comparable type of force constant, 16.5 mdynes/Å. for $Mo(CO)_6$. Thus, our nonrigorous force constants are qualitatively in the wrong ratio, though quantitatively the ratios differ rather little.

Acknowledgment.—The author is very grateful to Dr. Reinhard Schmutzler for his interest and kindness in supplying information about $Mo(PF_3)_3(CO)_3$.

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Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. VI.[1a] Reactions of Tetrasubstituted Biphosphines and a Biarsine with Monomeric Metal Carbonyls[1b]

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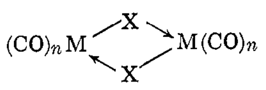
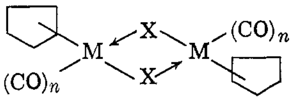
The reactions of tetramethylbiphosphine and -biarsine with the carbonyls of nickel, iron, chromium, molybdenum, and tungsten and of tetraphenylbiphosphine with nickel carbonyl have been studied and two types of binuclear complexes identified. The group VI metal carbonyls also give a third type of complex, which is apparently polymeric. The infrared and proton n.m.r. spectra of the complexes are discussed, and a few simple reactions are studied.

The reactions of tetrasubstituted biphosphines and tetramethylbiarsine with the dimeric metal carbonyls (cobalt and manganese[2]) and with the dimeric cyclopentadienyl metal carbonyls (iron,[3] nickel,[4] molybdenum,[4] and tungsten[4]) have recently been found to give, in general, dimeric bridged complexes of structures I and II, respectively.



I



II

In this paper, we describe the corresponding reactions of the monomeric carbonyls of nickel, iron, chromium, molybdenum, and tungsten. It was anticipated that, if these metal carbonyls were to react to give bridged complexes of type I, metal–metal bonding would also occur in order to allow the metals to achieve an inert gas configuration. In certain complexes of this general type, the molecule is folded along the line joining the bridging atoms, and it has been proposed that the metal–metal bond is bent.[5] One of our aims was to look for evidence of such folding using nuclear magnetic resonance spectroscopy.

While our investigation of the reactions of the group VI metal carbonyls was still incomplete, we learned that Chatt and his co-workers had prepared similar compounds.[6] We therefore curtailed our work on group VI, although in fact our investigation appears to complement that of Chatt, *et al.*, who used sealed tubes rather than solvents for their reactions and have in some cases isolated different products.

Experimental[7]

Infrared spectra were measured on a Beckmann IR-9 spectrophotometer. The nuclear magnetic resonance spectra were measured on a Varian Associates A-60 spectrometer, using tetramethylsilane as an internal standard. All the compounds described in this paper (except V) gave sharp n.m.r. spectra and are thus presumed to be diamagnetic. Methyl resonances were observed in the range τ 7.6–9.1 and phenyl resonances at about τ 2.65. Melting points were determined in evacuated capillaries unless otherwise stated and are uncorrected.

The phosphines and arsine were prepared as previously described.[3] The metal carbonyl compounds were obtained from commercial sources, except triiron dodecacarbonyl, which was prepared from iron pentacarbonyl.[8] All operations except the handling of the solid complexes were carried out under nitrogen. Chromatographic separations were carried out on Merck acid-washed alumina.

Preparation of the Complexes.—The complexes listed in Table I were prepared by reaction between the metal carbonyl (2 moles) and the biphosphine or biarsine ligand (1 mole). In the preparation of the iron complexes, $Fe(CO)_5$ was used for the complexes of type IV, and $Fe_3(CO)_{12}$ for $[Fe_2(CO)_6P_2(CH_3)_4]$. The reaction conditions, purification procedures, yields, and properties of the complexes are summarized in Table I. Analytical data are given in Table II, and infrared data in Tables III and IV.

The reactions involving iron carbonyls deposited black solids, which were pyrophoric when dry and were removed by filtration before evaporation of the reaction solvent. Black metal-like solids were also formed during the reactions of the group VI metal carbonyls in diglyme, and these could only be partially re-

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(1) (a) Part V: R. G. Hayter and L. F. Williams, *Inorg. Chem.*, **3**, 613 (1964); (b) presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 21–April 5, 1963.

(2) R. G. Hayter, *J. Am. Chem. Soc.*, **86**, 823 (1964).

(3) R. G. Hayter, *ibid.*, **85**, 3120 (1963).

(4) R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

(5) (a) L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, **2**, 328 (1963); (b) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961); (c) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, in press.

(6) J. Chatt, D. A. Thornton, and D. T. Thompson, private communications, and *J. Chem. Soc.*, in press.

(7) Microanalyses and molecular weight determinations were by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., Huffmann Microanalytical Laboratories, Wheatridge, Colo., Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mülheim, Germany, and Pascher Microanalytisches Laboratorium, Bonn, Germany.

(8) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Vol. II, Ferdinand Enke Verlag, Stuttgart, 1960, p. 1510.

TABLE I

PREPARATIVE DATA, PROPERTIES, AND PROTON N.M.R. SPECTRA OF THE COMPLEXES OF TYPES III, IV, AND V

	Preparation conditions						Proton n.m.r. spectrum		
Compound	Solvent[a]	Reflux time, hr.	Crystn. solvent	Yield, %	Color	M.p., °C.	τ	Multiplicity[o]	Solvent
$[Ni_2(CO)_6P_2(C_6H_5)_4]$	Heptane	1[b]	Benzene	82	Yellow	190–200[l]	...	...	...
$[Ni_2(CO)_6P_2(CH_3)_4]$	Benzene	1[b]	Pentane[d]	..	White	10–13	9.08	Triplet (5.1)	C_6H_6
$[Fe_2(CO)_8P_2(CH_3)_4]$	Benzene	16	CH_2Cl_2–pentane[e]	33	Yellow	140–145	8.83	Doublet (0.8)	C_6H_6
$[Fe\{P(CH_3)_2\}(CO)_3]_2$	ECH	40	C_6H_6–hexane[f]	55	Orange	221.5–222	8.07 8.48	1:2:1 triplet (5.8) 1:2:1 triplet (6.0)	$CHCl_3$
$[Fe\{As(CH_3)_2\}(CO)_3]_2$	ECH	18	C_6H_6–heptane[g]	69	Orange-red	210–211[m]	8.12 8.39	Singlet Singlet	CS_2
$[Cr_2(CO)_{10}P_2(CH_3)_4]$	ECH	64	Hexane[h]	12	Pale yellow	128–130	8.31	Triplet (3.4)	$CHCl_3$
$[Cr_2(CO)_{10}As_2(CH_3)_4]$	ECH	16	Hexane[i]	29	Pale yellow	108–110	8.31	Singlet	$CHCl_3$
$[Cr(CO)_4As_2(CH_3)_4]_m$			DMF–ethanol[i]	5	Yellow-orange	230[n]	...	...	...
$[Cr\{P(CH_3)_2\}(CO)_4]_2$	Diglyme	6[c]	Benzene	26	Red	302–303	7.70	Doublet (10.0)	$CHCl_3$
$[Mo_2(CO)_{10}P_2(CH_3)_4]$	MCH	43	C_6H_6–hexane	26	White	140–141	8.33	Triplet (5.1)	$CHCl_3$
$[Mo(CO)_4As_2(CH_3)_4]_m$	ECH	16	DMF–ethanol	23	Pale yellow	235[n]	...	...	...
$[Mo\{P(CH_3)_2\}(CO)_4]_2$	Diglyme	3[c]	Hexane[j]	20	Orange	228	7.73	Doublet (9.2)[p]	CS_2
$[Mo\{As(CH_3)_2\}(CO)_4]_2$	Diglyme	16[c]	Benzene	30	Orange	290	7.73	Singlet	$CHCl_3$
$[W_2(CO)_{10}P_2(CH_3)_4]$	Diglyme	16[c]	C_6H_6–hexane[k]	9	White	162–163	8.18	Triplet (4.1)	$CHCl_3$
$[W\{P(CH_3)_2\}(CO)_4]_2$			Hexane[k]	11	Orange	205	7.60	Doublet (9.4)[p]	CS_2
$[W\{As(CH_3)_2\}(CO)_4]_2$	Diglyme	16[c]	CH_2Cl_2–hexane	38	Orange	219–221	7.67	Singlet	$CHCl_3$

[a] ECH, ethylcyclohexane; MCH, methylcyclohexane; diglyme, bis(2-methoxyethyl) ether. [b] Reaction carried out at room temperature until gas evolution ceased. [c] Prior to reflux, the reaction mixture was held at 80–100° until sublimation of the metal carbonyl onto the cooler parts of the flask ceased. The solutions were then pale yellow due to the presence of the type III complexes. [d] Crystallization and isolation carried out at −78°. The complex, which is very sensitive to heat and oxidation, was dried in a nitrogen stream at 0° and finally by brief pumping at room temperature. [e] Previously chromatographed on alumina, being eluted by hexane. [f] Previously sublimed at 90° and 0.1 mm. Shorter reaction periods (*ca.* 16 hr.) give mixtures of $[Fe\{P(CH_3)_2\}(CO)_3]_2$ and $[Fe_2(CO)_8P_2(CH_3)_4]$, which cannot be readily separated by chromatography. $[Fe_2(CO)_8P_2(CH_3)_4]$ largely decomposes on attempted sublimation. [g] Previously chromatographed, being eluted by benzene. [h] Sublimes at 100° and 0.1 mm. [i] Crude product obtained by evaporation of ethylcyclohexane and removal of unreacted $Cr(CO)_6$ at 80° and 0.1 mm. Benzene extraction of the residue gave $[Cr_2(CO)_{10}As_2(CH_3)_4]$ and left $[Cr(CO)_4As_2(CH_3)_4]_m$. [j] Analytical sample obtained by sublimation at 85° and 0.2 mm. This reaction also gave a 15% yield of (hexane-insoluble) $[Mo_2(CO)_8P_2(CH_3)_4]$. [k] Extraction of the crude reaction product with hexane gave $[W\{P(CH_3)_2\}(CO)_4]_2$, the analytical sample being obtained by sublimation at 120° and 0.2 mm. The hexane-insoluble residue was almost pure $[W_2(CO)_{10}P_2(CH_3)_4]$. [l] Blackens above 100°. [m] With decomposition. [n] Decomposes without melting. [o] Splittings are given in brackets in c.p.s. The unqualified term "triplet" is used when the central absorption is weaker and broader than the outer peaks; the quoted splitting is then the separation between the two outer peaks. [p] An additional weak doublet having the same center of gravity was also observed. The splitting is 5.2 c.p.s. for $[Mo\{P(CH_3)_2\}(CO)_4]_2$ and 4.0 c.p.s. for $[W\{P(CH_3)_2\}(CO)_4]_2$.

moved by filtration. The diglyme therefore was first distilled off under vacuum (1 mm.), the solid residue dissolved in dichloromethane, and the solution treated with a few grams of alumina which absorbed the black solids; filtration then gave a clean solution.

The preparations of the complexes not obtained directly from a metal carbonyl are given below.

Di-μ-(diphenylphosphido)bis(dicarbonylnickel).—$[Ni_2(CO)_6P_2(C_6H_5)_4]$ (5.0 g.) was heated in mesitylene (200 ml.) for 3–4 days at 90–100°. The dark red solution was then filtered and allowed to cool. Black crystals slowly separated and, after 4 days, these were collected and washed with benzene to give 1.94 g. (42% yield) of substantially pure complex. The analytical sample was obtained by recrystallization from mesitylene as black plate-like crystals with a greenish metallic sheen (m.p. 170–190° dec.).

Measurement of magnetic susceptibility gave the following result: $10^6\chi_M = +168$, $10^6\chi_M$ (cor.) $= +427$, $\mu_{eff} = 1.02$ B.M.[9]

This reaction also appears to occur on heating $[Ni_2(CO)_6P_2(C_6H_5)_4]$ in most organic solvents. However, in refluxing benzene or toluene considerable quantities of metallic nickel and very low yields of the desired complex were obtained.

μ-Tetraphenylbiphosphinebis(bromo-π-allylnickel).—$[Ni_2(CO)_6P_2(C_6H_5)_4]$ (0.50 g., 0.76 mmole) was suspended in dry diethyl ether (30 ml.) and treated with allyl bromide (4.0 ml., excess). Gas evolution occurred at once and the yellow complex dissolved to give an orange solution, which soon began to deposit crystals. The reaction was complete in about 1 hr. and the product was filtered and washed with ether to give red prismatic crystals (decomposition with blackening at 110°). The compound is very air sensitive, especially in solution.

Di-μ-(dimethylphosphido)bis(bromotricarbonyliron).—A solution of $[Fe\{P(CH_3)_2\}(CO)_3]_2$ (1.0 g., 2.48 mmoles) in benzene (20 ml.) was stirred and treated dropwise with a solution of bromine in benzene (10 ml., 2.48 mmoles). A transient precipitate was observed, which redissolved to give a red solution. Stirring was continued for 0.5 hr., the solution evaporated, and the orange residue dissolved in chloroform and chromatographed. Benzene eluted a yellow band due to unreacted $[Fe\{P(CH_3)_2\}(CO)_3]_2$ and, more slowly, an orange band, which was finally eluted with chloroform. After evaporation of the eluate, the residue was crystallized from benzene–heptane to give orange prisms (m.p. 171–181° dec.; yield 20%).

The n.m.r. spectrum ($CHCl_3$ solution) shows a 1:2:1 triplet at τ 7.96, splitting = 6.6 c.p.s.

Di-μ-(dimethylarsenido)bis(bromotricarbonyliron) was similarly prepared and purified. After being eluted by benzene, the product was crystallized from dichloromethane–hexane as red crystals (decomposition above 160°; yield 27%).

The n.m.r. spectrum in chloroform shows a singlet at τ 8.15.

Di-μ-(dimethylarsenido)bis(iodotricarbonyliron) was similarly prepared and purified. Elution of the chromatogram with benzene gave an orange-brown band which yielded red crystals on evaporation. N.m.r. showed the product to be a mixture, containing small amounts of $[Fe\{As(CH_3)_2\}(CO)_3]_2$ and of an unidentified compound which shows two equal singlets at τ 7.79 and

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(9) The diamagnetic correction was obtained from Pascal's constants: P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., p. 91.

TABLE II: ANALYTICAL DATA

Type	Compound	Carbon, %		Hydrogen, %		Oxygen, %		Metal, %		Phosphorus, %		Molecular weight[e]	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
III	$[Ni_2(CO)_6P_2(C_6H_5)_4]$	54.9	55.5	3.1	3.35	14.6	14.9					656	593
IV	$[Ni\{P(C_6H_5)_2\}(CO)_2]_2$	56.1	56.25	3.4	3.4	10.7	10.9	19.6	19.4	10.3	10.1	600	559
III	$[Ni_2(CO)_6P_2(CH_3)_4]$	29.5	30.7	3.0	3.4	23.55	23.5	28.8	27.9			408	436
V	$[Ni_2Br_2(\pi\text{-}C_3H_5)_2P_2(C_6H_5)_4]$	49.4	49.7	4.1	4.4					8.5	8.35[a]		
III	$[Fe_2(CO)_8P_2(CH_3)_4]$	31.5	31.3	2.6	3.0	28.0	27.8	24.4	24.4	13.5	13.7	458	406
IV	$[Fe\{P(CH_3)_2\}(CO)_3]_2$	29.9	30.3	3.0	3.3	23.9	24.2	27.8	28.2	15.4	15.5	402	408
IV	$[Fe\{As(CH_3)_2\}(CO)_3]_2$	24.5	25.2	2.5	2.6	19.6	20.0	22.8	22.0			490	541
	$[FeBr\{P(CH_3)_2\}(CO)_3]_2$	21.4	21.5	2.15	2.1	17.1	16.8[b]					562	560[f]
	$[FeBr\{As(CH_3)_2\}(CO)_3]_2$	18.5	18.7	1.9	2.0	14.8	15.5[c]					650	624[f]
	$[FeI\{As(CH_3)_2\}(CO)_3]_2$	16.15	16.9	1.6	1.7	12.9	13.1[d]					743.5	725[f]
III	$[Cr_2(CO)_{10}P_2(CH_3)_4]$	33.2	32.8	2.4	2.3	31.6	32.1	20.55	20.7	12.2	12.3	506	542[f]
III	$[Cr_2(CO)_{10}As_2(CH_3)_4]$	28.3	28.4	2.0	2.3	26.9	28.2	17.5	17.5			594	607
	$[Cr(CO)_4As_2(CH_3)_4]_m$	25.7	25.4	3.2	3.3	17.1	17.1	13.9	14.5			4862[g]	4700[f]
IV	$[Cr\{P(CH_3)_2\}(CO)_4]_2$	32.0	31.8	2.7	2.8	28.4	28.3					450	433[f]
III	$[Mo_2(CO)_{10}P_2(CH_3)_4]$	28.3	28.0	2.0	1.85	26.9	27.15	32.3	32.65	10.4	10.8	594	605[f]
	$[Mo(CO)_4As_2(CH_3)_4]_m$	23.0	23.6	2.9	2.8	15.3	16.2	23.0	24.1			8359[h]	8500[f]
IV	$[Mo\{P(CH_3)_2\}(CO)_4]_2$	26.8	27.0	2.25	2.4	23.8	24.4	35.7	35.4	11.5	11.25	538	523
IV	$[Mo\{As(CH_3)_2\}(CO)_4]_2$	23.0	23.3	1.9	1.9	20.45	22.3	30.7	31.3			626	652[f]
III	$[W_2(CO)_{10}P_2(CH_3)_4]$	21.8	21.7	1.6	1.9	20.8	20.9			8.05	8.0	770	787
IV	$[W\{P(CH_3)_2\}(CO)_4]_2$	20.2	21.1	1.7	2.4	17.9	18.0	51.5	51.3	8.7	9.0	714	777
IV	$[W\{As(CH_3)_2\}(CO)_4]_2$	18.0	18.5	1.5	1.7	16.0	16.6	45.9	46.0			802	807[f]

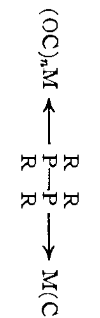
[a] Calcd.: Br, 21.9. Found: Br, 23.0. [b] Calcd.: Br, 28.5. Found: Br, 28.25. [c] Calcd.: Br, 24.6. Found: Br, 24.8. [d] Calcd.: I, 34.1. Found: I, 34.2. [e] Measured using a vapor pressure osmometer. Unless otherwise indicated benzene solutions were used. [f] Dibromomethane solution. [g] Calcd. for a degree of polymerization, m, of 13. [h] Calcd. for m = 20.

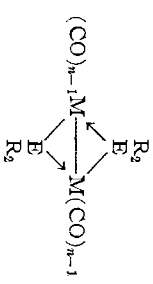
7.93 ($CHCl_3$ solution). Crystallization from dichloromethane–hexane gave the pure complex as reddish brown crystals (m.p. 141–143°; yield 15%).

The n.m.r. spectrum in chloroform solution shows a singlet at τ 7.86.

Discussion

Biphosphine and Biarsine Complexes.—In general, the biphosphine ligands react with the monomeric metal carbonyls in alicyclic or aliphatic hydrocarbon solvents to give binuclear complexes of the uncleaved ligand of structure III.[10] $[Fe_2(CO)_8P_2(CH_3)_4]$, however, is best prepared from triiron dodecacarbonyl and $P_2(CH_3)_4$ in boiling benzene. The analogous tetramethylbiarsine complexes are more difficult to obtain and only the chromium carbonyl derivative $[Cr_2(CO)_{10}As_2(CH_3)_4]$ has been isolated. Reaction also occurs between $Ni(CO)_4$ and $As_2(CH_3)_4$ with evolution of carbon monoxide, but no stable complex could be isolated. With iron pentacarbonyl, $As_2(CH_3)_4$ appears to form only the bridged complex $[Fe\{As(CH_3)_2\}(CO)_3]_2$.


III


IV

$M = Ni, n = 3$
$M = Fe, n = 4$
$M = Cr, Mo, W, n = 5$ $\Big\} R = CH_3$
$R = CH_3, C_6H_5$ $\Big\} E = P, As$

In some of the reactions of tetramethylbiphosphine or -biarsine with the group VI metal carbonyls in alicyclic hydrocarbon solvents, relatively insoluble products are also obtained. The arsine products are sufficiently soluble to be purified by crystallization and analysis indicates the composition $[M(CO)_4As_2(CH_3)_4]_m$ (M = Cr, Mo). These materials appear to be polymers in which metal tetracarbonyl groups are linked by tetramethylbiarsine ligands; terminal groups may be either $-M(CO)_5$ or $-As(CH_3)_2$. Molecular weight measurements indicate that m averages 13 when M = Cr and 20 when M = Mo.

The complexes of type III contain the zerovalent metals and their properties are similar to those of other monosubstituted metal carbonyl complexes. Thus, they are colorless or pale yellow compounds and show absorptions in their infrared spectra which are usually consistent with the proposed number of terminal carbonyl groups (Tables III and IV). The pentacarbonyl complexes of chromium, molybdenum, and tungsten have spectra in the carbonyl region similar to those reported for $LM(CO)_5$ (L = $C_6H_{11}NH_2$, C_5H_5N, R_3P; M = Cr, Mo, W),[11] although not all the expected bands

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[10] While this work was in progress, $[Ni_2(CO)_6P_2(CH_3)_4]$ was reported by L. A. Ross, Ph.D. dissertation, University of Indiana, 1962. The analogous perfluoro complex, $[Ni_2(CO)_6P_2(CF_3)_4]$, is also known (A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **80**, 2334 (1958)), and the preparation of $[Ni_2(CO)_6P_2(C_6H_5)_4]$ and $[Fe_2(CO)_8P_2(C_6H_5)_4]$ has been described (W. Schweckendiek, German Patent 1,072,244 (Dec. 31, 1959)).

[11] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963); R. Poilblanc and M. Bigorgne, *Bull. soc. chim. France*, 1301 (1962).

TABLE III
INFRARED SPECTRA OF THE NICKEL AND IRON COMPLEXES

	Absorption bands in the carbonyl region, cm.$^{-1}$		
Compound	Solution	Halocarbon mulls	Other absorption bands,[d] cm.$^{-1}$
$[Ni_2(CO)_6P_2(C_6H_5)_4]$	2066 (s), 2042 (s), 2000 (vs)[a]	2065 (vs), 1999 (vs), 1985 (sh), 1961 (m), 1955 (m)	3065 (w), 3042 (w), 1585 (w), 1570 (w), 1483 (w), 1480 (sh), 1438 (s), 1432 (s), 1312 (w), 1182 (w), 1089 (m), 1073 (w), 1028 (w), 1002 (w), 978 (w), 922 (w), 750 (m), 742 (s), 703 (m), 694 (s), 501 (m), 484 (m), 472 (m), 440 (s), 432 (sh)
$[Ni_2(CO)_6P_2(CH_3)_4]$[b]	2072 (vs), 1992 (vs), 1947 (m)		2983 (w), 2915 (w), 1423 (m), 1293 (m), 1287 (m), 949 (s), 916 (w), 890 (s), 879 (s), 826 (w), 736 (m), 689 (m), 478 (sh), 453 (s)
$[Ni\{P(C_6H_5)_2\}(CO)_2]_2$	2032 (vs), 2003 (vs)[a]	2030 (vs), 2022 (vs), 2000 (vs), 1994 (vs), 1968 (w), 1963 (w)	3065 (w), 3045 (w), 1582 (w), 1568 (w), 1477 (m), 1431 (s), 1308 (w), 1277 (w), 1185 (m), 1162 (m), 1133 (m), 1104 (m), 1090 (m), 1071 (m), 1042 (w), 1030 (m), 1000 (m), 922 (w), 857 (sh), 852 (m), 752 (s), 744 (m), 728 (w), 695 (s), 566 (w), 521 (s), 484 (s), 468 (m), 446 (s), 438 (sh)
$[Fe_2(CO)_8P_2(CH_3)_4]$	2048 (s), 1981 (m), 1946 (vs)[a]	2054 (s), 2015 (m), 2005 (m), 1970 (sh), 1950 (vs, br)	3008 (w), 2928 (w), 1423 (m), 1414 (m), 1410 (m), 1298 (m), 1292 (m), 1170 (w), 1158 (w), 1048 (w), 948 (m), 878 (s), 862 (m), 827 (w), 748 (m), 726 (m), 696 (m), 616 (vs), 521 (m), 492 (m), 484 (m), 438 (w)
$[Fe\{P(CH_3)_2\}(CO)_3]_2$	2050 (s), 2010 (vs), 1977 (vs), 1962 (vs)[a]	2044 (s), 2000 (vs), 1966 (vs), 1920 (m)	2915 (w), 2848 (w), 1420 (w), 1298 (w), 1287 (m), 1279 (m), 968 (sh), 947 (m), 898 (m), 854 (w), 842 (w), 725 (m), 709 (m), 615 (s), 606 (s), 629 (s), 531 (m), 523 (sh), 493 (m), 465 (w)
$[Fe\{As(CH_3)_2\}(CO)_3]_2$	2043 (s), 2004 (vs), 1973 (vs), 1961 (vs)[a]	2040 (s), 1998 (vs), 1966 (vs), 1954 (vs), 1939 (vs), 1912 (s)	2925 (w), 1414 (s), 1267 (w), 1253 (w), 1246 (w), 907 (m), 859 (m), 632 (m), 617 (s), 608 (s), 590 (m), 572 (s), 528 (w), 520 (w), 492 (w), 458 (m)
$[FeBr\{P(CH_3)_2\}(CO)_3]_2$	2080 (vs), 2038 (vs), 2010 (s)[c]	2080 (vs), 2040 (vs), 2002 (vs)	1438 (m), 1423 (m), 1408 (m), 1297 (m), 1281 (m), 952 (s), 947 (s), 908 (vs), 848 (m), 838 (sh), 727 (m), 688 (m), 604 (vs), 574 (vs), 528 (m), 506 (m), 488 (m), 465 (m)
$[FeBr\{As(CH_3)_2\}(CO)_3]_2$	2072 (vs), 2054 (s), 2008 (s)[c]	2074 (vs), 2038 (vs), 2010 (sh), 1998 (vs)	1440 (m), 1408 (m), 1263 (w), 1248 (m), 1170 (w), 1155 (w), 975 (w), 909 (s), 860 (sh), 862 (vs), 812 (m), 724 (m), 609 (vs), 597 (vs), 567 (vs), 520 (m), 488 (m), 462 (m), 440 (w)
$[FeI\{As(CH_3)_2\}(CO)_3]_2$	2066 (vs), 2028 (vs), 2006 (vs)[c]	2068 (vs), 2030 (vs), 2018 (vs), 2002 (vs), 1988 (vs), 1975 (sh), 1953 (w)	1417 (sh), 1406 (m), 1263 (w), 1250 (m), 1170 (w), 910 (s), 867 (vs), 814 (m), 738 (sh), 724 (m), 608 (vs), 602 (vs), 596 (vs), 567 (s), 522 (m), 492 (m), 464 (m)

[a] Carbon disulfide. [b] Liquid film. [c] 1,2-Dichloroethane. [d] Nujol mull 400–1300 cm.$^{-1}$, halocarbon mull 1300–4000 cm.$^{-1}$.

are always resolved. $[Fe_2(CO)_8P_2(CH_3)_4]$ shows three carbonyl bands, as does $[Fe(CO)_4P(C_6H_5)_3]$,[12] and hence probably has a structure in which the biphosphine joins two trigonal bipyramidal iron tetracarbonyl residues by substitution at the axial positions. The nickel tricarbonyl complexes have three instead of the expected two carbonyl bands.[13]

The proton n.m.r. spectra of the complexes III are also consistent with the proposed structures. The metal resonances usually occur as doublets with splittings of *ca.* 1–5 c.p.s. In the complexes which show the larger splittings, there is also visible a weak but complex central absorption, which is due to the effect of phosphorus–phosphorus coupling. The separation between the outer peaks of the doublet is then equal to the sum of the two methyl–phosphorus coupling constants.[14] Similar spectra have recently been observed for some disubstituted complexes of metal carbonyls with tris(dimethylamino)phosphine.[15]

Phosphorus- and Arsenic-Bridged Complexes.—In

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[12] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

[13] J. Chatt and F. A. Hart, *ibid.*, 1378 (1960).

[14] The resolution of the peaks comprising the complex central absorption is too poor to allow calculation of the individual methyl–phosphorus and phosphorus–phosphorus coupling constants (R. K. Harris, private communication).

[15] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

TABLE IV

INFRARED SPECTRA OF THE GROUP VI METAL COMPLEXES

Compound	Absorption bands in the carbonyl region, cm.$^{-1}$ Soln. in 1,2-dichloroethane	Halocarbon mulls	Other absorption bands,[a] cm.$^{-1}$
$[Cr_2(CO)_{10}P_2(CH_3)_4]$	2071 (m), 2059 (vs), 1948 (vs, br)	2060 (s), 1952 (vs), 1920 (vs)	1422 (m), 1300 (m), 1292 (m), 946 (m), 880 (s), 858 (w), 828 (w), 738 (m), 725 (w), 686 (s), 672 (vs), 651 (vs), 554 (w), 542 (w), 466 (s)
$[Mo_2(CO)_{10}P_2(CH_3)_4]$	2082 (sh), 2074 (s), 1994 (m), 1956 (vs, br)	2065 (vs), 1992 (vs), 1940 (vs, br)	2985 (w), 2920 (w), 1418 (m), 1298 (s), 1292 (s), 1003 (w), 948 (m), 920 (w), 877 (s), 826 (w), 837 (m), 686 (m), 607 (vs), 582 (vs), 526 (w)
$[W_2(CO)_{10}P_2(CH_3)_4]$	2080 (sh), 2070 (m), 1946 (vs, br), 1926 (sh)	2068 (vs), 1984 (m), 1950 (sh), 1940 (vs), 1915 (vs)	2930 (w), 1418 (m), 1298 (m), 1289 (m), 1056 (w), 1009 (w), 945 (m), 877 (m), 824 (w), 738 (m), 724 (sh), 686 (m), 598 (s), 571 (s), 448 (w), 416 (w)
$[Cr_2(CO)_{10}As_2(CH_3)_4]$	2065 (m), 1980 (s), 1943 (vs)	2060 (s), 1994 (s), 1952 (vs), 1875 (sh)	1415 (m), 1270 (m), 1262 (m), 938 (w), 904 (m), 844 (s), 810 (w), 726 (m), 672 (vs), 652 (vs), 588 (m), 551 (m), 543 (m), 462 (s)
$[Cr\{P(CH_3)_2\}(CO)_4]_2$	2013 (vs), 1950 (vs)	2014 (s), 1950 (vs), 1928 (vs)	1426 (m), 1414 (m), 1303 (w), 1288 (m), 950 (m), 947 (sh), 894 (m), 848 (m), 733 (m), 713 (s), 676 (s), 643 (vs), 638 (vs), 628 (vs), 533 (w), 496 (m), 467 (m)
$[Mo\{P(CH_3)_2\}(CO)_4]_2$	2026 (s), 1957 (vs, br)	2068 (w), 2025 (s), 1961 (vs), 1920 (sh)	2928 (w), 1421 (w), 1412 (m), 1298 (w), 1283 (m), 952 (m), 891 (m), 845 (w), 731 (w), 707 (m), 609 (w), 582 (s), 558 (m), 494 (m), 459 (m), 423 (m)
$[W\{P(CH_3)_2\}(CO)_4]_2$	2024 (vs), 1946 (vs, br)	2068 (m), 2028 (s), 1946 (vs, br)	1423 (m), 1412 (m), 1300 (w), 1285 (m), 997 (w), 952 (m), 896 (m), 878 (w), 709 (m), 599 (m), 579 (s), 557 (m), 502 (w), 460 (m)
$[Mo\{As(CH_3)_2\}(CO)_4]_2$	2026 (vs), 1956 (vs, br)	2018 (vs), 1987 (m), 1978 (s), 1960 (vs), 1929 (vs)	2920 (w), 1418 (m), 1403 (w), 1267 (w), 1252 (w), 911 (m), 853 (m), 605 (sh), 597 (m), 581 (s), 567 (m), 560 (m), 502 (w), 462 (m), 433 (m), 416 (m)
$[W\{As(CH_3)_2\}(CO)_4]_2$	2023 (vs), 1948 (vs, br)	2014 (vs), 1982 (m), 1952 (vs), 1922 (vs)	2932 (w), 2920 (w), 1416 (w), 1401 (w), 1265 (w), 1252 (w), 912 (m), 859 (m), 675 (m), 610 (w), 596 (m), 578 (s), 558 (m), 510 (w), 463 (m), 447 (w)
$[Cr(CO)_4As_2(CH_3)_4]_m$	2004 (s), 1908 (vs), 1884 (sh)	2008 (vs), 1986 (sh), 1924 (vs), 1875 (vs), 1835 (m)	3010 (w), 2930 (w), 1418 (m), 1265 (m), 892 (m), 858 (s), 838 (sh), 678 (s), 648 (s), 640 (s), 599 (w), 581 (w), 556 (w), 492 (m)
$[Mo(CO)_4As_2(CH_3)_4]_m$	2018 (s), 1919 (vs, br), 1890 (sh)	2025 (s), 1938 (s), 1885 (vs)	2930 (w), 1415 (m), 1266 (m), 1020 (w), 973 (w), 943 (w), 896 (m), 859 (s), 841 (sh), 726 (m), 620 (s), 600 (m), 585 (vs), 539 (m), 475 (m), 450 (m), 427 (m)

[a] Nujol mull 400–1300 cm.$^{-1}$, halocarbon mull 1300–4000 cm.$^{-1}$.

general cyclic complexes are obtained from reactions carried out at higher temperatures or for longer periods than those in which the biphosphine or biarsine complexes are formed. The group VI metal carbonyls are particularly reluctant to form cyclic complexes and all attempts at their preparation in hydrocarbon solvents were unsuccessful. However, in diglyme, the zerovalent complexes (III) are formed at about 80–100° (pale yellow solutions) and the cyclic compounds at the reflux temperature, 160° (dark red solutions). Considerable deposition of metal also occurs at the higher temperature (particularly in the phosphine reactions) so that the reaction time cannot be indefinitely extended without considerable decrease in yield. The cyclic complexes are more highly colored (orange or red) than the corresponding zerovalent complexes and can usually be more readily sublimed under vacuum.

$[Ni\{P(C_6H_5)_2\}(CO)_2]_2$ (IV, M = Ni, R = C_6H_5) is obtained by heating $[Ni_2(CO)_6P_2(C_6H_5)_3]$ in mesitylene at 90–100° for several days. Attempts to prepare the corresponding methyl compound by heating $[Ni_2(CO)_6P_2(CH_3)_4]$ were unsuccessful, decomposition with blackening occurring even at slightly elevated temperatures. The $P_2(CH_3)_4$ complex, unlike $[Ni_2(CO)_6P_2(C_6H_5)_4]$, also did not undergo the desired reaction on irradiation with ultraviolet light.

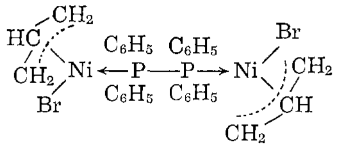
The infrared spectrum of $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$ shows two strong bands in the terminal carbonyl region, as expected for a tetrahedral or *cis* planar dicarbonyl complex. No absorption was observed in the bridging carbonyl region, and, since molecular weight measurements indicate a dimer, bridging must occur through phosphorus. The n.m.r. spectrum indicates V to be diamagnetic, at least in chloroform solution, while in the solid a magnetic moment corresponding to $\mu_{eff} = 1.02$ B.M. was found. The weak paramagnetism may be due at least in part to a small amount of surface oxidation of the crystals which are slightly air-sensitive. In any case, these observations indicate a considerable degree of electron pairing between the two formally univalent nickel atoms. The presence of metal–metal bonding is also consistent with the intense color and metallic sheen of the crystalline complex. The conversion of $[Ni_2(CO)_6P_2(C_6H_5)_4]$ into $[Ni\{P(C_6H_5)_2\}(CO)_2]_2$ thus appears to be an internal valency disproportionation reaction, nickel being oxidized from zero- to univalent and the ligand reduced from the neutral to the anionic state.

Both tetramethylbiphosphine and tetramethylbiarsine react with iron pentacarbonyl under suitable conditions to give tricarbonyl complexes, $[Fe\{E(CH_3)_2\}(CO)_3]_2$ (IV, M = Fe, R = CH_3, E = P, As), which are analogous to well-known sulfur-bridged complexes $[Fe(SR)(CO)_3]_2$.[16] A recent X-ray structure determination has shown that $[Fe(SC_2H_5)(CO)_3]_2$ has a folded structure, in which it has been proposed that a bent metal–metal bond occupies the vacant octahedral positions of the iron atoms.[5a] The infrared spectra of $[Fe\{E(CH_3)_2\}(CO)_3]$ in the region typical of carbonyl stretching vibrations (Table III) are very similar to those of $[Fe(SR)(CO)_3]_2$, indicating that the phosphorus and arsenic complexes also have a folded structure.[17] The n.m.r. spectra of $[Fe\{E(CH_3)_2\}(CO)_3]_2$ show two different methyl resonances of equal intensity, the number of resonances being consistent with the proposal of a folded structure. Thus, one of the two methyl groups attached to each of the bridging E atoms projects on the same side of E as the vacant octahedral position, while the second methyl group projects away from this vacant position. Two environments are therefore available for the methyl groups,[18] and, when E = As, two singlets are observed, and, when E = P, two triplets. The triplet pattern in cyclic complexes of this type is attributed to relatively strong phosphorus–phosphorus coupling,[3] and it is interesting to note that the pattern is not noticeably affected by folding the four-membered ring.

The bridged complexes of the group VI metals (IV, M = Cr, Mo, W) have a structure in which folding is not expected since the metals are each surrounded by six ligands in octahedral array. The metal–metal bond therefore lies in the plane of the ring and those properties of the complexes which are determined by geometry should be similar to those of $[Mn\{E(CH_3)_2\}(CO)_4]_2$.[2] In agreement with this, the n.m.r. spectra of these compounds show a single methyl resonance consistent with a symmetrical structure in which all the methyl groups are equivalent. The methyl resonance in $[M\{P(CH_3)_2\}(CO)_4]_2$ is a doublet (M = Cr) or a doublet with two weak central peaks (M = Mo, W). This is surprising in view of our previous experience with transition metal complexes containing rings of this type in which the methyl resonance has always been a 1:2:1 triplet.[1,3,4] The conditions for triplet formation were discussed in an earlier paper[3] and the absence of triplets here suggests that either (a) J_{HP} is large or (b) J_{PP} is unusually small. However, J_{HP} was found to be 10.0 c.p.s. in $[Cr\{P(CH_3)_2\}(CO)_4]_2$, a not unusually large value.[19] If the alternative (b) is accepted, it is not immediately obvious why J_{PP} is smaller than in, say, $[Mn\{P(CH_3)_2\}(CO)_4]_2$, which has a triplet methyl resonance.[2]

The infrared spectra (Table IV) of $[M\{E(CH_3)_2\}(CO)_4]_2$ (M = Cr, Mo, W) show two strong bands in the carbonyl region, one sharp at about 2020 cm.$^{-1}$ and the other broad at about 1950 cm.$^{-1}$, instead of the four bands expected for a *cis*-$[ML_2(CO)_4]$ complex.[11,20] The 1950 cm.$^{-1}$ band is presumably due to the accidental superposition of three out of the four predicted bands. A similar superposition was observed in the spectra of $[Mn(ER_2)(CO)_4]_2$ (E = P, As; R = CH_3, C_6H_5), where only three of the expected four bands were resolved.[2]

Some Reactions of the Complexes.—$[Ni_2(CO)_6P_2(C_6H_5)_4]$ reacts with allyl bromide to give a dark red complex which, by analysis and by analogy with the corresponding reaction of $[Ni(CO)_3\{P(C_6H_5)_3\}]$,[21] has the structure V. The infrared spectrum of V confirmed the absence of carbonyl groups, but the extreme air sensitivity of the complex, especially in solution, prevented reliable measurements of molecular weight and n.m.r. spectrum being obtained. $[Ni_2(CO)_6P_2(CH_3)_4]$ reacted similarly to give a dark red very readily oxidized complex, which was not fully characterized.



V

The complexes $[Fe\{E(CH_3)_2\}(CO)_3]_2$ absorb a molecule of bromine or iodine to give orange or red crystalline compounds of general formula $[FeX\{E(CH_3)_2\}(CO)_3]_2$ (E = P, As; X = Br, I). In these reactions, the halogens presumably interact with the electrons of the metal–metal bond and do not attack the heterocyclic ring. The resulting E-bridged complexes therefore probably have a structure in which two octahedral iron atoms are joined by an edge. Complexes of this

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(16) (a) W. Hieber and C. Scharfenberg, *Chem. Ber.*, **73**, 1012 (1940); S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, 3890 (1960); (b) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

(17) Chatt and Thornton have independently reached a similar conclusion (ref. 6) from infrared and dipole moment data.

(18) In one of the isomers of $[Fe(SCH_3)(CO)_3]_2$, both methyl groups have the same environment, while in the other they have different environments: R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

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(21) R. F. Heck, J. C. W. Chien, and D. S. Breslow, *Chem. Ind.* (London), 986 (1961).

type may exist in five isomeric forms, depending on the relative positions of the halogen atoms and carbonyl groups. However, only in the two isomers in which the halogen atoms occupy mutually *trans* apical or equatorial positions on the respective iron atoms can all the methyl groups have equivalent environments, as indicated by the single methyl resonances observed in the n.m.r. spectra. The infrared spectra of the complexes show three carbonyl stretching vibrations and do not help in distinguishing between the two isomers.

It was recently reported that $Fe(CO)_5$ reacts with $(CF_3)_2PI$ to give a dark red crystalline complex $[FeI\{P(CF_3)_2\}(CO)_3]_2$.[22] It is possible that this complex has a structure analogous to $[FeX\{E(CH_3)_2\}(CO)_3]_2$.

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Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. VII.[1] Complexes Derived from Iron Dicarbonyl Dinitrosyl

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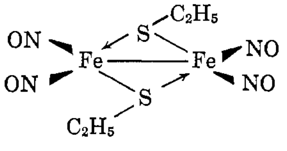
The reactions of R_4E_2 ($E = P$, $R = CH_3$, C_6H_5; $E = As$, $R = CH_3$) with $[Fe(CO)_2(NO)_2]$ yield the dark red E-bridged complexes, $[Fe(ER_2)(NO)_2]_2$. The tetramethylbiphosphine complexes, $[Fe_2(CO)_2\{P_2(CH_3)_4\}(NO)_4]$ and $[Fe_2\{P_2(CH_3)_4\}_2(NO)_4]$, can also be prepared. $Hg[Fe(CO)_3NO]_2$ reacts with R_4E_2 to give mixtures of complexes, most of which are better prepared by other routes.

Our previous investigations in this series[1] have yielded a number of phosphorus- and arsenic-bridged dimeric complexes of metals of the first transition series. The ligands, other than those forming the bridge, have usually been carbon monoxide and/or cyclopentadienyl. In this paper we report bridged complexes of iron which contain nitric oxide as a terminal ligand.

Sulfur-bridged nitrosyl complexes of iron have been known for some time[2] and the structure of Roussin's red ethyl ester $[Fe(SC_2H_5)(NO)_2]_2$ (I) has been determined.[3] The iron atoms were found to have approximately tetrahedral coordination and the ring to be a planar rhombus. The ethyl groups are *trans* with respect to each other. The only analogous previously known complex containing a bridging group V element is $[Fe(NH)(NO)_2]_2$.[4] This compound has been shown to contain bridging imino groups, but the geometry of the molecule has not been established with certainty and the ring may be folded, as suggested for the corresponding carbonyl complex, $[Fe(NH)(CO)_3]_2$, which has a relatively high dipole moment (3.3 D.).



I

Attempts to prepare phosphorus- and arsenic-bridged nitrosyl complexes by displacement of carbon monoxide from a suitable carbonyl complex (for example, $[Fe\{P(CH_3)_2\}(CO)_3]_2$[1]) by nitric oxide were not successful. We have therefore investigated the reactions of P_2R_4 ($R = CH_3$, C_6H_5) and of $As_2(CH_3)_4$ with iron dicarbonyl dinitrosyl and find that the formation of bridged complexes occurs under conditions similar to those found in analogous metal carbonyl reactions.[1]

Experimental

Microanalyses and molecular weight determinations were by Schwarzkopf Microanalytical Laboratories. Infrared spectra were measured on a Beckman IR-9 spectrophotometer using Nujol (400–1300 cm.$^{-1}$) and halocarbon (1300–4000 cm.$^{-1}$) mulls. Proton n.m.r. spectra were obtained with a Varian Associates A-60 spectrometer, using tetramethylsilane as an internal standard. Unless otherwise stated, the compounds gave sharp spectra, methyl resonances being observed in the range τ 7.7–8.4. Melting points were determined in evacuated capillaries and are uncorrected.

The biphosphine and biarsine ligands,[5] $[Fe(CO)_2(NO)_2]$, and $Hg[Fe(CO)_3NO]_2$[6] were prepared by previously described methods. All operations except the manipulation of the solid complexes were carried out under nitrogen. Merck acid-washed alumina was used for chromatographic purifications.

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