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Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. II. Cyclopentadienylnickel, -molybdenum, and -tungsten Complexes[1,2]

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The cyclopentadienyl metal carbonyls of molybdenum, tungsten, and nickel react with tetrasubstituted biphosphines and biarsines to give P- and As-bridged complexes, respectively. These are of the type $[C_5H_5M(ER_2)(CO)_n]_2$ (M = Mo or W, n = 2, E = P or As, R = CH_3; M = Ni, n = 0, E = P or As, R = CH_3 or C_6H_5). $P_2(C_6H_5)_4$ reacts with $[C_5H_5Mo(CO)_3]_2$ to give $[C_5H_5Mo\{P(C_6H_5)_2\}(CO)]_3$. The reaction of $(CH_3)_2PCl$ with $Na[C_5H_5Mo(CO)_3]_2$ yields the hydrido complex $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$. The infrared and nuclear magnetic resonance spectra of the complexes are discussed.

During our investigations of phosphorus- and arsenic-bridged complexes of transition metals, we have found that cyclopentadienyliron dicarbonyl dimer reacts with tetrasubstituted biphosphines and biarsines to give complexes of the type $[C_5H_5Fe(ER_2)(CO)]_2$ (E = P, R = CH_3 or C_6H_5, E = As, R = CH_3).[1] These were shown to contain four-membered Fe_2E_2 rings and to exhibit geometric isomerism. It was therefore of interest to study the reactions of the R_4E_2 ligands with other dimeric cyclopentadienyl metal carbonyl compounds, *i.e.*, those of the group VI metals and nickel. Of the series of group VI metal compounds, $[C_5H_5Mo(CO)_3]_2$ was selected for detailed study, because of its availability; the reactions of the corresponding tungsten compound were also investigated, but in less detail.

Sulfur-bridged complexes derived from the cyclopentadienyl carbonyls of chromium,[3] molybdenum,[3,4] tungsten,[4] and nickel[5] have recently been reported and we were also interested in comparing their properties with the corresponding phosphorus- and arsenic-bridged complexes.

Experimental

Microanalyses and molecular weight determinations were by Schwarzkopf Laboratories, Woodside, N. Y.; Huffman Microanalytical Laboratories, Wheatridge, Colo.; and Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mulheim, Germany. Melting points were determined in evacuated capillaries and are uncorrected.

Infrared spectra were obtained using a Beckmann IR-9 spectrophotometer. Proton nuclear magnetic resonance spectra were measured with Varian Associates A-60 and HR-60 spectrometers, using tetramethylsilane as an internal reference. All the compounds described in this paper give sharp n.m.r. spectra and are thus presumed to be diamagnetic.

All reactions, crystallizations, and the handling of the phosphines and arsines were carried out under nitrogen. Chromatographic separations were carried out on Merck acid-washed alumina.

The phosphine and arsine compounds were prepared as previously described,[1] using established methods or slight modifications thereof. Cyclopentadienylnickel carbonyl dimer[6] and cyclopentadienyltungsten tricarbonyl dimer[7] were prepared by published methods. Cyclopentadienyl molybdenum tricarbonyl dimer was prepared as described below.

Molybdenum hexacarbonyl (100 g.) and dicyclopentadiene (200 ml.) were heated together under reflux. The purple color of $[C_5H_5Mo(CO)_3]_2$ soon appeared in solution. $Mo(CO)_6$ slowly sublimed out of the reaction mixture and was returned to the reaction vessel by scraping with a brass wire which was inserted into the condenser. After about 3 hr., all the $Mo(CO)_6$ was consumed, as shown by the cessation of sublimation, and the reaction mixture was cooled. Hexane (200 ml.) was added and the purple crystalline product separated from unreacted dicyclopentadiene first by decantation and finally by filtration. Thorough washing with hexane was necessary to remove the last traces of dicyclopentadiene. The yield of $[C_5H_5Mo(CO)_3]_2$ was 85%, and its purity (as indicated by comparison of its infrared spectrum with the literature[7]) was sufficiently good so that it could be used directly for reactions.

Sodium cyclopentadienylmolybdenum tricarbonyl was prepared in tetrahydrofuran (freshly distilled from $LiAlH_4$) from $[C_5H_5Mo(CO)_3]_2$ and sodium amalgam as described below.

Di-μ-(dimethylarsenido)-di-π-cyclopentadienyltetracarbonyldimolybdenum.—$[C_5H_5Mo(CO)_3]_2$ (3.76 g., 7.66 mmoles), tetramethylbiarsine (1.61 g., 7.66 mmoles), and toluene (150 ml.) were refluxed together for 24 hr. The dark red solution was filtered and evaporated, leaving a red solid, which was dissolved in chloroform and chromatographed. The chromatogram was washed with hexane and eluted with benzene to give an orange-red band. The eluate was evaporated to dryness and the residual solid crystallized from benzene–hexane to give dark red crystals (m.p. 309–310° dec.; yield, 65%).

Anal. Calcd. for $C_{18}H_{22}As_2Mo_2O_4$: C, 33.6; H, 3.4; Mo, 29.8; O, 9.9; mol. wt., 644. Found: C, 33.8; H, 3.6; Mo, 31.4; O, 10.1; mol. wt. (C_6H_6), 633.

The n.m.r. spectrum of the compound in chloroform shows peaks at 4.69 (cyclopentadienyl protons) and 8.46 τ (methyl protons) with relative intensities of 5:6, respectively.

This compound was also prepared as follows from $Na[C_5H_5Mo(CO)_3]_2$ and dimethylchloroarsine.

$[C_5H_5Mo(CO)_3]_2$ (4.35 g., 8.9 mmoles) in tetrahydrofuran (150 ml.) was stirred vigorously with sodium amalgam (prepared from sodium (0.535 g., 23.2 g.-atoms) and mercury (10 ml.)) until the purple solution changed to pale yellow (30 min.). The excess amalgam was then drained off through a stopcock in the bottom of the reaction vessel and dimethylchloroarsine (2.50 g., 17.8 mmoles) was added dropwise to give an immediate yellow precipitate. After stirring for 1 hr., the solution was orange-red. The solvent was evaporated at 15 mm., toluene (75 ml.) was added, and the solution was refluxed for 3.5 hr. to give a red solution.

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[1] Part I: R. G. Hayter, *J. Am. Chem. Soc.*, in press.

[2] Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963.

[3] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[4] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

[5] W. K. Schropp, *J. Inorg. Nucl. Chem.*, **24**, 1688 (1963).

[6] J. F. Tilney-Bassett, *J. Chem. Soc.*, 577 (1961).

[7] G. Wilkinson, *J. Am. Chem. Soc.*, **76**, 209 (1954).

After filtration, the solution was evaporated and the residual solid dissolved in methylene chloride and chromatographed. Elution with hexane gave a yellow eluate which deposited yellow crystals on cooling. This compound was shown to be $Hg[C_5H_5Mo(CO)_3]_2$ by analysis and by comparison of its m.p. and infrared and n.m.r. spectra with those of an authentic specimen prepared from $Na[C_5H_5Mo(CO)_3]$ and mercuric cyanide.[8]

Anal. Calcd. for $C_{16}H_{10}HgMo_2O_6$: C, 27.8; H, 1.5; Found: C, 28.3; H, 1.9.

The n.m.r. spectrum of $Hg[C_5H_5Mo(CO)_3]_2$ in chloroform consists of a singlet at 4.57 τ due to the cyclopentadienyl protons.

Elution of the chromatogram with benzene gave a red-brown band. Evaporation of the eluate gave red crystals contaminated with $Hg[C_5H_5Mo(CO)_3]_2$. Crystallization from benzene–heptane gave pure $[C_5H_5Mo\{As(CH_3)_2\}(CO)_3]_2$ (yield, 5%), which was identified by its m.p. and infrared and n.m.r. spectra.

Di-μ-(dimethylphosphido)-di-π-cyclopentadienyltetracarbonyldimolybdenum.—$[C_5H_5Mo(CO)_3]_2$ (5.60 g., 11.5 mmoles), tetramethylbiphosphine (1.40 g., 11.5 mmoles), and toluene (75 ml.) were refluxed together for 16 hr. to give an orange-red solution. After filtration, the solution was evaporated to a sticky red-brown solid. Washing with cold acetone gave an intense brown solution and left orange crystals. These were crystallized several times from chloroform–hexane to give the pure product as orange plates (decomposes at 210°; yield, 31%).

Anal. Calcd. for $C_{18}H_{22}Mo_2O_4P_2$: C, 38.9; H, 4.0; Mo, 34.5; O, 11.5; P, 11.1; mol. wt., 556. Found: C, 38.7; H, 4.0; Mo, 34.2; O, 11.4; P, 11.2; mol. wt. (CH_2Br_2), 521.

The n.m.r. spectrum of this compound in deuteriochloroform consists of a triplet at 4.73 τ (cyclopentadienyl protons, J_{HP} = 0.8 c.p.s.) and a triplet at 8.33 τ (methyl protons, J_{HP}[9] = 4.5 c.p.s.).

μ-(Dimethylphosphido)-hydridodi-π-cyclopentadienyltetracarbonyldimolybdenum.—A solution of $Na[C_5H_5Mo(CO)_3]$ (32.8 mmoles) in tetrahydrofuran (150 ml.) was prepared as described above. Dimethylchlorophosphine (3.17 g., 32.8 mmoles) was then added dropwise with stirring to give a transient yellow precipitate. After stirring for 1 hr., the solvent was removed at 15 mm. If the reaction mixture were worked up at this stage, the only isolable product would be $Hg[C_5H_5Mo(CO)_3]_2$ (which was isolated and identified as described above in an independent experiment). Toluene (75 ml.) was added and the solution refluxed overnight. After filtration, the solution was evaporated to dryness at 15 mm. and the residual solid dissolved in chloroform and chromatographed. Elution with benzene gave an orange band, which afforded orange crystals on evaporation of the eluate. These were recrystallized from benzene–hexane to give the pure compound as orange-red rods (m.p. 215°; yield, 35%).

Anal. Calcd. for $C_{16}H_{17}Mo_2O_4P$: C, 38.7; H, 3.45; Mo, 38.7; O, 12.9; P, 6.2; mol. wt., 496. Found: C, 38.9; H, 3.5; Mo, 38.1; O, 13.0; P, 6.6; mol. wt. (C_6H_6), 504.

The n.m.r. spectrum of this compound in benzene solution shows a doublet at 5.31 τ (cyclopentadienyl protons, $J_{HP} \approx 0.3$ c.p.s.), a double doublet at 8.38 τ (methyl protons, splittings = 9.9 c.p.s. (J_{HP}) and 0.4 c.p.s.), and a doublet at 21.73 τ (Mo–H proton, J_{HP} = 36.6 c.p.s.). The first two resonances have relative intensities of 10:6, respectively. In chloroform solution, the cyclopentadienyl resonance occurs at 4.86 τ (J_{HP} = 0.4 c.p.s.) and the methyl resonance at 8.10 τ (J_{HP} = 9.9 c.p.s.).

Under similar conditions, $Na[C_5H_5W(CO)_3]_2$ and $(CH_3)_2PCl$ react to give a 40% yield of $Hg[C_5H_5W(CO)_3]_2$[8] as the only isolable product. The n.m.r. spectrum in chloroform shows a peak at 4.50 τ due to the cyclopentadienyl protons.

Tri-μ-(diphenylphosphido)-tri-π-cyclopentadienyltricarbonyltrimolybdenum.—$[C_5H_5Mo(CO)_3]_2$ (5.00 g., 10.2 mmoles) was added to tetraphenylbiphosphine (10.2 mmoles) in toluene (150 ml.) and the solution refluxed for 20 hr. On cooling, the intense green solution deposited dark green crystals, which were filtered and washed with toluene and hexane (yield, 4.45 g.). The compound was only very sparingly soluble in organic solvents and portions were crystallized from boiling toluene (0.24 g. dissolved in 100 ml.) to give dark green plates (m.p. 336–343° dec.). The crystals turn brown on prolonged exposure to air.

Anal. Calcd. for $C_{54}H_{45}Mo_3O_3P_3$: C, 57.8; H, 4.0; Mo, 25.6; O, 4.3; P, 8.3; mol. wt., 1123. Found: C, 58.7; H, 4.2; Mo, 25.15; O, 5.0, 4.9; P, 8.0; mol. wt. (C_6H_6), 907; (CH_2Br_2), 1000.

The compound was insufficiently soluble in most organic solvents to give an n.m.r. spectrum and solutions in halogenated solvents slowly turned orange or brown, indicating decomposition.

Di-μ-(dimethylphosphido)-di-π-cyclopentadienyltetracarbonylditungsten.—$[C_5H_5W(CO)_3]_2$ (1.50 g., 2.1 mmoles), tetramethylbiphosphine (0.30 g., 2.48 mmoles), and ethylcyclohexane (50 ml.) were refluxed together for 24 hr. The resulting orange solution was filtered and evaporated at 15 mm. and the residual solid crystallized from acetone to give orange prisms (decomposes at 255°; yield, 20%).

Anal. Calcd. for $C_{18}H_{22}O_4P_2W_2$: C, 29.5; H, 3.0; O, 8.7; P, 8.5; mol. wt., 732. Found: C, 29.7; H, 3.0; O, 9.6; P, 9.1; mol. wt. (C_6H_6), 758.

The n.m.r. spectrum of this compound in chloroform consists of peaks at 4.61 τ (cyclopentadienyl protons, triplet, J_{HP} = 0.4 c.p.s.) and 8.13 τ (methyl protons, triplet, J_{HP}[9] = 4.4 c.p.s.).

Di-μ-(diphenylphosphido)-di-π-cyclopentadienyldinickel.—$[C_5H_5NiCO]_2$ (5.00 g., 16.5 mmoles) was added to tetraphenylbiphosphine (16.5 mmoles) in toluene (150 ml.) and the solution refluxed for 16 hr. The solution was then cooled, filtered, and evaporated to dryness at 15 mm. The brown solid residue was crystallized from toluene to give dark brown needles of the pure product (m.p. 264–265° dec.; yield, 65%).

Anal. Calcd. for $C_{34}H_{30}Ni_2P_2$: C, 66.1; H, 4.9; Ni, 19.0; P, 10.0; mol. wt., 618. Found: C, 66.0; H, 5.1; Ni, 18.9; P, 9.7; mol. wt. (C_6H_6), 528.

The n.m.r. spectrum in $CDCl_3$ shows complex bands at 2.2 and 2.75 τ due to the phenyl protons and a triplet at 5.16 τ (cyclopentadienyl protons, J_{HP} = 0.6 c.p.s.).

Di-μ-(dimethylphosphido)-di-π-cyclopentadienyldinickel.—Tetramethylbiphosphine (1.35 g., 11.0 mmoles) was added to $[C_5H_5NiCO]_2$ (3.34 g., 11.0 mmoles) in toluene (75 ml.) and the solution refluxed for 66 hr. The dark red solution was then filtered and evaporated to dryness at 15 mm., leaving an oily red solid. Hexane (10 ml.) was added and, after cooling in a refrigerator, the solid product was filtered and dried. Sublimation at 140° and 0.2 mm. gave red-brown crystals (m.p. 217–220° dec.; yield, 32%). A second sublimation gave the analytical sample. The compound decomposes slowly on exposure to air.

Anal. Calcd. for $C_{14}H_{22}Ni_2P_2$: C, 45.5; H, 6.0; Ni, 31.8; P, 16.8; mol. wt., 370. Found: C, 45.9; H, 5.9; Ni, 31.0; P, 15.7; O, 0.0; mol. wt. (C_6H_6), 328.

The n.m.r. spectrum in carbon disulfide solution shows bands at 5.13 (cyclopentadienyl protons, singlet) and 8.67 τ (methyl protons, triplet, J_{HP}[9] = 6.6 c.p.s.) of integrated relative intensities 5:6, respectively.

Di-μ-(dimethylarsenido)-di-π-cyclopentadienyldinickel.—Tetramethylbiarsine (1.60 g., 7.61 mmoles) was added to a solution of $[C_5H_5NiCO]_2$ (2.32 g., 7.61 mmoles) in toluene (75 ml.) and refluxed for 20 hr. The yellow-black solution was then cooled, filtered, and evaporated, leaving a black crystalline solid, which was crystallized from hexane to give black crystals of the complex (decomposes at 240°; yield, 60%).

Anal. Calcd. for $C_{14}H_{22}As_2Ni_2$: C, 36.75; H, 4.85; Ni, 25.7; mol. wt., 458. Found: C, 36.7; H, 4.9; Ni, 25.9; mol. wt. (C_6H_6), 497.

The n.m.r. spectrum in CS_2 solution shows singlet bands at 5.10 (cyclopentadienyl protons) and 8.79 τ (methyl protons) with relative intensities 5:6, respectively.

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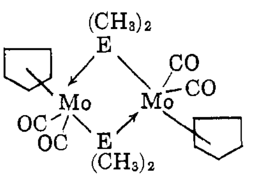
[8] E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. anorg. allgem. Chem.*, **282**, 47 (1955).

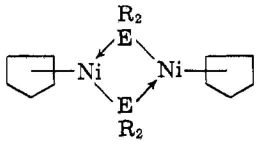
[9] (a) This is not a true coupling constant, since it is the average of the coupling constants of the methyl protons to the near and far phosphorus nuclei (structures I and II, E = P, R = CH_3); (b) for a more detailed discussion of this effect, see ref. 1 and R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

Discussion

In general, the cyclopentadienyl metal carbonyl dimers of molybdenum and nickel react with tetrasubstituted biphosphines and biarsines to give complexes of types I and II, respectively. These compounds form a series with the previously reported iron complexes,[1] of general formula $[C_5H_5M(ER_2)(CO)_n]_2$ ($M = Mo$, $n = 2$; $M = Fe$, $n = 1$; $M = Ni$, $n = 0$). The tungsten compound $[C_5H_5W\{P(CH_3)_2\}(CO)_2]_2$, which has a structure similar to I, was prepared from $[C_5H_5W(CO)_3]_2$ and $(CH_3)_4P_2$. Recently reported sulfur-bridged complexes of molybdenum,[4] tungsten,[4] and nickel[5] have structures analogous to I and II with $-SR$ groups replacing $-ER_2$.



I ($E = P$, As)

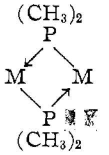


II ($E = P$, $R = CH_3$, C_6H_5; $E = As$, $R = CH_3$)

Evidence for the structure of the molybdenum, tungsten, and nickel compounds is obtained from their infrared and n.m.r. spectra. The infrared spectra of the complexes of type I are very similar, especially in the carbonyl region (Table I and Fig. 1). In solution, two strong bands are found in the region expected for terminal carbonyl absorption (a third weak band may be a combination mode) and none in the bridging carbonyl region. The nickel complexes show no absorption due to carbonyl groups in the region 1700–2200 cm.$^{-1}$.

The compounds reported in this paper have not been found to show geometric isomerism, unlike the corresponding iron complexes, $[C_5H_5Fe(ER_2)(CO)]_2$.[1] Such isomerism might be expected for the molybdenum and tungsten compounds, although not for the nickel analogs. Geometric isomerism has been suggested for the sulfur-bridged $[C_5H_5Mo(SCH_3)(CO)_2]_2$ in order to account for the infrared and n.m.r. spectra.[4] The n.m.r. spectra of the present series of compounds show features which are similar to those observed in the analogous iron compounds of *trans* configuration.[1] Thus, $[C_5H_5Mo\{As(CH_3)_2\}(CO)_2]_2$ and $[C_5H_5Ni\{As(CH_3)_2\}]_2$ both show two singlet absorptions due to the equivalent cyclopentadienyl and methyl protons, respectively. Even the crude reaction mixtures gave no evidence for small amounts of other isomers.

The spectra of the analogous phosporus compounds show cyclopentadienyl resonances in the range 4.6–5.2 τ, usually in the form of a triplet due to coupling of the protons of the π-cyclopentadienyl rings to two equivalent phosphorus atoms, each of nuclear spin $^1/_2$. This splitting is small (<1 c.p.s.) and was not observed in $[C_5H_5Ni\{P(CH_3)_2\}]_2$. When $R = CH_3$, the methyl resonance occurs in the range 8.1–8.7 τ as a well defined 1:2:1 triplet. The triplet pattern can be attributed to strong phosphorus–phosphorus coupling in the ring[1,9b] and appears to be a characteristic feature of such a grouping, having been observed when M = Fe,[1] Mn,[10] Mo, W, and Ni.



The reaction of tetraphenylbiphosphine with $[C_5H_5$-

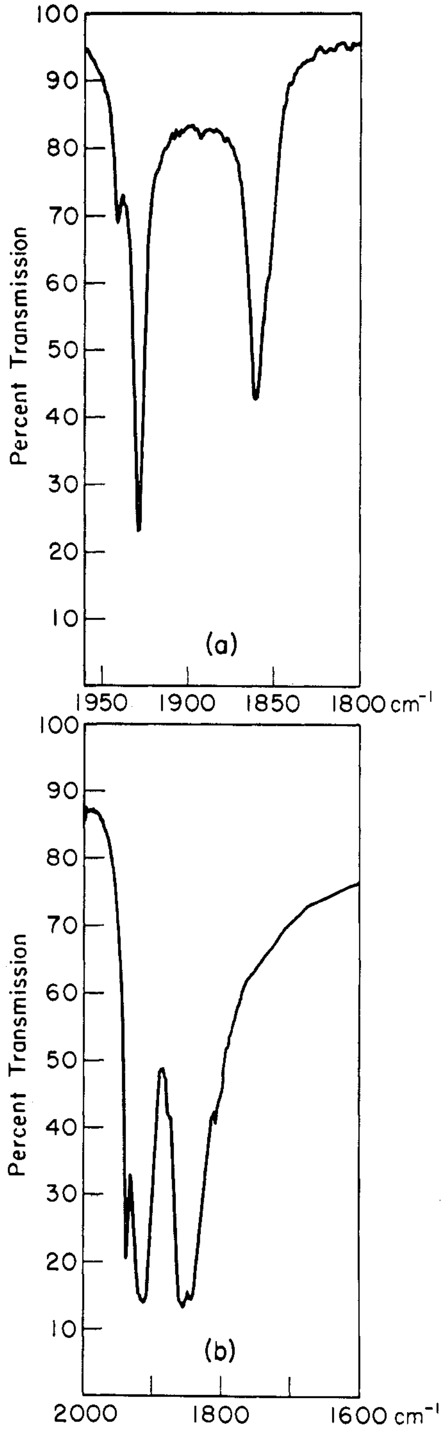


Fig. 1.—Infrared spectra of $[C_5H_5Mo\{P(CH_3)_2\}(CO)_2]_2$ in the carbonyl region: (a) carbon disulfide solution, (b) halocarbon mull. These spectra are typical of complexes of the type $[C_5H_5M\{E(CH_3)_2\}(CO)_2]_2$ ($M = Mo$, W; $E = P$, As).

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[10] R. G. Hayter, *Z. Naturforsch.*, **18b**, 581 (1963).

TABLE I

INFRARED SPECTRA OF THE PHOSPHORUS- AND ARSENIC-BRIDGED COMPLEXES OF MOLYBDENUM, TUNGSTEN, AND NICKEL

	Absorption bands in the carbonyl region, cm.$^{-1}$		
Compound	CS_2 solution	Halocarbon mull	Other absorption bands, cm.$^{-1a}$
$[C_5H_5Mo\{As(CH_3)_2\}(CO)_2]_2$	1939 (w), 1927 (vs), 1859 (vs)	1937 (s), 1912 (vs), 1858 (vs), 1842 (vs)	2908 (w), 1418 (m), 1352 (w), 1258 (w), 1242 (w), 1104 (w), 1056 (m), 1004 (m), 918 (w), 882 (m), 859 (s), 843 (m), 830 (m), 817 (vs), 807 (s), 794 (s), 724 (m), 601 (m), 588 (m), 573 (m), 560 (s), 550 (s), 523 (s), 508 (m), 493 (m), 482 (w), 466 (m)
$[C_5H_5Mo\{P(CH_3)_2\}(CO)_2]_2$	1941 (w), 1929 (vs), 1860 (vs)	1938 (s), 1912 (vs), 1856 (vs), 1844 (vs)	3115 (w), 2995 (w), 2950 (w), 2900 (w), 1422 (m), 1410 (w), 1354 (w), 1292 (w), 1283 (w), 1274 (m), 1258 (w), 1105 (w), 1055 (m), 1012 (m), 1006 (m), 933 (s), 902 (s), 883 (w), 855 (w), 840 (w), 830 (m), 810 (vs), 709 (m), 701 (m), 682 (w), 671 (m), 600 (m), 568 (m), 558 (s), 532 (s), 518 (m), 508 (m), 496 (s), 486 (m), 468 (s)
$[C_5H_5W\{P(CH_3)_2\}(CO)_2]_2$	1933 (w), 1921 (vs), 1848 (vs)	1930 (vs), 1906 (vs), 1846 (vs), 1831 (vs)	3120 (w), 2998 (w), 2955 (w), 2904 (w), 1423 (s), 1411 (m), 1355 (w), 1296 (w), 1287 (w), 1278 (m), 1106 (w), 1062 (w), 1057 (m), 1014 (w), 1005 (m), 937 (m), 908 (s), 888 (w), 860 (w), 847 (w), 838 (m), 818 (s), 725 (w), 714 (w), 704 (w), 675 (m), 596 (w), 552 (m), 547 (m), 537 (m), 524 (m), 510 (w), 499 (w), 490 (m), 472 (m), 465 (m)
$[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$	1935 (vs), 1872 (vs)	2018 (m), 1930 (vs), 1859 (vs)	3108 (w), 3090 (w), 2998 (w), 2962 (w), 2910 (w), 1422 (s), 1412 (m), 1356 (m), 1292 (w), 1278 (m), 1111 (w), 1063 (w), 1010 (m), 942 (m), 890 (s), 842 (m), 834 (w), 809 (s), 722 (m), 703 (m), 612 (m), 596 (m), 566 (m), 539 (m), 522 (m), 508 (s), 470 (s)
$[C_5H_5Mo\{P(C_6H_5)_2\}(CO)]_3$	...	1852 (vs)	3040 (w), 1581 (w), 1564 (w), 1477 (w), 1428 (w), 1418 (w), 1300 (w), 1263 (w), 1180 (w), 1155 (w), 1104 (w), 1092 (m), 1061 (m), 1023 (m), 1004 (m), 968 (w), 835 (m), 806 (s), 800 (s), 742 (vs), 697 (vs), 620 (w), 612 (w), 552 (m), 537 (vs), 526 (m), 494 (vs), 482 (s), 467 (m), 444 (s)
$[C_5H_5Ni\{P(C_6H_5)_2\}]_2{}^b$	...	...	3060 (w), 3042 (w), 2995 (w), 1581 (s), 1568 (m), 1475 (vs), 1432 (vs), 1405 (m), 1348 (m), 1300 (w), 1172 (m), 1157 (w), 1087 (m), 1065 (w), 1052 (w), 1025 (m), 1017 (m), 998 (w), 986 (w), 972 (w), 920 (w), 887 (w), 848 (sh), 837 (m), 830 (m), 792 (vs), 784 (vs), 766 (m), 741 (vs), 693 (vs), 620 (w), 529 (vs), 503 (vs), 483 (w), 462 (m), 448 (m), 433 (m)
$[C_5H_5Ni\{P(CH_3)_2\}]_2{}^b$	...	...	3088 (w), 2980 (w), 2912 (w), 1405 (m), 1373 (w), 1268 (m), 1248 (w), 1108 (w), 1035 (w), 1013 (m), 986 (m), 935 (s), 902 (vs), 838 (m), 830 (m), 792 (s), 781 (vs), 712 (m), 675 (vs), 608 (w), 554 (w), 483 (m), 458 (w)
$[C_5H_5Ni\{As(CH_3)_2\}]_2{}^b$	...	...	3090 (w), 2985 (w), 2960 (w), 2912 (w), 1408 (m), 1376 (w), 1348 (w), 1243 (w), 1232 (w), 1112 (w), 1048 (m), 1018 (m), 983 (m), 894 (m), 888 (m), 844 (s), 833 (s), 780 (vs), 728 (m), 580 (m), 570 (m)

[a] Nujol mull 400–1300 cm.$^{-1}$, halocarbon mull 1300–4000 cm.$^{-1}$. [b] These compounds show a spurious peak at 1670 cm.$^{-1}$ in their mull spectra, which is not present when Nujol is used as the mulling agent. This may be due to reaction with the halocarbon.

$Mo(CO)_3]_2$ does not give a complex of type I, but instead a dark green crystalline complex, for which analyses and molecular weight data indicate the composition $[C_5H_5Mo\{P(C_6H_5)_2\}(CO)]_3$. Owing to its low solubility, good n.m.r. spectra were not obtained, although the sharp tetramethylsilane reference peak indicated the diamagnetism of the compound. In the infrared spectrum (Table I), a single band is observed in the carbonyl region at a frequency (1852 cm.$^{-1}$) where both terminal and bridging carbonyl groups may absorb.[11] Terminal carbonyl absorption in this region has previously been found in substituted derivatives of the group VI metal carbonyls, when the substituting ligands (*e.g.*, tertiary phosphines) make less demand on the metal d-electrons than do the carbonyl groups.[11,12] This effect may also be operating here, particularly since there is only one carbonyl group to compete for

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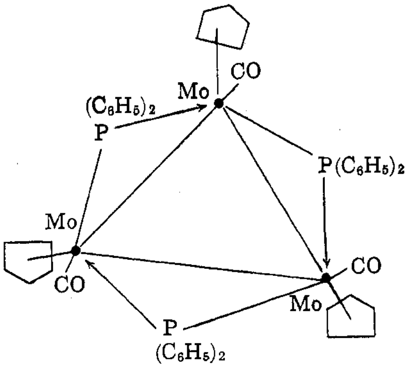
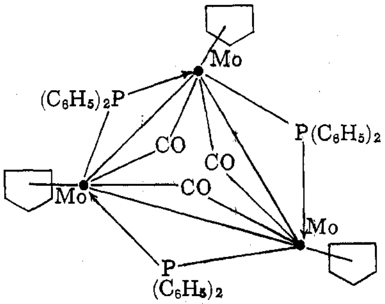
(11) F. A. Cotton, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 5.

(12) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

the d-electrons of each molybdenum atom. However, the data presently available do not allow us to distinguish with certainty between structures III and IV. Metal-metal bonding is assumed in both structures in order to allow each molybdenum atom to attain an inert gas configuration.



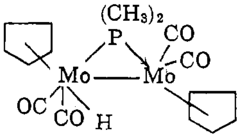
III



IV

It is also possible that this compound may contain Mo–H hydrogen instead of one or more of the metal–metal bonds, and this hydrogen would escape detection by elemental analysis. There was no evidence for any absorption due to $\nu_{\mathrm{Mo-H}}$ in the infrared spectrum, but, unfortunately, the low solubility prevented a more definite conclusion being drawn from the n.m.r. spectrum in the characteristic transition metal hydride region.[13]

The crude reaction product from $[C_5H_5Mo(CO)_3]_2$ and $P_2(CH_3)_4$ shows in its n.m.r. spectrum the presence of two compounds in approximately equal amounts. One was isolated and identified as I (E = P, R = CH_3) and the other was found to be identical (by n.m.r.) with the compound (V) obtained from $Na[C_5H_5Mo(CO)_3]$ and $(CH_3)_2PCl$. The infrared spectrum of V (Table I) shows two strong bands in the terminal carbonyl region, while no absorption in the bridging carbonyl region was observed. The n.m.r. spectrum is very similar to that of the analogous compound $[(C_5H_5)_2Fe_2H\{P(CH_3)_2\}(CO)_2]$, and can be similarly interpreted.[1] Thus the cyclopentadienyl resonance is a doublet, the methyl resonance is a double doublet, and the Mo–H hydrogen[14] shows doublet absorption at 21.73 τ. The doublet pattern of each absorption band probably arises from spin–spin coupling between the single phosphorus nucleus in the molecule and the respective protons. The small (0.4 c.p.s.) additional splitting of the methyl resonance is probably due to a slight nonequivalence of the methyl groups.[1] The location of the unique hydrogen atom is uncertain and it may be equally associated with both metal atoms.[15] Structure V is then an extreme form of the molecule.



V

A major product in the reaction of $Na[C_5H_5Mo(CO)_3]$ (prepared from $[C_5H_5Mo(CO)_3]_2$ and sodium amalgam) with $(CH_3)_2AsCl$ and with $(CH_3)_2PCl$ under certain conditions (see Experimental section) is $Hg[C_5H_5Mo(CO)_3]_2$. The mercury presumably comes from the finely divided metal which remains after the removal of excess amalgam. The following reactions may then occur

$$2Na[C_5H_5Mo(CO)_3] + 2(CH_3)_2AsCl + Hg \longrightarrow Hg[C_5H_5Mo(CO)_3]_2 + As_2(CH_3)_4 + 2NaCl$$

$$Hg[C_5H_5Mo(CO)_3]_2 + As_2(CH_3)_4 \longrightarrow Hg + [C_5H_5Mo\{As(CH_3)_2\}(CO)_2]_2 + 2CO$$

In the case of $(CH_3)_2PCl$, either the mercury derivative or the hydrido complex are obtained, depending on the conditions. In partial confirmation of the proposed reaction scheme, it has been found that $P_2(CH_3)_4$ and $Hg[C_5H_5Mo(CO)_3]_2$ react in refluxing toluene to give a mixture of I (E = P, R = CH_3) and V in the approximate ratio 1:4.

There are other examples known of the formation of mercury derivatives of metal carbonyls in reactions involving sodium amalgam and certain chloro compounds.[16] It has also been found that $Co_2(CO)_8$ reacts directly with mercury to give $Hg[Co(CO)_4]_2$,[17] so that formation of mercury derivatives may occur in some cases even in the absence of sodium and a chloro compound.

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(13) M. L. H. Green, *Angew. Chem.*, **17**, 719 (1960).

(14) The origin of this hydrogen is at present unknown and is the subject of further investigation.

(15) Evidence has recently been presented suggesting that the single hydridic hydrogen in $[(C_5H_5)_2W_2H(CO)_6]^+$ is undergoing rapid intramolecular exchange between the two metal atoms (A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3635 (1962)).

(16) R. B. King, private communication.

(17) S. V. Dighe and M. Orchin, *Inorg. Chem.*, **1**, 965 (1962).