Table III

Analysis of Residue after Extraction of Filtrate from Reaction between KCN and $K_2[Ni(CN)_4]$ (Molar ratio 2:1)

Oxidation no. of Ni	Ni, %	CN, %	K, %	Atomic ratios K/CN	Atomic ratios CN/Ni	Empirical formula
0.05	18.50 ± 0.12	32.07 ± 0.21	....	..	3.92	
0.02	18.48 ± 0.02	32.54 ± 0.30	48.83 ± 0.32	3.96	3.97	$K_{3.96}Ni(CN)_{3.97}$

Table IV

Analysis of Residue after Extraction of Filtrate from Reaction between Ni, $K_2[Ni(CN)_4]$ and KCN (Molar ratios 1:14)

Oxidation no. of Ni	Ni, %	CN, %	K, %	Atomic ratios CN/Ni	Atomic ratios K/Ni	Empirical formula
1.07	21.23 ± 0.09	....	....	..	..	....
1.07	21.60 ± .02	36.71 ± .43	41.49 ± .13	3.84	2.88	$K_{2.88}Ni(CN)_{3.84}$
1.16	21.61 ± .00	37.56 ± .52	42.30 ± .21	3.93	2.93	$K_{2.93}Ni(CN)_{3.93}$

Another novel reaction is the one at 450–480° between nickel, potassium tetracyanonickelate(II) and potassium cyanide in the molar ratios 1:1:4. As the data of Table IV indicate, the lower valent nickel complex obtained from this reaction is potassium tetracyanonickelate(I), $K_3[Ni(CN)_4]$. This ox-blood red substance was isolated in 50–80% yield. It would be expected that this compound would be paramagnetic, with a spin-only moment of about 1.73 Bohr magnetons corresponding to one unpaired electron. Our product was paramagnetic, but the moment found varied in the range of 2.98–3.32 Bohr magnetons. No definite explanation can be offered for the high moment obtained, but it is conceivable that traces of elementary nickel, which is ferromagnetic, were present in the product. The fact that $K_3[Ni(CN)_4]$ is stable at 480°, whereas $K_4[Ni_2(CN)_6]$ undergoes disproportionation, strongly suggests that it is the material which contaminates the $K_4[Ni(CN)_4]$ formed in the reaction between nickel, mercury(II) cyanide and potassium cyanide.

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Organic Derivatives of Chromium, Molybdenum and Tungsten Carbonyls

By Thomas A. Magee, Clifford N. Matthews, Tze Seng Wang and John H. Wotiz

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The reaction of the Group VIB metal hexacarbonyls and arene–metal tricarbonyls with trivalent Group VA ligands has been studied. Fifteen compounds described by the generic formula $(R_3A)_xM(CO)_{6-x}$ have been prepared. Correlations have been drawn between the position of the metal carbonyl stretching frequency in the infrared spectrum and the number and type of the substituting ligand.

We have previously reported[1] the preparation of compounds formed by the reaction of trivalent Group VA compounds (such as tertiary phosphines and phosphites) with carbonyl compounds of Group VIB metals. The products, obtained in high yield, were stable, non-volatile, monomeric compounds described by the generic formula $(R_3A)_xM(CO)_{6-x}$ where R_3A is a trialkyl or triaryl phosphine, phosphite, arsine or stibine; M is chromium, molybdenum or tungsten; and x is 1, 2 or 3, depending on the substituting ligand and the reaction conditions employed. We now wish to describe some additional compounds of this type, together with details concerning the preparation and infrared spectra of all of the reported compounds.

Until recent years the only substituted carbonyl compounds of the Group VIB metals which had been reported were those in which nitrogen served as the donor atom.[2] This is in contrast with other transition elements, particularly those of Group VIII, for which a variety of compounds containing other donor atoms has been described [*e.g.*, bis-(triphenylphosphine)-nickel dicarbonyl[3] and triphenylphosphinemanganese tetracarbonyl[4]]. However, in addition to our earlier report,[1] several investigators recently have described substituted carbonyl compounds of the Group VIB metals in which the ligand donor atoms are phosphorus, arsenic or antimony.[5-11]

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The fifteen compounds prepared in the present investigation are listed in Table I. The general method for their preparation consisted of heating the reactants in diglyme (bis-2-methoxyethyl ether) at the reflux temperature until, in the case of the metal hexacarbonyls, all of the hexacarbonyl had been consumed. Filtration of the cooled reaction mixture gave clear solutions whose color was dependent on the metal involved. The products were obtained by removal of the solvent by distillation under reduced pressure. When the product was solid, purification was effected by repeated recrystallizations from a mixture of chloroform and ethanol.

In the case of the metal hexacarbonyls, either one or two of the carbon monoxide groups were displaced by the substituting ligand through reactions of the type

$$x\text{R}_3\text{A} + \text{M(CO)}_6 \xrightarrow[160-165^\circ]{\text{diglyme}} (\text{R}_3\text{A})_x\text{M(CO)}_{6-x} + x\text{CO}$$

The magnitude of x was dependent primarily on the stoichiometry of the reaction and, to a lesser extent, on the ligand involved and the reaction time. The disubstituted compounds seem to be the preferred derivatives of $Cr(CO)_6$. They were formed in each instance in which an excess of the displacing ligand was used. In addition, both the mono- and the tris-triphenylphosphite compounds (VII and IX) underwent disproportionation to the bis compound VIII on continued heating in solution. In the case of XI, a derivative of $Mo(CO)_6$, three of the carbon monoxide groups were displaced. This was the only example observed of direct displacement of three carbon monoxide groups by other than an aromatic ring.

With arene–chromium tricarbonyls, displacement of the aromatic ring by three ligand molecules occurred

$$\text{C}_6\text{H}_6\text{Cr(CO)}_3 + 3\text{R}_3\text{A} \xrightarrow[160-165^\circ]{\text{diglyme}} (\text{R}_3\text{A})_3\text{Cr(CO)}_3 + \text{C}_6\text{H}_6$$

Whiting[9] has reported similar results while other investigators[7,8] have prepared analogous compounds by similar reactions with cycloheptatriene derivatives of the metal hexacarbonyls.

Infrared Spectra.—The infrared spectra of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ have been reported previously.[12-14] In the gas phase a strong sharp band at 2000 cm.$^{-1}$ and a weak band at 1965 cm.$^{-1}$ were observed in the spectrum of $Cr(CO)_6$. Since the hexacarbonyl is a symmetrical molecule, only one band in the carbonyl stretching region would be predicted. The source of the additional weak band at 1965 cm.$^{-1}$ has been the subject of some speculation, although a generally accepted explanation has yet to be advanced. In the present investigation the spectra of carbon tetrachloride solutions of the three hexacarbonyls contained only

TABLE I

		Physical form	M.p., °C.[a]	Yield Crude	Yield Pure	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chromium Calcd.	Chromium Found	Phosphorus Calcd.	Phosphorus Found	M. wt. Calcd.	M. wt. Found
I	$(C_6H_5)_3PCr(CO)_5$	Pale yel. crystals	127–128	84	31	60.8	60.8	3.3	3.3	11.5	11.3	6.8	6.8	454	458
II	$[(C_6H_5)_3P]_2Cr(CO)_4$	Yel. powd.	250–252	36	12	69.8	68.5	4.4	4.4	7.6	7.8	9.0	9.2		
III	$(C_6H_5)_3PMo(CO)_5$	Wh. cryst.	138–139	91	52	55.5	55.6	3.0	3.0	[b]		6.2	5.7	498	495
IV	$(C_6H_5)_3PW(CO)_5$	Pale yel. crystals	146–147	84	42	47.2	47.0	2.6	2.7	[c]		5.3	5.0	586	593
V	$(C_6H_5)_3AsCr(CO)_5$	Yel. cryst.	135–135.5	96	55	55.4	55.4	3.0	3.0	10.5	9.3	[d]			
VI	$(C_6H_5)_3SbCr(CO)_5$	Yel. cryst.	147–149	83	43	50.7	50.6	2.8	2.7	9.5	9.3	[e]			
VII	$(C_6H_5O)_3PCr(CO)_5$	White cryst.	59.5–60	81	45	55.0	55.0	3.0	3.1	10.3	10.2	6.2	6.2	502	495
VIII	$[(C_6H_5O)_3P]_2Cr(CO)_4$	White cryst.	148–149	89	67	61.2	60.8	3.8	4.0	6.6	6.6	7.9	7.8		
IX	$[(C_6H_5O)_3P]_3Cr(CO)_3$	White cryst.	126–126.5	69	30	64.2	64.4	4.2	4.6	4.9	5.0	8.7	8.2		
X	$[(C_6H_5O)_3P]_2Mo(CO)_4$	White cryst.	110–111	97	32	58.0	57.7	3.7	3.7	[f]		7.5	7.2		
XI	$[(C_6H_5O)_3P]_3Mo(CO)_3$	White cryst.	142–143	59	11	61.6	61.4	4.1	3.7	[g]		8.4	8.7		
XII	$(C_4H_9)_3PCr(CO)_5$	Chartreuse liquid	[h]	100	..	51.8	51.5	6.9	7.2	13.2	12.9	7.9	7.5		
XIII	$(NCCH_2CH_2)_3PCr(CO)_5$	Wh. cryst.	136–137	62	23	43.7	43.8	3.1	3.0	13.5	13.3	8.1	7.7[i]		
XIV	$[(C_4H_9O)_3P]_2Cr(CO)_4$	Gr. liquid	[j]	105	..	50.6	51.3	8.1	9.2	7.8	8.2	9.3	9.4	664	660
XV	$[(C_4H_9O)_3P]_3Cr(CO)_3$	Gr. liquid	[k]	100	..	52.8	52.8	9.2	9.1	5.9	6.1	10.5	10.4		

[a] Melting points were taken using a mechanically stirred oil-bath. They are corrected. [b] % Molybdenum: calcd., 19.3; found, 19.5. [c] % Tungsten: calcd., 31.4; found, 31.5. [d] % Arsenic: calcd., 15.1; found, 14.9. [e] % Antimony: calcd., 22.3; found, 22.3. [f] % Molybdenum: calcd., 11.6; found, 10.9. [g] % Molybdenum: calcd., 8.6; found, 9.4. [h] Decomposes without distilling at 215° (0.05 mm.); n^{26}D 1.5417. [i] % Nitrogen: calcd., 10.9; found, 10.9. [j] Decomposes without distilling at 230° (0.1 mm.); n^{25}D 1.4893. [j] Decomposes without distilling at 230° (0.1 mm.).

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TABLE II[a]

	Compound	Wave numbers, cm.$^{-1}$				
I	$(C_6H_5)_3PCr(CO)_5$	2066m	1988w	1942vs		653s
II	$[(C_6H_5)_3P]_2Cr(CO)_4$	2012w	1949w	1897vs		653m
III	$(C_6H_5)_3PMo(CO)_5$	2074m	1988w	1946vs		
IV	$(C_6H_5)_3PW(CO)_5$	2075m	1980sh	1938vs		
V	$(C_6H_5)_3AsCr(CO)_5$	2066m	1988sh	1942vs		653m
VI	$(C_6H_5)_3SbCr(CO)_5$	2065m	1988sh	1943vs		653m
VII	$(C_6H_5O)_3PCr(CO)_5$	2080m	2000sh	1960vs		651m
VIII	$[(C_6H_5O)_3P]_2Cr(CO)_4$	2038w	1976w	1930vs		666m
IX	$[(C_6H_5O)_3P]_3Cr(CO)_3$	2008w		1912vs		647m
X	$[(C_6H_5O)_3P]_2Mo(CO)_4$	2055w	1990m	1941vs		
XI	$[(C_6H_5O)_3P]_3Mo(CO)_3$	2020m		1923vs		
XII	$(C_4H_9)_3PCr(CO)_5$	2062m		1934vs	1872w	655m
XIII	$(NCCH_2CH_2)_3PCr(CO)_5$	2063m	1988sh	1938vs		655m
XIV	$[(C_4H_9O)_3P]_2Cr(CO)_4$	2024w	1960w	1906vs	1872s	659w
XV	$[(C_4H_9O)_3P]_3Cr(CO)_3$	2028w	1961m	1908s	1876vs	659w
	$Cr(CO)_6$			1980vs		663
	$Mo(CO)_6$			1980vs		
	$W(CO)_6$			1980vs		

[a] vs = very strong; s = strong; w = weak; m = medium; sh = shoulder.

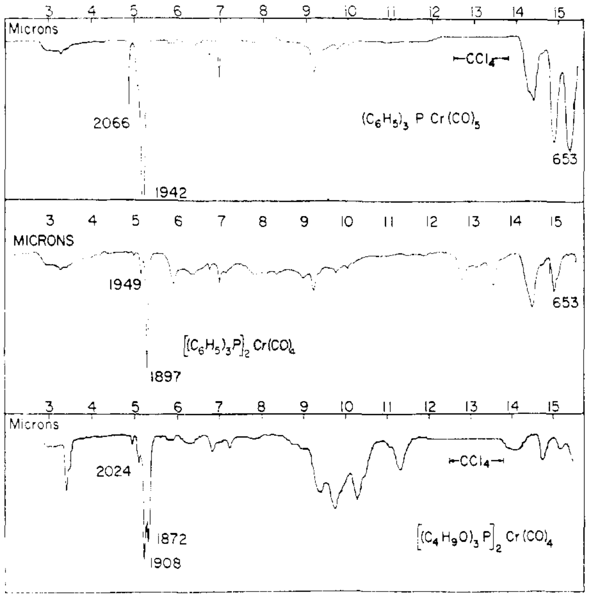

Fig. 1.—Infrared spectra of $(C_6H_5)_3PCr(CO)_5$, $[(C_6H_5)_3P]_2$-$Cr(CO)_4$ and $[(C_4H_9O)_3P]_2Cr(CO)_4$.

a strong sharp band at 1980 cm.$^{-1}$ which is attributable to the fundamental stretching vibration of the carbonyl group.

In compounds containing a single ligand molecule with phosphorus, arsenic or antimony as donor atom, the intense fundamental absorption band was observed in the 1960–1934 cm.$^{-1}$ region. In addition a sharp band of medium intensity occurred in the region of 2080 to 2060 cm.$^{-1}$ In the majority of cases another band appeared as a shoulder on the high frequency side of the intense fundamental (*cf.* Fig. 1). The general pattern of this type of complex was quite characteristic and was independent of the nature of the substituting ligand.

The disubstituted metal hexacarbonyls may exist in two stereoisomeric forms. Poilblanc and Bigorgne,[11] working with analogous derivatives of molybdenum hexacarbonyl, isolated both isomeric forms from their reaction mixture. They found that by heating either isomer for an extended period of time an equilibrium mixture was obtained which contained a *cis*:*trans* isomer ratio of 1:4. Hieber and Peterhans,[10] who have prepared II by heating triphenylphosphine with $Cr(CO)_6$ in the absence of a solvent, identified the product as the *trans* isomer on the basis of its infrared spectrum which contained only one intense carbonyl absorption band at 1893 cm.$^{-1}$. The sample of II prepared by us appeared to be identical with a sample of bis-(triphenylphosphine)-chromium tetracarbonyl kindly furnished us by Professor Hieber in regard to melting point, mixed melting point, infrared spectrum and X-ray powder diffraction pattern.[15] It was thus the *trans* isomer (Fig. 1). Among the other bis-substituted compounds, VIII and X apparently also possess the *trans* configuration. XIV however shows two strong absorption peaks in the metal carbonyl region (Fig. 1). Rigorous purification of the green liquid XIV was not possible since the material underwent decomposition during attempted distillations.

Similar results were observed in the infrared spectra of those compounds containing three ligand molecules with phosphorus as the donor atom. The triphenylphosphite derivatives IX and XI possess only one intense band in the region of the fundamental while with XV, in which tributylphosphite serves as ligand, two intense bands were observed. As in the case of the bis-substituted compounds, two geometrical isomers may exist. The formation of IX and XV from the arene–chromium tricarbonyl suggests that the three carbon monoxide groups are mutually *cis*,[8] although the possibility of rearrangement during the reaction cannot be excluded. The presence of two intense bands in the metal carbonyl stretching region in both the bis and tris compounds in which tributylphosphite is the ligand (XIV, XV) has not yet been explained.

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(15) An earlier sample prepared in this Laboratory contained two strong absorption bands at 1941 and 1890 cm.$^{-1}$, as well as two weak bands at 2062 and 2008 cm.$^{-1}$. It has not been conclusively established whether this represents the existence of the *cis* isomer or the presence of an impurity.

Factors affecting the values of C–O stretching frequencies in substituted metal carbonyls, such as the degree of multiple bonding in the metal–carbon bond and the influence on this of other ligands present in the molecule, have been discussed previously.[16–18] In the present study the positions of the C–O stretching frequencies were observed to be a function both of the number and the nature of the Group VA ligand molecule. A successive increase in the number of ligand molecules from zero to three produced a steady shift of the C–O absorption peaks toward lower frequencies, *e.g.*, $Cr(CO)_6$, VII, VIII, IX.

In those compounds containing equal numbers of phosphorus ligands the position of the C–O stretching frequency was affected by the nature of the organic substituent on the phosphorus. In order of decreasing carbonyl absorption frequency of their derivatives the organic groups may be listed in the sequence $C_6H_5O— > C_6H_5— > C_4H_9O— \overline{>} C_4H_9— = NCCH_2CH_2—$. Meriwether and Fiene,[18] who have reported similar shifts in the spectra of nickel carbonyl–phosphorus complexes, relate the changes in position of the absorption bands to the ability of the ligand molecules to accept back donation of electrons from the metal, thus forming partial double bonds, rather than to their inherent basicity. In general our results were in agreement with theirs, although the shifts were of smaller magnitude.

Few conclusions could be drawn as to the effect of a change in the central metal atom on the carbonyl stretching frequency. For the series of mono-triphenylphosphine complexes, I, III and IV, the differences in the 2000 cm.$^{-1}$ region were slight and within the experimental limitations of the spectral determinations. With the bis-triphenylphosphite derivatives IX and XI there were, respectively, 11 and 12 cm.$^{-1}$ shifts toward higher frequency as the central metal atom was changed from chromium to molybdenum. This may be interpreted either as indicating that the inductive effects of the ligands are less significant due to the larger size of the metal atom or alternatively that molybdenum is less inclined toward back donation of electrons to the ligand donor atom than is chromium. The first explanation would seem to be the more probable.

In the 650 cm.$^{-1}$ region, however, there were definite differences in the spectra of derivatives of the three metals. The spectra of all of the chromium compounds possessed a band in the region of 666-643 cm.$^{-1}$; the spectra of the molybdenum and tungsten compounds were void of absorption in this region. Shufler, *et al.*,[12] in a study of $Cr(CO)_6$, reported a band at 668 cm.$^{-1}$ as being due either to a Cr-C stretching vibration or to a C–O bending vibration. The fact that these bands appeared only in the spectra of chromium compounds whereas the C–O stretching frequencies for compounds of all three metals appeared in the same region around 2000 cm.$^{-1}$ tends to support the assignment of the band around 650 cm.$^{-1}$ to a Cr–C stretching vibration.

It was of interest to note that the spectra of I, V and VI were essentially identical in the carbonyl stretching region, indicating that P, As and Sb are equivalent in their ligand donor properties. A similar conclusion was reached by Abel, Bennett and Wilkinson[8] in the case of tris-substituted compounds of the type $L_3Mo(CO)_3$ where L is a ligand molecule with a Group VA element as donor atom, *e.g.*, $(C_6H_5)_3P$.

Experimental

Preparation of Complexes.—Method A. Triphenylphosphine-chromium Pentacarbonyl.—A mixture of 52.6 g. (0.2 mole) of triphenylphosphine, 50 g. (0.23 mole) of chromium hexacarbonyl and 500 ml. of diglyme was heated to reflux for 4 hr. The hexacarbonyl, which sublimed into the condenser throughout the reaction, was returned to the reaction vessel intermittently by means of a copper wire ramrod. The reaction mixture was allowed to cool, filtered and the solvent removed by distillation under reduced pressure to give 76 g. (84%) of green-yellow crystals. These were recrystallized three times from a mixture of chloroform and ethanol. The resulting pale yellow crystals weighed 28 g. (31%) and melted at 127–128°.

Anal. Calcd. for $C_{23}H_{15}PCrO_5$: C, 60.8; H, 3.3; Cr, 11.5; P, 6.8; mol. wt., 454. Found: C, 60.8; H, 3.3; Cr, 11.3; P, 6.8; mol. wt., 458.

Method B. Tris-triphenylphosphite-chromium Tricarbonyl.—The reaction of 27 g. (0.1 mole) of durene-chromium tricarbonyl and 310 g. (1.0 mole) of triphenylphosphite was carried out by heating the mixture at 240° for 1.5 hr., during which time durene was observed to sublime into the condenser. The green liquid reaction product was dissolved in chloroform, filtered and placed in an evaporating dish. After the chloroform had evaporated, the excess triphenylphosphite was decanted. Filtration of the residue yielded 74 g. (69%) of green tinted white crystals. Two recrystallizations from chloroform–ethanol gave 32 g. (30%) of white crystals, m.p. 126–126.5°. These were sensitive to light and underwent slow decomposition unless stored in the dark.

Anal. Calcd. for $C_{57}H_{45}P_3CrO_{12}$: C, 64.2; H, 4.2; Cr, 4.9; P, 8.7. Found: C, 64.4; H, 4.6; Cr, 5.0; P, 8.2.

Durene-chromium tricarbonyl was prepared by the method of Whiting,[9] *et al.*, in 53% crude yield. Two recrystallizations from chloroform–ethanol gave 43% of bright yellow crystals, m.p. 98–99°.

Anal. Calcd. for $C_{13}H_{14}CrO_3$: C, 57.8; H, 5.2; Cr, 19.2. Found: C, 57.8; H, 5.3; Cr, 18.8.

Infrared Spectra.—The spectra of 0.025 *M* solutions of these compounds were obtained on a Perkin-Elmer Model 21 recording spectrophotometer employing a cell thickness of 0.1 mm. For frequency values in the region 5000 to 1350 cm.$^{-1}$, carbon tetrachloride was used as the solvent; for those from 1350 to 640 cm.$^{-1}$, carbon disulfide. Because tris-(2-cyanoethyl)-phosphine-chromium pentacarbonyl (XIII) was not sufficiently soluble in these solvents, its spectrum was obtained in a tetrahydrofuran solution. The pertinent bands of the absorption spectra are listed in Table II.

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