in the octahedral geometry about W1: P1–W1–P6 = 67.5 (1)°, P1–W1–P2 = 78.7 (2)°, and P6–W1–C3 = 160.3 (7)°. The second tungsten atom, W2, has four carbonyl ligands and one five-membered chelate ring with P4 and P5. The five-membered chelate rings also have relatively compressed P–W–P angles with similar values: P4–W2–P5 = 79.8 (2)° and P1–W1–P2 = 78.7 (2)°. The compressed P–W–P chelate angles arise from the relatively long W–P bond lengths, which range from 2.446 (5) to 2.494 (5) Å. The W–W separation in **1** is 6.666 (1) Å and is roughly what one would expect for this open-mode geometry. The other bond distances are in the usual ranges and will not be discussed further.

The P1–C44–P6 methylene bridge angle is 95.2 (8)° and is comparable to that seen for other chelated M(η^2-PCH$_2$P) units[8] as well as the mononuclear FeCl(CO)(η^4-eHTP)$^+$ species.[9] Unlike those in the $M_2(CO)_6$(eHTP) compounds, or the symmetrically coordinated eHTP complexes $Co_2(CO)_4(eHTP)^{2+}$ and $M_2Cl_2(eHTP)^{2+}$ (M = Ni, Pd, Pt), which have central P–CH$_2$–P angles in the range 122–130°, the central methylene bridge angle in **1** is a normal 109 (1)°. This results from the fact that the P1–CH$_2$–P4 bridge is involved in a five-membered ring system formed by the bonding of P1 to C44, which restricts the opening of the bridge angle by intraligand repulsions. The bimetallic eHTP species *mer,mer*-Cr_2Cl_6(eHTP) has an asymmetric eHTP coordination mode with one (diethylphosphino)ethylene group from each internal phosphine bridging to the opposite metal atom, giving rise to fused five- and seven-membered ring systems.[5] The central

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[8] Cf: (a) Darensbourg, D. J.; Zalewski, D. J.; Plepys, C.; Campana, C. *Inorg. Chem.* **1987**, *26*, 3727. (b) Cotton, F. A.; Falvello, L. R.; Poli, R. *Polyhedron* **1987**, *6*, 1135. (c) Foy, R. M.; Kepert, D. L.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans* **1980**, 440.

[9] Askham, F. R.; Saum, S. E.; Stanley, G. G. *Organometallics* **1987**, *6*, 1370.

methylene group in *mer,mer*-Cr_2Cl_6(eHTP) also has a normal P–CH_2–P angle of 115.2 (4)° for essentially the same reasons because it is part of a seven-membered ring system. Indeed, the closest analogy for **1** is to the multibridging structure seen for *mer,mer*-Cr_2Cl_6(eHTP) (vide infra).

The spectroscopic data for $W_2(CO)_7(C_{19}H_{43}P_5)$ are fully consistent with the solid-state structure. The infrared spectrum displays five ν_{CO} bands at 2010, 1918, 1870, 1825, and 1800 cm^{-1}, while the $^{31}P\{^1H\}$ spectrum, shown in Figure 2, shows all five inequivalent phosphorus atoms. The ^{31}P spectrum of **6**, in spite of its apparent complexity, turns out to be a relatively straightforward first-order system with the following P–P coupling constants: J_{P1-P2} = 15 Hz, J_{P1-P6} = 15 Hz, J_{P1-P4} = 16 Hz, J_{P2-P6} = 23 Hz, and J_{P4-P6} = 2 Hz. The spectrum has been successfully simulated by using these coupling constants.

One interesting feature of the ^{31}P NMR spectrum is the discrepancy between the assigned peak positions and those expected from chelating ring effects.[10] It is well-known that trivalent phosphorus atoms involved in four-membered chelate rings experience a pronounced shielding effect of ca. 52 ppm. Phosphines that participate in five-membered chelates, on the other hand, encounter a deshielding effect of ca. 33 ppm. Furthermore, these effects are usually additive. On the basis of these ring-shift effects, P6 should be the furthest upfield, since it is only involved in a single four-membered chelate, thus experiencing the maximum shielding effect. P1, on the other hand, is involved in both four- and five-membered chelate rings with the deshielding five-membered-chelate-ring effect cancelling out a fair bit of the four-membered-ring downfield shift. Our assignments, however, have P1 located at −24.8 ppm and P6 at 29.1 ppm—exactly opposite from that expected from the ring-shift effects. We believe, however, that the coupling constants confirm our peak assignments: the pseudo-quartet pattern at −24.8 ppm (see Figure 2) is consistent with essentially equivalent 15-Hz coupling to three other phosphorus centers, and *only* P1 is in the proper position to experience this type of coupling to P2, P6, and P4. We have explored a variety of other possible coupling schemes, and only the one proposed is consistent with the coupling patterns observed.

The fact that P1 is involved in both four- and five-membered tungsten chelate rings *and* the five-membered P1–P4 ring system represents an interesting combination of ring effects. It has been reported that phosphorus atoms involved in *non*-metal-containing ring systems are, on occasions, subject to noticeable shielding/deshielding effects.[10] Phosphorus atoms in five-membered *non*-metallacyclic rings, for example, experience nuclear shielding, while deshielding is seen for five-membered metallacycles. This shielding non-metallacyclic rings effect would work to shift the P1 resonance further upfield. Another factor that may be working to switch the positions of P1 and P6 is the fact that moving down a metal triad can significantly enhance the chelate nuclear-shielding effect, as clearly demonstrated with the mononuclear complexes $M(CO)_4(\eta^2\text{-dppm})$: the tungsten species has a ^{31}P signal at −23.7 ppm, while the molybdenum and chromium analogues have signals at 0.0 and +23.6 ppm, respectively.[10,11] Furthermore, there is a difference between the W–P bond distances for phosphorus atoms P1 and P6: W1–P1 = 2.446 (5) Å and W1–P6 = 2.511 (4) Å. The fact that the W1–P1 bond distance is shorter by 0.07 Å should imply that P1 is experiencing a higher shielding effect from the tungsten atom than P6, which, once again, works in the proper direction to explain the relative chemical shift positions of P1 and P6. The W–P coupling constants J_{W-P1} = 94 Hz and J_{W1-P6} = 87 Hz are also consistent with and supportive of this bond strength/shielding argument.

A natural question that arises is, how does **1** form? Although this is the first time any fragmentation has been observed for eHTP, we have never before subjected a metal/eHTP system to the relatively vigorous reaction conditions of refluxing xylene (bp ca. 140 °C). Several obvious possibilities such as simple thermal fragmentation of $W_2(CO)_6$(eHTP) or eHTP can be easily ruled out by refluxing xylene solutions of each for 1 week and not observing any fragmentations. eHTP has considerable thermal stability, as indicated by the fact that it is isolated by vacuum distillation at 205 °C with no sign of thermal fragmentations. We have, however, noted that occasionally during the preparation of $W_2(CO)_6$(eHTP), by reaction of $W(CO)_6$ and eHTP in refluxing xylene, small amounts of a fine black precipitate are formed in the intermediate stages of the reaction. This black material is metallic tungsten, and whenever it forms, the production of **1** has been *consistently* observed.

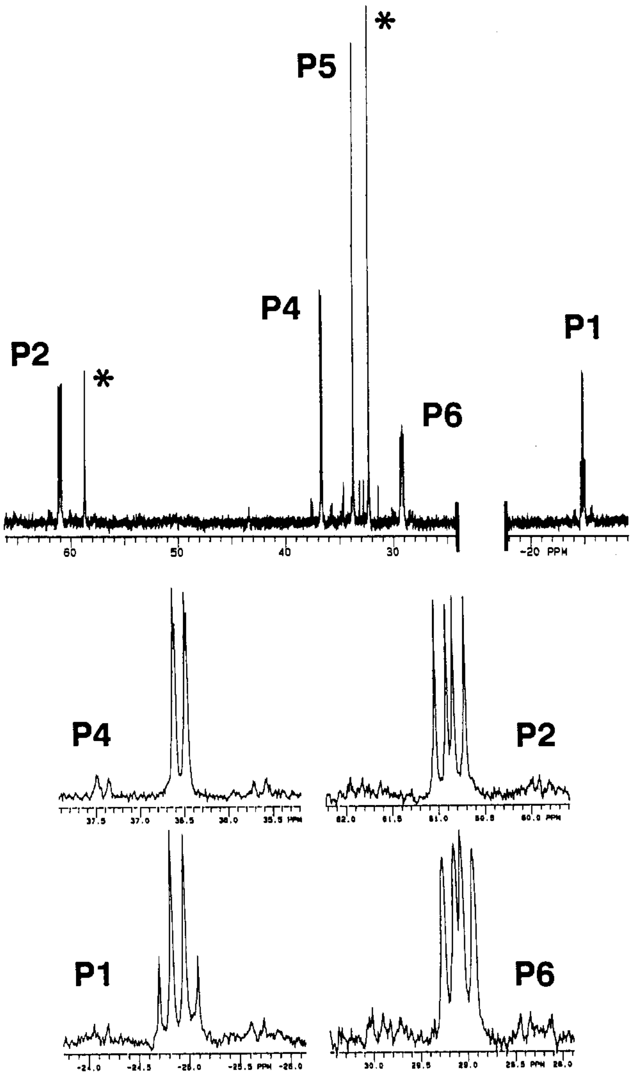

Figure 2. $^{31}P\{^1H\}$ NMR spectra of $W_2(CO)_7(C_{19}H_{43}P_5)$. Peaks marked with a star belong to the starting material $W_2(CO)_6$(eHTP). The labeling scheme for the peaks corresponds to that used in the ORTEP plot in Figure 1. Expanded views of the ^{31}P NMR peaks (except that for P5, which is a singlet) for **1** are shown below the full spectrum.

We have not, unfortunately, been able to determine the conditions that lead to the formation of the metallic tungsten, but it generally formed in about half of the reactions we ran. This variability may suggest that a surface-mediated container-type effect is responsible for the formation of the tungsten metal. $W_2(CO)_6$(eHTP) can also be prepared by reacting (η^6-cycloheptatriene)tricarbonyltungsten or preformed (η^6-xylene)tricarbonyltungsten with eHTP under milder conditions with *no* formation of **1**, whereas the direct reaction of $W(CO)_6$ and eHTP under less vigorous conditions (refluxing toluene) gives no products at all after several days of reaction. Furthermore, the addition of finely divided tungsten metal (obtained from an extended reflux of $W(CO)_6$ in xylene) to the reaction mixture of $W(CO)_6$ and eHTP in refluxing xylene did *not* produce **1**.

On the basis of this limited information, we propose that there is a homolytic fragmentation of one of the P_{int}–$CH_2CH_2PEt_2$ arms

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(10) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(11) Grim, S. O.; Barth, B.; Briggs, W.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1095.

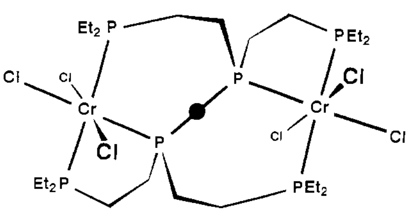
induced by some type of small reactive tungsten species that is generated during the formation of bulk tungsten metal. The in situ formation of metallic particles of tungsten metal in our reaction mixture must proceed through the initial formation of small-molecular-sized tungsten clusters that are probably unsaturated and quite reactive. Since the addition of bulk tungsten does not result in the formation of **1**, it appears quite likely that **1** is formed by interaction of eHTP with the small precursor tungsten monomer or cluster species that assemble to form the bulk metal.

The fragmentation of polyphosphine ligands induced by reactive impurities has been observed for the more sterically encumbered tris(phosphine) ligand $HC(PPh_2)_3$ (tripod), where it is believed that both nickel metal and O_2 can promote the fragmentation of $Ni(CO)_2$(tripod) and subsequent hydrogen abstraction to give the (diphenylphosphino)methane- (dppm-) bridged dimer $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$.[12] Mague and co-workers, as well as ourselves, have noted that oxygen-free solutions of the iron analogue, $Fe(CO)_3$(tripod), can be refluxed in toluene for extended periods with no sign of tripod fragmentation.[13] Moreover, Mague has noted that the use of impure $Fe_3(CO)_{12}$ in reactions with tripod does cause fragmentation, yielding iron–dppm carbonyl dimers.[14]

If small reactive clusters of tungsten metal are responsible for the fragmentation of eHTP, one would expect a variety of other fragmented phosphine products to be present. Although the precipitate generated contains only $W_2(CO)_6$(eHTP) and **1**, ^{31}P NMR spectroscopy demonstrates that there is a relatively complex mixture of unidentifiable tungsten-bound and -unbound phosphorus-containing products in the yellow xylene solution. **1** is the only fragmentation product that precipitates out of the xylene solution and is easily isolated. On the basis of the relative yields and ^{31}P NMR spectra, it is also the major fragmentation product.

Photochemistry. Our interest in preparing closed-mode M–M-bonded eHTP dimers naturally made us consider the prospect for photodissociating one or two of the carbonyl groups to produce an unsaturated species that would be sufficiently sterically nonhindered to allow rotation about the central methylene group to form a closed-mode complex. Although the photodissociation of carbonyls from a relatively electron-rich $M(CO)_3(P)_3$ moiety seemed somewhat unlikely, we nevertheless decided to examine the photolysis of the $M_2(CO)_6$(eHTP) family.

Although the Cr, Mo, and W hexacarbonyl–eHTP complexes form an isomorphous structural set, the photochemical reactivity varies quite dramatically from $Cr_2(CO)_6$(eHTP) to $Mo_2/W_2(CO)_6$(eHTP). The chromium hexacarbonyl eHTP complex was photolyzed by using a mercury lamp in CH_2Cl_2 at 20 °C for 24 h. The initially colorless solution began turning green after 15 min and darkened to purple after 1 h. Filtration of the final dark purple solution followed by column chromatography allowed the isolation of the major burgundy-colored air-stable paramagnetic product in 50–70% yields. The IR spectrum and unit cell dimensions of this product exactly match that of the previously characterized Cr(III) complex *mer,mer*-Cr_2Cl_6(eHTP), the structure of which is[5]



The bis(phosphino)methane unit is bridging the two Cr(III) centers with one (diethylphosphino)ethyl arm attached to each metal center in the traditional fashion. The second (diethylphosphino)ethyl arm is used to form a bis(phosphino)ethane bridge between the two Cr atoms. This forms a rigid system of four fused metallacycles having five- and seven-membered chelate rings. This complex was previously prepared from the direct reaction of 2 equiv of $CrCl_3\cdot 3THF$ with eHTP.

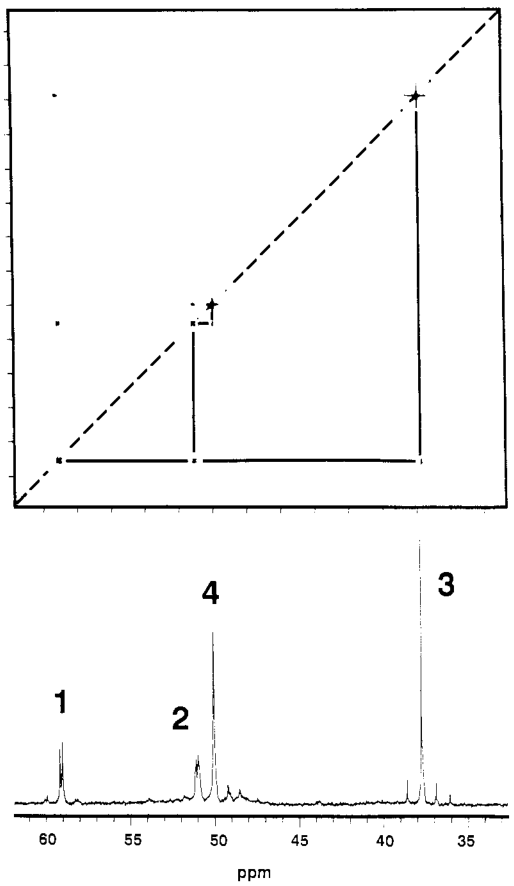


Figure 3. $^{31}P\{^1H\}$–$^{31}P\{^1H\}$ COSY two-dimensional NMR spectrum (top) and one-dimensional $^{31}P\{^1H\}$ NMR spectrum (bottom) for $W_2Cl_4(CO)_4$(eHTP). The ppm scale on the one-dimensional spectrum also applies to the two-dimensional spectrum. Peaks 1 and 2 are assigned to the two internal phosphorus atoms, while peaks 3 and 4 indicate the external phosphorus atoms. See text for further discussion.

It is well-known that the photolysis of CH_2Cl_2 can produce radical species that are capable of causing oxidations and chlorinations.[14] Specifically, the oxidation of metal carbonyls in the presence of organic halides has been observed a number of times.[15,16] Although the irradiation of $M_2(CO)_6(eHTP)/CH_2Cl_2$ samples by a mercury lamp is likely to proceed by such a CH_2Cl_2-activated process, CH_2Cl_2 radicals are unlikely to form under ambient conditions. Yet we find that $Cr_2(CO)_6$(eHTP) exhibits similar photoreactions under a much milder *hν* environment. The extreme photosensitivity of $Cr_2(CO)_6$(eHTP) is evidenced by the fact that solutions left standing under the normal fluorescent lighting in the laboratory gradually turn purple over the course of 1 week. Placing a sample of $Cr_2(CO)_6$(eHTP) in direct sunlight (Pyrex glass) effects the transformation in a matter of 8–12 h. One possible scenario is that the reaction is proceeding by electron transfer from an excited metal complex to CH_2Cl_2.

The irradiation of $W_2(CO)_6$(eHTP) over 5 days produces a yellow diamagnetic solution that, on the basis of ^{31}P NMR spectra of the reaction mixture, contains only one tungsten–eHTP-containing product. The ^{31}P NMR spectrum and two-dimensional ^{31}P–^{31}P COSY spectrum of the product are shown in Figure 3.

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(12) Osborn, J. A.; Stanley, G. G.; Bird, P. H. *J. Am. Chem. Soc.* **1988**, *110*, 2117.

(13) (a) Mague, J. T.; Dessens, S. E. *J. Organomet. Chem.* **1984**, *262*, 347. (b) Mague, J. T. Private communication. (c) Bahsoun, A.; Osborn, J. A. Unpublished results.

(14) Calvert, J. G.; Pitts, J. N., Jr. In *Photochemistry*; Wiley & Sons: New York, 1966; p 522.

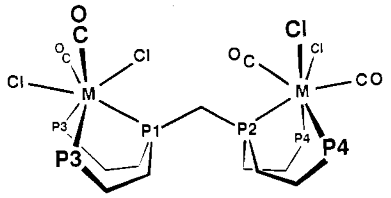
(15) Kochi, J. K. In *Organometallic Mechanisms and Catalysis*; Academic Press, Inc.: New York, 1978; p 194.

(16) Rhee, I.; Ryan, M.; Tsutsumy, S. *J. Organomet. Chem.* **1967**, *9*, 361.

(17) Saum, S. E.; Askham, F. R.; Laneman, S. A.; Stanley, G. G. *Polyhedron*, submitted for publication.

The pattern of peaks in the ^{31}P NMR spectrum is extremely similar to that seen for heterobimetallic eHTP complexes[17] and points to an eHTP conformation similar to that seen in the starting $W_2(CO)_6(eHTP)$ dimer but with two different metal environments. Peaks 1 and 2 in the ^{31}P NMR spectrum represent the two internal phosphorus atoms, and the ^{31}P–^{31}P COSY spectrum shows that they are indeed coupled to each other. Peak 1 is also connected to peak 3, which has a relative integration ratio of 1:2, consistent with the assignment of peak 3 as the two external phosphorus atoms on the same half of eHTP as the internal phosphorus atom P1 (peak 1). There is no measurable coupling between P1 and the two P3 atoms in the one-dimensional ^{31}P spectrum, although they are magnetically connected since there is a cross peak between them on the ^{31}P–^{31}P COSY spectrum. The lack of observable coupling between the P1 and P3 atoms is due, no doubt, to the presence of coupling pathways through the metal center and ligand framework that are similar in magnitude and opposite in sign.[18] The phosphorus atom represented by peak 2 in the ^{31}P spectrum is coupled to peak 4, and there is an integration ratio of 1:2. There is a small amount of observable coupling present between P2 and P4, which gives a barely resolvable doublet for P4 and an ill-resolved pattern for P2. Both P1 and P2 are shifted downfield from P3 and P4, consistent with the involvement of P1 and P2 in two five-membered chelate rings.[10]

On the basis of the ^{31}P NMR and IR spectra and work on related mononuclear compounds (vide infra), we propose that the structure of the photoproduct is the chlorinated open-mode bimetallic tungsten(II) system $W_2Cl_4(CO)_4(eHTP)$. Each metal center has a 7-coordinate capped octahedral geometry, but there is a different relative orientation of ligands to the facial set of three phosphine ligands for each metal center. On one tungsten atom the two external phosphorus atoms are trans to two chloride ligands, while the internal phosphorus atom is trans to a carbonyl ligand. The second carbonyl ligand is occupying a symmetrical face-capping position adjacent to the two chloride ligands. The other 7-coordinate tungsten center also has a facial set of three phosphine ligands, but now, the two external phosphorus atoms are trans to the two carbonyl ligands, while the internal phosphorus atom is trans to a chloride ligand. The second chloride ligand is also in a symmetrical face-capping position that is adjacent to the two carbonyl ligands. One possible structure is shown schematically as follows:



Note that in any proposed structure it is important to maintain a mirror plane of symmetry that relates the two external phosphine groups, as only a single peak is observed for these two phosphorus atoms. Our choice of the inverted W-shaped *syn,syn*-$M_2(eHTP)$ conformation is based on molecular models which indicate that this conformation is probably best suited to accommodate the relatively crowded coordination geometry about each metal center. If the molecule is adopting this configuration, it is undoubtedly twisted so that the inwardly pointing Cl and CO ligands are not pointed at one another. The increased J_{W-P} coupling constants of ca. 212 Hz for this compound are also consistent with the formation of a higher W oxidation state.

The relative positions of the ^{31}P NMR signals are consistent with the structure proposed above. The mononuclear eHTP complex $FeCl(CO)(\eta^4\text{-eHTP})^+$, for example, has one of the internal phosphorus atoms trans to a carbonyl group, while the other is trans to a chloride ligand.[9] The phosphine trans to the carbonyl has an upfield chemical shift position of +28.9 ppm (H_3PO_4 reference), while the phosphorus atom trans to the chloride has a position shifted further downfield at +59.3 ppm. Analogous chemical shift trends are also seen in RhCl(CO)(dppe).[19] Using these general upfield and downfield shifts, we can tentatively assign the ^{31}P NMR spectrum of $W_2Cl_4(CO)_4(eHTP)$ as follows: peak 1 corresponds to the internal eHTP phosphorus atom that is trans to a chloride; peak 2 indicates the other internal phosphorus center that is trans to a carbonyl ligand; peak 3 corresponds to the symmetry-related pair of external phosphorus atoms that are trans to carbonyl ligands; and peak 4 indicates the remaining two external phosphorus atoms that are trans to chloride anions.

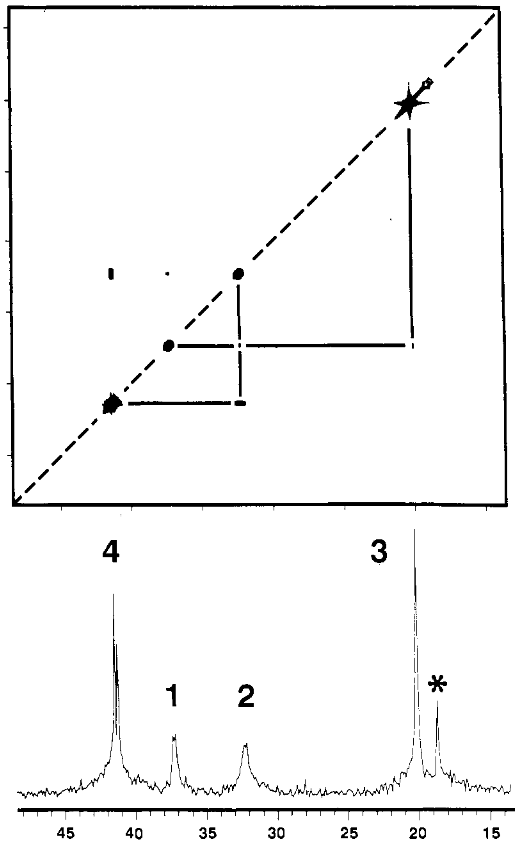


Figure 4. $^{31}P\{^1H\}$–$^{31}P\{^1H\}$ COSY two-dimensional NMR spectrum (top) and one-dimensional $^{31}P\{^1H\}$ NMR spectrum (bottom) for $Mo_2Cl_4(CO)_4(eHTP)$. The ppm scale on the one-dimensional spectrum also applies to the two-dimensional spectrum. Peaks 1 and 2 are assigned to the two internal phosphorus atoms, while peaks 3 and 4 indicate the external phosphorus atoms. The peak marked with a star indicates an unidentified impurity. See text for further discussion.

Further evidence for this formulation comes from the well-known 7-coordinate $MX_2(CO)_2(PR_3)_3$ (M = Mo, W) compounds,[20] which are typically formed from the reaction of $MX_2(CO)_4$ with phosphines,[21] although the related reaction of $MX_2(PR_3)_3$ with carbon monoxide is also known.[22] Similarly, the different reaction of I_2 with $M(CO)_4(P_2)$ type complexes has been recently reported,[23] and it is very likely that $M(CO)_3(P_3)$ compounds would be readily oxidized by halogens to give $MX_2(CO)_2(P_3)$ type products. This, however, is the first example of a photochemical chlorination of a $M(CO)_3P_3$ system to form a $MCl_2(CO)_2P_3$ complex using the relatively inert halocarbon

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(18) Grim, S. O.; Barth, R. C.; Mitchell, J. D.; Del Gaudio, J. *Inorg. Chem.* **1977**, *16*, 1776.

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CH_2Cl_2. All of the $M_2(CO)_6(eHTP)$ complexes, for example, are thermally very stable in CH_2Cl_2.

The fact that Mo(II) and W(II) oxidation states and 7-coordinate diamagnetic systems are quite common and rather stable strongly supports the proposed formulation for the tungsten photoproduct. Drew, in his extensive review on 7-coordinate metal complexes,[20a] stated that although structures for $MX_2(CO)_2$(triphos) compounds (where triphos represents a tridentate, bischelating phosphine ligand) were not known, their geometries were most likely capped octahedral in nature.

The IR spectrum of $W_2Cl_4(CO)_4(eHTP)$ is consistent with the structure shown above. Four ν_{CO} bands are observed, with three of the bands (1920, 1830, and 1810 cm^{-1}) having approximately equal intensities, while the highest energy peak (1955 cm^{-1}) is about 40% as intense as the other carbonyl bands. The two equally intense ν_{CO} peaks (1920 and 1810 cm^{-1}) would correspond to the carbonyl ligands that are trans to the external phosphine ligands and should have an idealized OC–M–CO angle of around 100–112°, while the carbonyl ligands on the other tungsten center should have a larger OC–M–CO angle of ca. 125°, which should give an intensity ratio of the two resulting carbonyl bands of ca. 33%, and this is in good qualitative agreement with the observed values.[21] It is interesting to note that the insoluble yellow solid that is occasionally produced in the photolysis has only two similar-intensity ν_{CO} bands at 1950 and 1830 cm^{-1}. This may correspond to an isomeric form of $W_2Cl_4(CO)_4(eHTP)$ that has the *same* coordination environment about each tungsten center.

The irradiation of $Mo_2(CO)_6(eHTP)$ appears to proceed in a manner similar to that seen for the tungsten analogue. After 5 days of photolysis a yellow solution is formed that occasionally has some yellow precipitate as well. The infrared spectrum of the soluble yellow species is nearly identical with that of $W_2Cl_4(CO)_4(eHTP)$ and shows four ν_{CO} bands at 1970, 1920, 1830, and 1810 cm^{-1} as well as peaks characteristic of eHTP. The one-dimensional ^{31}P NMR and two-dimensional ^{31}P–^{31}P COSY spectra of the molybdenum photoproduct are also quite similar to those for tungsten and are shown in Figure 4. The spectra clearly indicate the presence of two different molybdenum environments, as seen in the tungsten system. Peaks 1 and 2 represent the internal phosphorus atoms, while peaks 3 and 4 indicate the external phosphine groups on each half of the complex. The main difference between the ^{31}P NMR spectra for the Mo and W compounds is that peak 4 is shifted downfield from both peaks 1 and 2. On the basis of the spectral data, we propose that the soluble molybdenum photoproduct is $Mo_2Cl_4(CO)_4(eHTP)$ and has two different ligand environments about each metal center, as discussed above for the tungsten system. The yellow precipitate that occasionally forms (ν_{CO} = 1970, 1830 cm^{-1}) in the photolysis of $Mo_2(CO)_6(eHTP)$ would also appear to be an isomeric form of $Mo_2Cl_4(CO)_4(eHTP)$ in which each metal center has the same ligand geometry, just as was seen in the tungsten reaction.

The limited solubility of the starting $M_2(CO)_6(eHTP)$ compounds in essentially only CH_2Cl_2 limited the photochemical studies and led, perhaps not unexpectedly, to the chlorination reactions described. The difference between the Cr and Mo/W reaction pathways is consistent with the general chemistry of the related mononuclear systems, even though this is the first reported example of photochemical chlorinations using CH_2Cl_2 for producing seven-coordinate $MCl_2(CO)_2(P_3)$ type complexes. The apparent absence of any M–M cooperative interactions leads us to believe that we should concentrate our efforts on the binuclear reaction chemistry of lower coordinate later transition metal dimer complexes. The synthesis, characterization, and reactivity studies of group VIII dimers based on eHTP and tetratertiary phosphine ligand derivatives[24] will be reported in future papers.

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Supplementary Material Available: Infrared spectra for the yellow soluble and insoluble $M_2Cl_4(CO)_4(eHTP)$ (M = Mo, W) photoproducts and tables of crystal and data collection parameters, anisotropic thermal parameters, and all bond distances and angles for the W complex (8 pages); a listing of calculated and observed structure factors for $W_2(CO)_7(C_{19}H_{43}P_5)$ (9 pages). Ordering information is given on any current masthead page.

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Competing Formation of Bridging Diphenylphosphido and Bridging (Diphenylphosphino)cyclopentadienyl Ligands during the Reaction of $[M(CO)_5PPh_2]^-$ (M = Cr, Mo, W) with $CpRu(CO)_2Cl$. X-ray Structure of $(CO)_5W(\mu\text{-}C_5H_4PPh_2)Ru(CO)(\mu\text{-}CO)_2Ru(CO)Cp\cdot CH_2Cl_2$

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The reaction of $[M(CO)_5PPh_2]^-$ with $CpRu(CO)_2Cl$ (M = Cr, Mo, W) is highly dependent on the metal. When M = Mo or W, the products isolated are $(CO)_5M(\mu\text{-}C_5H_4PPh_2)Ru(CO)(\mu\text{-}CO)_2Ru(CO)Cp$ (M = Mo (**2**), W (**3**)). **3**·CH_2Cl_2 crystallizes in the triclinic space group C_i-$P\bar{1}$ with cell dimensions a = 12.184 (4) Å, b = 14.952 (2) Å, c = 9.545 (2) Å, α = 96.46 (1)°, β = 92.94 (2)°, γ = 77.39 (2)°, and Z = 2. The structure was solved and refined to R and R_w values of 0.044 and 0.056, respectively, by using 4813 reflections. Experimental results suggest that the first step of the formation of **2** and **3** is a nucleophilic attack of $[M(CO)_5PPh_2]^-$ on the cyclopentadienyl ligand of $CpRu(CO)_2Cl$.

Introduction

The synthesis of and the study of the reactivity of heterobimetallic complexes are now well-established areas of activity in organometallic chemistry.[1] Among the motivations for such study is the hope that combining metals with different chemical properties would lead to synergic effects and to new chemical reactivity. In this field, we are presently interested in the synthesis of heteropolymetallic systems associating group 6 and group 8 metals. Such systems associate metals with quite different properties, e.g. oxophilicity for group 6 and hydrogen activation for group 8, which

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(1) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Chapter 40.

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