for example, AgLiPc or CuLiPc.[10]

Dimerization is very common in the chemistries of both phthalocyanines and porphyrins; however, it seems unlikely that at the low concentrations used (ca. 10^{-5} M) in these coordinating solvents (DMA and Me_2SO) and with the very narrow bandwidths observed throughout the sequence of spectra in Figure 1, that the dimer concentration is at all significant. Ring-to-ring dimerization of phthalocyanines appears to result in rather broad bands; see, for example, the comparison between the spectra of H_2Pc in chloronaphthalene and H_2Pc as a sublimed film in ref 11. Tetrasulfanated phthalocyanine solutions are found to be monomeric in Me_2SO[12,13] even though dimerization occurs readily in other solvents at much lower concentrations.

Porphyrins (P) readily form the D_{4h} species H_4P^{2+} in acidic media, with, in general, noncoordinating solvents.[14] For example, trifluoroacetic acid is commonly used to produce H_4P^{2+} complexes in solvents such as benzene.[15] Solvents with a high dielectric constant, such as *N*,*N*-dimethylformamide and Me_2SO, have been shown to reduce the tendency of H_4P^{2+} formation.

Addition of 0.1 mL of concentrated trifluoroacetic acid to a 2.5 mL solution of Li_2Pc in DMA or Me_2SO results in the formation of H_2Pc (characterized by the twin Q bands). No other species could be detected in the absorption spectrum.

This finding further supports our conclusion that the final species formed by the demetalation of Li_2Pc by distilled water, Figure 2, is the D_{4h} H_2Pc rather than the cationic H_4Pc^{2+} complex. The geometry of this H_2Pc species is, then, similar to that of Li_2Pc and Na_2Pc for which typical MPc spectra are observed.

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Registry No. Li_2Pc, 25510-41-2; H_2Pc, 574-93-6.

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Polydentate Ligands Containing Phosphorus. 4. Group 6 Metal Carbonyl Derivatives of *N*-(Diphenylphosphino)methyl Derivatives of Ethylenediamine[1]

Samuel O. Grim,*[2] Dilip P. Shah, and Luis J. Matienzo

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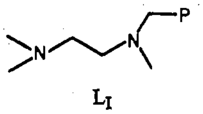
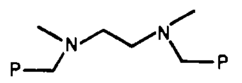
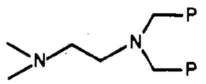
Neutral polydentate ligands can exhibit a wide variety of coordination behaviors, which can influence stereochemistry and other properties of the resulting complexes. Over the years numerous groups have investigated polydentate ligands of group 5 donor atoms.[3-6] Some time ago we[7] synthesized some previously unreported *N*-(diphenylphosphino)methyl derivatives of ethylenediamine by a well-established synthetic route.[8,9] This paper reports on some of the complexes of the group 6 metal carbonyls with these ligands: $Ph_2PCH_2N(CH_3)CH_2CH_2N(CH_3)_2$, L_I, *N*-[(diphenylphosphino)methyl]-*N*,*N'*,*N'*-trimethylethylenediamine; $Ph_2PCH_2N(CH_3)CH_2CH_2N(CH_3)CH_2PPh_2$, L_{IIs}, *N*,*N'*-bis[(diphenylphosphino)methyl]-*N*,*N'*-dimethylethylenediamine; $(Ph_2PCH_2)_2NCH_2CH_2N(CH_3)_2$, L_{IIu}, *N*,*N*-bis[(diphenylphosphino)methyl]-*N'*,*N'*-dimethylethylenediamine; and $(Ph_2PCH_2)_2NCH_2CH_2N(CH_2PPh_2)_2$, L_{IV}, *N*,*N*,*N'*,*N'*-tetrakis[(diphenylphosphino)methyl]ethylenediamine.



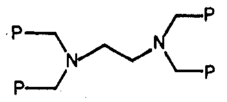
L_I



L_{IIs}



L_{IIu}



L_{IV}

With these ligands, numerous types of coordination behavior can be displayed. For example, the symmetrical bis(phosphine) ligand, L_{IIs}, could conceivably be a mono-, di-, tri-, or tetradentate ligand. If monodentate, then there is a possibility of ambidentate behavior, i.e., N- or P-coordination. If bidentate, then there is the possibility of N,N- (5-membered chelate ring), N,P- (4- or 7-membered chelate ring), or P,P- (9-membered chelate ring) coordination. Further possibilities would result from tri- and tetradentate behavior. In addition, one molecule of ligand might bind to more than one metal center, leading to bridging and possibly to oligomeric coordination compounds. Each of the ligands in this study can display this complex behavior, including the possibility of hexadentate coordination in L_{IV}.

Results and Discussion

In this investigation we have used only soft metals which have a stronger tendency to bind with the soft phosphine donor atoms rather than with the harder amine nitrogen. The following compounds have been synthesized and characterized: $L_ICr(CO)_5$, $L_IMo(CO)_5$, $L_IW(CO)_5$, $L_{IIu}Cr(CO)_4$, $L_{IIu}Mo(CO)_4$, $L_{IIu}W(CO)_4$, $L_{IIu}[W(CO)_5]_2$, $L_{IIs}Cr(CO)_4$, $L_{IIs}Mo(CO)_4$, $L_{IIs}W(CO)_4$, $L_{IIs}[Cr(CO)_5]_2$, $L_{IIs}[Mo(CO)_5]_2$, $L_{IIs}[W(CO)_5]_2$, $L_{IV}[Cr(CO)_4]_2$, $L_{IV}[Mo(CO)_4]_2$, $L_{IV}[W(CO)_4]_2$, $L_{IV}Cr(CO)_4$, $L_{IV}Mo(CO)_4$, $L_{IV}[Cr(CO)_4][Mo(CO)_4]$, and $L_{IV}[W(CO)_5]_4$. The gentle methods of synthesis and specifically chosen stoichiometries of the reactants have resulted in these fairly simple coordination compounds in which only phosphorus is directly coordinated to the transition metal. Generally, this conclusion has been reached by examination of the ^{31}P NMR spectra of the compounds, although occasionally the ^1H NMR spectra also aided in the structural assignments or corroborated the ^{31}P results. The ^{31}P NMR data are given in Table I.

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Table I. Phosphorus-31 NMR Data for the Group 6 Metal Carbonyl Complexes of N-Substituted [(Diphenylphosphino)methyl]ethylenediamines

compd	δ_P[a]	Δ[b]	$^1J_{WP}$, Hz
L_I	−26.6		
$L_ICr(CO)_5$	47.0	73.6	
$L_IMo(CO)_5$	31.5	58.1	
$L_IW(CO)_5$	13.6	40.2	242
L_{IIs}	−26.9		
$L_{IIs}Cr(CO)_4$	44.1	71.0	
$L_{IIs}Mo(CO)_4$	27.1	54.0	
$L_{IIs}W(CO)_4$	10.7	37.6	238
$L_{IIs}[Cr(CO)_5]_2$	48.9	75.8	
$L_{IIs}[Mo(CO)_5]_2$	30.5	57.4	
$L_{IIs}[W(CO)_5]_2$	13.5	40.4	243
L_{IIu}	−27.2		
$L_{IIu}Cr(CO)_4$	38.6	65.8	
$L_{IIu}Mo(CO)_4$	17.1	44.3	
$L_{IIu}W(CO)_4$	−4.0	23.2	224
$L_{IIu}[W(CO)_5]_2$	15.4	42.6	233
L_{IV}	−28.1		
$L_{IV}[Cr(CO)_4]_2$	39.1	67.2	
$L_{IV}[Mo(CO)_4]_2$	17.1	45.2	
$L_{IV}[W(CO)_4]_2$	−3.9	24.2	
$L_{IV}[Cr(CO)_4][Mo(CO)_4]$	16.7	44.8	
	27.1	55.2	
$L_{IV}[W(CO)_5]_4$	12.6	40.7	

[a] Positive chemical shifts are deshielded from 85% H_3PO_4.
[b] Coordination chemical shift $\Delta = \delta_{\text{complex}} - \delta_{\text{free ligand}}$.

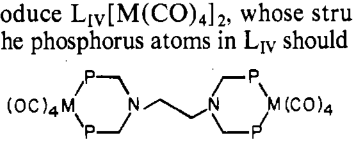
L_I reacts with $[Et_4N][M(CO)_5I]$[10] where M is Cr or Mo, and with $(PhNH_2)W(CO)_5$[11] at room temperature to form the monodentate phosphorus-coordinated $L_IM(CO)_5$ compounds. These oily complexes failed to crystallize, but they were characterized by their ^{31}P NMR and infrared spectra. In each case only one ^{31}P resonance is present which is shifted downfield from that of the free ligand upon coordination by 73.6, 58.1, and 40.2 ppm, respectively, for the Cr, Mo, and W complexes. These coordination shifts are noticeably larger than for the usual tertiary phosphine complex of the type $LM(CO)_5$, for which the coordination shifts range from 61–67 ppm (Cr), 42–47 ppm (Mo), and 22–27 ppm (W) when L is a range of ligands such as Ph_3P, n-$BuPh_2P$, n-Bu_2PhP, n-Bu_3P, Me_3P, Ph_2MeP, etc.[12,13] The reason for these unusually large coordination shifts for monodentate tertiary phosphine ligands is not clear.

L_{IIs} reacts with $Mo(CO)_6$ and $W(CO)_6$ in refluxing toluene in a 1:1 molar ratio to produce $L_{IIs}M(CO)_4$. The reaction of $(C_7H_8)Cr(CO)_4$,[14] where C_7H_8 is norbornadiene, with L_{IIs} results in the analogous Cr complex, and indeed the C_7H_8 complexes of Mo and W also react with L_{IIs} in a clean reaction to produce $L_{IIs}M(CO)_4$. The structure of this complex is somewhat surprising. The ^{31}P NMR spectrum of each compound exhibits only one ^{31}P resonance (except for the ^{183}W satellites in the W complex) with coordination shifts of 71.0, 54.0, and 37.6 ppm, respectively for the Cr, Mo, and W compounds. This indicates that both phosphorus atoms are coordinated to produce a 9-membered chelate ring instead of a 4-membered chelate ring with one phosphorus and one nitrogen donor atom. The protons of the methyl group on nitrogen are shielded upon coordination of the ligand, whereas if coordination were through nitrogen, deshielding would be expected.[15] This behavior exemplifies the strong preference of the soft Lewis acids for the soft phosphorus base in spite of the fact that an unusually large chelate ring must result. A molecular weight determination confirmed that the Mo compound is monomeric and not a ligand-bridged dimeric species. Finally, an X-ray structural determination proved the structure for the molybdenum compound.[16] It should be noted that the chelate ring effect[17–19] on the ^{31}P coordination chemical shift in these 9-membered chelate rings is only slight, about 3–5 ppm smaller (i.e., −3 to −5 ppm) than the coordination shifts for analogous ligands behaving in a monodentate fashion (vide infra). The chelate ring effect is the difference between the coordination shift in the chelate complex and the coordination shift in a monodentate complex of the type $LM(CO)_5$ or *cis*-$L_2M(CO)_4$.[20] This compares with other chelate ring effects, which are about −12 to −20 ppm for 4-membered chelate rings, +25 to +35 ppm for 5-membered chelate rings, and −2 to −8 ppm for 6-membered chelate rings[20–22] in the chromium, molybdenum, tungsten carbonyl series. L_{IIs} also reacts with $[Et_4N][Cr(CO)_5I]$, $[Et_4N][Mo(CO)_5I]$, and $(PhNH_2)W(CO)_5$ in a 1:2 molar ratio to produce $L_{IIs}[M(CO)_5]_2$. The ^{31}P coordination shifts in these compounds are 75.8, 57.4, and 40.4 ppm, respectively, for the Cr, Mo, and W compounds. These values are in good agreement with those of the monodentate L_I complexes.

L_{IIu} reacts with $M(CO)_6$ in refluxing diethylene glycol dimethyl ether (diglyme) in an equimolar ratio to produce $L_{IIu}M(CO)_4$, where M is Cr, Mo, or W. For these compounds, each ^{31}P NMR spectrum exhibits one downfield resonance, indicating again that both phosphorus atoms in a molecule of ligand are coordinated equivalently, in this case in a 6-membered chelate ring. The ^{31}P coordination shifts of 65.8, 44.3, and 23.2 ppm for Cr, Mo, and W, respectively, are somewhat greater than those of the analogous complexes of 1,3-bis(diphenylphosphino)propane (59, 38, and 17 ppm, respectively) but still correspond to a chelate ring effect of about −9 to −17 ppm, which is slightly larger in magnitude than expected. Actually, a comparison of the ^{31}P shifts for $L_{IIu}W(CO)_4$ and $L_{IIu}[W(CO)_5]_2$ indicates a chelate ring effect of −19.4 ppm, probably the largest magnitude so far observed for a 6-membered ring.

$L_{IIu}[W(CO)_5]_2$ was prepared by the 1:2 molar ratio reaction of L_{IIu} with $(PhNH_2)W(CO)_5$. The ^{31}P coordination shift of 42.6 ppm agrees with the other compounds in this study in which phosphorus is bonded to a tungsten pentacarbonyl group.

L_{IV} reacts with $M(CO)_6$ in 1:2 molar ratio in refluxing diglyme to produce $L_{IV}[M(CO)_4]_2$, whose structure is illustrated in I. The phosphorus atoms in L_{IV} should be chemically very similar to those in $L_{IIu}M(CO)_4$, illustrated in II. Indeed,



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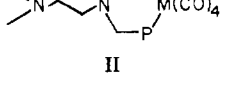

II

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Table II. Proton NMR Data for L_{IIs} and L_{IIu} Complexes[a]

compd	δ_{CH_3}	$\delta_{CH_2CH_2}$	δ_{PCH_2N}	$\delta_{C_6H_5}$[b]
L_{IIs}	2.41	2.69	3.28 d ($^2J_{PCH}$ = 3.1 Hz)	7.35, 7.45
$L_{IIs}Cr(CO)_4$	1.72	2.32	3.48	7.22, 7.36
$L_{IIs}Mo(CO)_4$	1.82	2.38	3.50	7.39, 7.55
$L_{IIs}W(CO)_4$	1.72	2.32	3.45	7.20, 7.35
$L_{IIs}[Cr(CO)_5]_2$	1.72	2.17	3.20	7.20, 7.26
$L_{IIs}[Mo(CO)_5]_2$	1.86	2.20	3.35	7.25, 7.35
$L_{IIs}[W(CO)_5]_2$	1.78	2.18	3.40	7.22, 7.35
L_{IIu}	2.18	2.28, 3.01	3.60 d ($^2J_{PCH}$ = 3.2 Hz)	7.58, 7.77
$L_{IIu}Cr(CO)_4$	2.10	2.20, 2.70	3.40	7.20, 7.36
$L_{IIu}Mo(CO)_4$	2.13	2.22, 2.73	3.50	7.35, 7.52
$L_{IIu}W(CO)_4$	2.09	2.18, 2.68	3.45	7.18, 7.34

[a] Measured in $CDCl_3$ with δ values in ppm downfield from Me_4Si. [b] The second value is a shoulder on the first, the major phenyl peak.

the ^{31}P chemical shifts (coordination shifts in parentheses) for $L_{IV}[M(CO)_4]_2$, are 39.1 (67.2), 17.1 (45.2), and −3.9 (24.1) ppm for the Cr, Mo, and W compounds, respectively, whereas those of $L_{IIu}M(CO)_4$ are 38.6 (65.8), 17.1 (44.3), and −4.0 (23.2) ppm, respectively for Cr, Mo, and W.

Two different metal moieties can be coordinated to L_{IV} stepwise, e.g.

$$L_{IV} \xrightarrow{C_7H_8Cr(CO)_4} L_{IV}[Cr(CO)_4] \xrightarrow{C_7H_8Mo(CO)_4} L_{IV}[Cr(CO)_4][Mo(CO)_4]$$

Earlier examples of two different metals coordinated to one ligand have been reported.[2,3] In addition, the reaction of L_{IV} with $(PhNH_2)W(CO)_5$ in a 1:6 molar ratio produces $L_{IV}[W(CO)_5]_4$, as a very insoluble product. This is an unusually high molecular weight (2148.5) monomeric coordination compound with four metal atoms per ligand. The L_{IV} complexes are generally only slightly soluble so that all the NMR data were not obtained. In certain cases, NMR measurements on the crude reaction mixtures gave reasonable values, but after the compounds had crystallized they were no longer sufficiently soluble to obtain reasonable spectra.

Infrared data in the carbonyl stretching region, which are consistent with the stoichiometries and structural assignments, are given in the Experimental Section. ^1H NMR data for the L_{IIs} and L_{IIu} ligands are given in Table II. It should be noted that the PCH_2N methylene protons in the complexes are a slightly broadened singlet with no resolvable (at 60 MHz) P–H coupling observed. Protons on carbons α to phosphorus in diamagnetic coordination compounds usually exhibit a detectable and often sizeable coupling to phosphorus,[12,24] and these compounds are somewhat unusual in that respect, although this decoupling effect has been observed previously[24,25] and discussed theoretically for both P–H and P–C[26] coupling in tertiary phosphine and phosphite complexes.

The results described here are probably only the simplest of the many varieties of compounds which could be prepared with these ligands. For example, none of these compounds contain a coordinated nitrogen, which could be capable of coordination via chelation,[27] as, e.g., in $L_IM(CO)_5$, to produce a 4-membered ring of the type $L_IM(CO)_4$ or of coordination to different, and harder, Lewis acids such as Zn(II) etc. Such studies will be done in due course.

In summary, coordination compounds of polydentate, [(diphenylphosphino)methyl]ethylenediamine ligands with the group 6 metal carbonyls are described. Included in these are unusual compounds containing a 9-membered chelate ring and one containing four metal atoms bonded to one molecule of ligand. Phosphorus-31 NMR data are used as the principal method for structural assignment.

Experimental Section

^{31}P NMR measurements were made on a Varian Associates XL-100-12 Fourier transform spectrometer as previously described.[28] The chemical shifts are given as positive if deshielded from the standard 85% H_3PO_4. ^1H NMR spectra were obtained with a Varian A-60A spectrometer on $CDCl_3$ solutions and an internal reference of tetramethylsilane.

Microanalyses were performed by Dr. F. Kasler of the University of Maryland. Melting points were taken with a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained on $CHCl_3$ solutions of the carbonyl complexes with a Digilab Model FTS-14 IR spectrometer using NaCl cells with 0.55-mm sample thickness. The bands are accurate to ±1 cm^{-1}.

The polydentate ligands were prepared as described in the literature,[7] as were the three $C_7H_8M(CO)_4$ compounds[14,29] and $PhNH_2W(CO)_5$,[11] $[Et_4N][Cr(CO)_5I]$,[14] and $[Et_4N][Mo(CO)_5I]$.[14]

$L_ICr(CO)_5$. L_I (1.16 g, 3.9 mmol) and 3.9 mmol of $[Et_4N][Cr(CO)_5I]$ were dissolved in 10 mL of $CHCl_3$–CH_3OH and stirred overnight under N_2 at room temperature (rt). After removal of the solvents an oil remained which was purified by chromatography with C_6H_6 on an alumina column. It failed to crystallize from various solvents even at −80 °C. IR stretches are at 2064, 1979, and 1939 cm^{-1}.

$L_IMo(CO)_5$ was prepared similarly. It has IR bands at 2066, 1985, 1952, and 1943 cm^{-1}.

$L_IW(CO)_5$ was prepared from 3.9 mmol of L_I and 3.0 mmol of $PhNH_2W(CO)_5$ in 25 mL of C_6H_6 by stirring under N_2 for 24 h. It also is an oil with IR bands at 2075, 1975, and 1935 cm^{-1}.

$L_{IIu}[W(CO)_5]_2$. L_{IIu} (2.0 mmol) and 2.5 g (5.0 mmol) of $(PhNH_2)W(CO)_5$ were stirred under N_2 in 25 mL of C_6H_6 at rt for 24 hr. After removal of the solvent via rotary evaporation, the resulting oil was recrystallized from CH_2Cl_2–CH_3OH. The yellow crystals, mp 148–150 °C, were obtained in 70% yield (1.62 g); IR stretches at 2073, 1980, and 1935 cm^{-1}. Anal. Calcd for $C_{40}H_{34}N_2O_{10}P_2W_2$: C, 42.43; H, 3.03; N, 2.47; P, 5.47. Found: C, 41.88; H, 3.40; N, 3.14; P, 4.90.

$L_{IIu}Cr(CO)_4$. L_{IIu} (0.97 g, 2.0 mmol) and 0.44 g (2.0 mmol) of $Cr(CO)_6$ were heated at an oil bath temperature of 145–150 °C under N_2 in an apparatus[12] that allowed the volume of evolved CO to be measured. The flask was shaken at times to return the sublimed $Cr(CO)_6$ to the reaction vessel. After completion of the reaction (several hours), the solvent was removed at reduced pressure, the residue was dissolved in CH_2Cl_2, and the product was precipitated by the addition of hexane. The light yellow product, mp 137–138 °C, was collected in 39% yield (0.50 g). It has IR CO frequencies at 2010, 1927, and 1890 cm^{-1}. Anal. Calcd for $C_{34}H_{34}CrN_2O_4P_2$: C, 62.96; H, 5.28; N, 4.32; P, 9.55. Found: C, 62.50; H, 5.34; N, 3.89; P, 9.83.

$L_{IIu}Mo(CO)_4$. This compound was prepared from L_{IIu} and $Mo(CO)_6$ as described above by heating for about 2 h with an oil bath temperature of 110–120 °C. The colorless crystals, mp 148–149 °C, with IR bands at 2022, 1933, and 1905 cm^{-1}, were obtained in 54% yield. Anal. Calcd for $C_{34}H_{34}MoN_2O_4P_2$: C, 58.97; H, 4.95; N, 4.05; P, 8.95. Found: C, 58.76; H, 5.20; N, 3.80; P, 8.70.

$L_{IIu}W(CO)_4$. This yellow compound, mp 158–160 °C, was prepared analogously to the Mo analogue in 66% yield. The CO stretches are at 2018, 1923, and 1872 cm^{-1}. Anal. Calcd for $C_{34}H_{34}N_2O_4P_2W$: C, 52.33; H, 4.39; N, 3.59; P, 7.94. Found: C, 52.57; H, 4.60; N, 3.32; P, 8.17.

$L_{IIs}Mo(CO)_4$. L_{IIs} (1.65 g, 3.38 mmol) and $Mo(CO)_6$ (0.894 g, 3.38 mmol) were heated under N_2 at refluxing temperature in 25 mL of toluene for 2 h. Removal of the solvent resulted in an oil which was dissolved in CH_2Cl_2 and precipitated with pentane. After re-

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crystallization from CH_2Cl_2–C_5H_{12}, a yield of 1.90 g (80%) of product, mp 175–177 °C, was obtained with IR bands at 2023, 1933, and 1905 cm^{-1}. Anal. Calcd for $C_{34}H_{34}MoN_2O_4P_2$: C, 58.97; H, 4.95; N, 4.05; P, 8.95; mol wt 692.5. Found: C, 59.12; H, 5.20; N, 4.02; P, 9.06; mol wt 691.

$L_{IIs}W(CO)_4$. This compound was prepared analogously from $W(CO)_6$ (3.5 mmol) and L_{IIs} (3.5 mmol) in 25 mL of diglyme for 2 h at a bath temperature of 155–160 °C. The yellow product, mp 203–205 °C, was recrystallized from CH_2Cl_2–C_5H_{12} in 37% yield. The CO stretching frequencies are 2017, 1916, and 1897 cm^{-1}. Anal. Calcd for $C_{34}H_{34}N_2O_4P_2W$: C, 52.33; H, 4.39; N, 3.59; P, 7.94. Found: C, 51.45; H, 4.51; N, 3.43; P, 7.70.

$L_{IIs}Cr(CO)_4$. $(C_7H_8)Cr(CO)_4$ (1.05 g, 4.1 mmol) and 2.05 g (4.2 mmol) of L_{IIs} were stirred for several days under N_2 in 25 mL of benzene. After removal of the solvent, the oily residue was dissolved in CH_2Cl_2 and greenish yellow crystals precipitated upon addition of CH_3OH. The product, mp 122–124 °C, with CO stretches at 2020, 1920, and 1903 cm^{-1}, was formed in 37% yield. Anal. Calcd for $C_{34}H_{34}CrN_2O_4P_2$: C, 62.96; H, 5.28; N, 4.32; P, 9.55. Found: C, 62.31; H, 5.56; N, 4.09; P, 9.74.

$L_{IIs}[Cr(CO)_5]_2$. $Cr(CO)_6$ (1.76 g, 8.0 mmol) and L_{IIs} (1.92 g, 4.0 mmol) were heated in 25 mL of diglyme at an oil bath temperature of 155–160 °C for 2 h. Excess $Cr(CO)_6$ was removed by filtration, and the filtrate was concentrated by rotary evaporation. The resulting oil was dissolved in CH_2Cl_2 and an off-white precipitate, mp 126–127 °C, formed on addition of CH_3OH, in 38% yield. The compound has IR stretches at 2068, 1983, and 1940 cm^{-1}. Anal. Calcd for $C_{40}H_{34}Cr_2N_2O_{10}P_2$: C, 55.31, H, 3.95; N, 3.22; P, 7.13. Found: C, 54.86; H, 4.14; N, 3.00; P, 7.42.

$L_{IIs}[Mo(CO)_5]_2$. $[Et_4N][Mo(CO)_5I]$ (1.0 g, 2.0 mmol) and 0.5 g (1.0 mmol) of L_{IIs} were stirred under N_2 at rt in 20 mL of $CHCl_3$ for 24 h. The mixture was evaporated to dryness, and the residue dissolved in CH_2Cl_2 and reprecipitated with CH_3OH. After being washed with H_2O, the white crystals, mp 135–137 °C, with IR bands at 2073, 1990, and 1943 cm^{-1}, represented an 80% yield. Anal. Calcd for $C_{40}H_{34}Mo_2N_2O_{10}P_2$: C, 50.23; H, 3.58; N, 2.93; P, 6.48. Found: C, 49.86; H, 3.76; N, 3.00; P, 6.58.

$L_{IIs}[W(CO)_5]_2$. The compound was prepared as above from 0.5 g (1.0 mmol) of L_{IIs} and 0.84 g (2.0 mmol) of $(C_6H_5NH_2)W(CO)_5$ in 25 mL of C_6H_6. Yellow crystals, mp 147–149 °C, were recrystallized from CH_2Cl_2–CH_3OH in 68% yield. The compound has IR bands at 2072, 1980, and 1933 cm^{-1}. Anal. Calcd for $C_{40}H_{34}N_2O_{10}P_2W_2$: C, 42.43; H, 3.03; N, 2.47; P, 5.47. Found: C, 42.30; H, 3.30; N, 2.40; P, 5.61.

$L_{IV}[Cr(CO)_4]_2$. L_{IV} (0.85 g, 1.0 mmol) and 0.5 g (2.2 mmol) of $Cr(CO)_6$ were heated in 10 mL of diglyme for 2 h in an oil bath at 170–175 °C. After removal of the solvent, the crude product was washed several times with CH_2Cl_2–acetone solution. The yellow compound (55%), dec pt >180 °C, is only sparingly soluble in organic solvents. It has CO stretches at 2011, 1928, and 1893 cm^{-1}. Anal. Calcd for $C_{62}H_{52}Cr_2N_2O_8P_4$: C, 63.06; H, 4.44; N, 2.37; P, 10.49. Found: C, 62.55; H, 4.65; N, 2.28; P, 10.27.

$L_{IV}[Mo(CO)_4]_2$. The reaction between $Mo(CO)_6$ and L_{IV} was carried out in 10 mL of toluene at an oil bath temperature of 120 °C. The resulting white crystals, dec pt >250 °C, with IR bands at 2025, 1935, 1907, and 1896 (sh) cm^{-1}, are insoluble in CH_2Cl_2, EtOH, C_6H_6, and acetone. The yield was 70%. Anal. Calcd for $C_{62}H_{52}Mo_2N_2O_8P_4$: C, 58.64; H, 4.13; N, 2.21; P, 9.76. Found: C, 58.40; H, 4.27; N, 2.15; P, 9.77.

$L_{IV}[W(CO)_4]_2$. The yellow compound, dec pt >250 °C, was prepared in 62% yield from $W(CO)_6$ and L_{IV} in diglyme at a bath temperature of 180 °C for 3 h. It is also only sparingly soluble in organic solvents. The CO stretches are at 2018, 1919, and 1895 cm^{-1}. Anal. Calcd for $C_{62}H_{52}N_2O_8P_4W_2$: C, 51.55; H, 3.63; N, 1.94; P, 8.58. Found: C, 51.03; H, 3.82; N, 1.86; P, 8.75.

$L_{IV}Cr(CO)_4$. L_{IV} (2.3 g, 2.7 mmol) and 0.7 g (2.7 mmol) of $C_7H_8Cr(CO)_4$ were stirred under N_2 in 40 mL of C_6H_6 for 24 h at room temperature. After concentration via rotary evaporation, the residue was dissolved in CH_2Cl_2 and reprecipitated by the addition of CH_3OH. The slightly greenish powder, mp 105–108 °C, after recrystallization from CH_2Cl_2–CH_3OH, weighed 1.76 g (64%). The IR CO bands are at 2006, 1913, and 1887 cm^{-1}. Anal. Calcd for $C_{58}H_{52}CrN_2O_4P_4$: C, 68.50; H, 5.15; N, 2.75; P, 12.18. Found: C, 67.97; H, 5.20; N, 2.51; P, 11.70.

$L_{IV}[Cr(CO)_4][Mo(CO)_4]$. $C_7H_8Mo(CO)_4$ (0.3 g, 1 mmol) and 1.0 g (1.0 mmol) of L_{IV} $Cr(CO)_4$ were stirred under N_2 in 50 mL of C_6H_6 for 72 h. The greenish white precipitate which formed was recrystallized from acetone. The yield was 40%. Anal. Calcd for $C_{62}H_{52}CrMoN_2O_8P_4$: C, 60.79; H, 4.28; N, 2.29; P, 10.11. Found: C, 60.42; H, 4.26; N, 2.26; P, 10.50.

$L_{IV}[W(CO)_5]_4$. L_{IV} (0.85, 1.0 mmol) and 2.5 g (6.0 mmol) of $PhNH_2W(CO)_5$ were stirred in 30 mL of benzene. The solution was concentrated by rotary evaporation, and a ^{31}P NMR spectrum was taken of the crude reaction mixture (a supersaturated solution). Yellow crystals, with CO stretching frequencies of 2073, 1980, and 1935 cm^{-1}, formed in 72% yield. Anal. Calcd for $C_{74}H_{52}N_2O_{20}P_4W_4$: C, 41.37; H, 2.44; N, 1.30; P, 5.77. Found: C, 41.89; H, 2.71; N, 1.84; P, 5.95.

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Registry No. L_I, 43133-27-3; L_{IIs}, 43133-28-4; L_{IIu}, 43133-29-5; L_{IV}, 43133-31-9; $L_ICr(CO)_5$, 73926-17-7; $L_IMo(CO)_5$, 73926-18-8; $L_IW(CO)_5$, 73940-54-2; $L_{IIu}Cr(CO)_4$, 73926-19-9; $L_{IIu}Mo(CO)_4$, 73926-20-2; $L_{IIu}W(CO)_4$, 73940-55-3; $L_{IIu}[W(CO)_5]_2$, 73940-56-4; $L_{IIs}Cr(CO)_4$, 73926-21-3; $L_{IIs}Mo(CO)_4$, 58904-31-7; $L_{IIs}W(CO)_4$, 73926-22-4; $L_{IIs}[Cr(CO)_5]_2$, 73926-23-5; $L_{IIs}[Mo(CO)_5]_2$, 73926-24-6; $L_{IIs}[W(CO)_5]_2$, 73926-25-7; $L_{IV}[Cr(CO)_4]_2$, 73926-26-8; $L_{IV}[Mo(CO)_4]_2$, 73926-27-9; $L_{IV}[W(CO)_4]_2$, 73940-57-5; $L_{IV}Cr(CO)_4$, 73926-29-1; $L_{IV}Mo(CO)_4$, 54340-53-3; $L_{IV}[Cr(CO)_4][Mo(CO)_4]$, 73926-28-0; $L_{IV}[W(CO)_5]_4$, 73926-30-4; $[Et_4N][Cr(CO)_5I]$, 14780-98-4; $[Et_4N][Mo(CO)_5I]$, 14781-00-1; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $PhNH_2W(CO)_5$, 16969-72-5; $(C_7H_8)Cr(CO)_4$, 12146-36-0; $(C_7H_8)Mo(CO)_4$, 12146-37-1.

Correspondence

Alternative Bonding Models for an Unusual Metallocarborane Containing a Wedging B–H Group

Sir:

The skeletal geometries of many seemingly disparate polyhedral cagelike molecules may be rationalized and predicted by a set of simple, empirical electron-counting rules.[1] In this regard, a commonly accepted rationalization[2] (supposedly[2b,c] based on Mingos' capping principle[3]) for the peculiar skeletal geometry of $CpCoFeMe_4C_4B_8H_8$[4] (Cp = η^5-C_5H_5, Me = CH_3) (Figure 1) is that the double-face-capping (wedging) BH vertex *suggested* by the molecular structure determination[2a] is a direct result of a hyperdeficiency[5] of two

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(4) See Figure 1 for a drawing of the molecular structure and atom numbering scheme for $CpCoFeMe_4C_4B_8H_8$.