reactions with solutions of $Na^+(C_{12}H_{10})\cdot^-$. The methylation of $(CH_3)_3B_3N_3(CH_3)H_2$ in the presence of $Na^+(C_{12}H_{10})\cdot^-$ indicates that an alkali metal borazine derivative has been formed. The absence of hydrogen evolution in the reaction of the B-methylborazine with $Na^+(C_{12}H_{10})\cdot^-$ suggests that the biphenylide ion acts as a base removing a proton from the borazine to give an anion (eq 4) which can be subsequently alkylated

$$C_{12}H_{10}\cdot^- + (CH_3)_3B_3N_3(CH_3)H_2 \longrightarrow C_{12}H_{11}\cdot + (CH_3)_3B_3N_3(CH_3)H^- \quad (4)$$

$$(CH_3)_3B_3N_3(CH_3)H^- + CH_3I \rightleftharpoons (CH_3)_3B_3N_3(CH_3)_2H + I^- \quad (5)$$

(eq 5). The red color of the solution is attributed to the presence of a carbanion formed by the reaction of the biphenyl radical, formed according to eq 4, with excess $Na^+(C_{12}H_{10})\cdot^-$ (eq 6).[10] The equilibria rep-

$$C_{12}H_{11}\cdot + C_{12}H_{10}\cdot^- \rightleftharpoons C_{12}H_{11}^- + C_{12}H_{10} \quad (6)$$

resented by eq 4 and 6 must be reversible in the presence of substances that are easily reduced, as indicated by the isolation of coupled products when either $Mn(CO)_5Br$, $(C_6H_5)_3SnCl$, or $(C_6H_5)_2PCl$ was added to solutions of $Na^+(C_{12}H_{10})\cdot^-$ containing B-methylborazines. The isolation of $Mn_2(CO)_{10}$, $(C_6H_5)_6Sn_2$, and $(C_6H_5)_4P_2$, respectively, indicates that reduction occurs (eq 7) rather than the expected re-

$$2C_{12}H_{10}\cdot^- + 2MX \longrightarrow 2C_{12}H_{10} + MM + 2X^- \quad (7)$$
$$(MX = Mn(CO)_5Br, (C_6H_5)_3SnCl, (C_6H_5)_2PCl)$$

action of the borazine anion with halo compounds (*cf.* eq 5). The data presented here suggest that it is unlikely that a B-methylborazine radical anion is formed in these systems and are consistent with the fact that borazines of this type do not give a polarographic reduction wave, in contrast with the B-phenylborazines.[9]

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Low-Frequency Infrared Spectral Studies on Triphenylphosphine, -arsine, and -stibine Derivatives of Iron and Molybdenum Carbonyl Complexes

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Monosubstituted derivatives of iron carbonyl, $Fe(CO)_4\cdot L$, are expected[1] to have four possible configurations based on the position of L in trigonal-bipyramidal and rectangular-pyramidal structures of iron pentacarbonyl, $Fe(CO)_5$. Cotton and Parish made an attempt to study the configuration of monotriphenylphosphine iron tetracarbonyl, $Fe(CO)_4(C_6H_5)_3P$. On the basis of the number of carbonyl stretching vibrations observed for this monosubstituted iron carbonyl complex, they were able to conclude that $Fe(CO)_4\cdot L$ species are very probably trigonal bipyramidal and the model with the L in an axial position (C_{3v}) is strongly favored. An attempt has been made to establish the structure of $Fe(CO)_4\cdot L$ derivatives by analyzing the 700–200-cm^{-1} region. Triphenylphosphine, -arsine, and -stibine have been used as the substituting ligands (L). The structural configurations for the $Mo(CO)_5\cdot L$ and the $Fe(CO)_3\cdot 2L$ types of complexes are well established.[1,2] As an extension to the above studies, infrared spectra of $Mo(CO)_5\cdot L$ and $Fe(CO)_3\cdot 2L$ complexes using triphenylphosphine, -arsine, and -stibine ligands (L) have been recorded in the low-frequency region for a discussion of the metal-ligand (M–L) vibrations in the substituted iron and molybdenum carbonyl complexes.

Experimental Section

Iron and molybdenum carbonyls were purchased from Alfa Inorganics, Inc., and were used as such for preparing complexes. Reagent grade tetrahydrofuran from Fisher Chemicals was refluxed over lithium aluminum hydride and distilled. The middle fraction of the distillate was used as solvent. Triphenylphosphine (LP), -arsine (LA), and -stibine (LS) were obtained from K & K Laboratories and were dried under vacuum before use. All of the compounds were handled in a drybox flushed with nitrogen, and the reactions were carried out under a nitrogen atmosphere. The iron and molybdenum carbonyl complexes were prepared by the methods described in the literature,[3,4] and their compositions were confirmed by their melting points and elemental analyses. The infrared spectra of the complexes and the ligands were taken in the form of Nujol mulls supported on cesium iodide disks. A Perkin-Elmer 621 double-beam infrared spectrophotometer was used for recording the spectra.

Results and Discussion

The infrared spectral data of substituted iron and molybdenum carbonyl complexes have been summarized in Table I. The selection rules for stretching and deformation modes of vibration for possible configurations of the substituted metal carbonyls as derived by standard group theoretical methods[2,5] have been given in Table II. The C–M–C bending vibrations occur at frequencies below the range we have studied and therefore have not been considered in Table II. Low-frequency infrared spectra of the ligands LP, LA, and LS are well assigned[6] and can be nicely distinguished from the rest of the spectra.

Four possible structures have been proposed[1] for the $Fe(CO)_4\cdot L$ complexes derived from the trigonal-bipyramidal (TBP) and the rectangular-pyramidal (RP) configurations of iron pentacarbonylFe, $(CO)_5$.

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

[2] R. J. H. Clark, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **26**, 269 (1965).

[3] A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, **2**, 151 (1963).

[4] T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 204 (1965).

[5] F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, Inc., New York, N. Y., 1964, p 245.

[6] D. H. Brown, A. Mohammad, and D. W. A. Sharp, *Spectrochim. Acta*, **21**, 659 (1965).

TABLE I

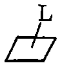
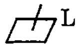
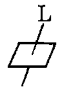
FAR-INFRARED SPECTRAL BANDS OF IRON AND MOLYBDENUM CARBONYLS AND THEIR PROBABLE ASSIGNMENTS

Complex[a,b]	ν(M–C), cm^{-1}	δ(M–C–O), cm^{-1}	Ligand vibrations,[c,d] cm^{-1}
$Fe(CO)_4 \cdot LP$	435 m, 480 m, sh, 490 m, sh	520 s, 530 s, sh, 610 s, sh, 620 s	240 w, 425 w, 505 m, 615 s
$Fe(CO)_4 \cdot LA$	445 m, sh, 472 m, 485 m	505 m, sh, 510 m, 607 s, sh, 615 s	(315, 325) m, (445, 460) m, 615 s
$Fe(CO)_4 \cdot LS$	435 m, 480 m, 488 m	510 m, 520 m, sh, 605 s, sh, 615 s	(268, 275), m, (443, 448) m, 615 m
$Fe(CO)_3 \cdot 2LP$	515 s	580 s, 630 s	240 w, 435 b, w, 500 m, 612 w
$Mo(CO)_5 \cdot LA$	375 s, 392 m, 400 m, sh	435 m, 580 s, 603 s, 670 m	(305, 315) m, sh, (470, 475) s, 615 w
$Mo(CO)_5 \cdot LS$	370 s, 390 m, 395 m, sh	425 m, 575 s, 603 s, 650 m	265 s, 445 s, 615 w

[a] LA = triphenylarsine, LP = triphenylphosphine, LS = triphenylstibine; s = strong, m = medium, w = weak, sh = shoulder. [b] Two very weak bands at ~405 and 425 cm^{-1} are observed in all the three monosubstituted complexes which seem to be the overtones or the combinations of the low-lying bending modes. [c] In addition to these ligand vibrations, two bands at ~720 cm^{-1} (out-of-plane hydrogen deformation) and ~680 cm^{-1} (out-of-plane ring deformation) were also observed in all of the complexes which are not listed in ref 6. [d] A very weak band at ~615 cm^{-1} is observed in the infrared spectra of pure ligands LA, LP, and LS (Whiffen's s band[6]); the strong bands at ~615 cm^{-1} in the complexes have been assumed to be due to combined δ(M–C–O) and the weak ligand vibration (Whiffen's s bands).

TABLE II

SPECIES OF VIBRATIONAL MODES OF SUBSTITUTED IRON AND MOLYBDENUM CARBONYLS[a]

Molecule	Configuration		Symmetry	Species of ν(M–C)	Species of δ(M–C–O)	Total no. of ir-active ν(M–C) and δ(M–C–O) bands expected	Species of ν(M–L)
$Fe(CO)_4 \cdot L$		I	C_{4v}	$\underline{A_1} + B_2 + \underline{E}$	$\underline{A_1} + A_2 + B_1 + B_2 + \underline{2E}$	5	$\underline{A_1}$
		II	C_s	$\underline{3A'} + \underline{A''}$	$\underline{4A'} + \underline{4A''}$	12	$\underline{A'}$
		III	C_{3v}	$\underline{2A_1} + \underline{E}$	$\underline{A_1} + A_2 + \underline{3E}$	7	$\underline{A_1}$
		IV	C_{2v}	$\underline{2A_1} + \underline{B_1} + \underline{B_2}$	$\underline{2A_1} + 2A_2 + \underline{2B_1} + \underline{2B_2}$	10	$\underline{A_1}$
$Fe(CO)_3 \cdot 2L$		V	D_{3h}	$A_1' + \underline{E'}$	$A_2' + \underline{A_2''} + \underline{E'} + E''$	3	$A_1' + \underline{A_2''}$
$Mo(CO)_5 \cdot L$		VI	C_{4v}	$2A_1 + B_1 + \underline{E}$	$\underline{A_1} + A_2 + B_1 + B_2 + \underline{3E}$	7	$\underline{A_1}$

[a] The infrared active vibrations are underlined.

Configuration I has been completely eliminated on the basis of the number of carbonyl stretching vibrations[1] and is expected to have five bands in the far-infrared region studied (Table II). These bands include the Fe–C stretching and the Fe–C–O in-plane and out-of-plane bending vibrations. Configurations II and IV having group symmetries C_s and C_{2v} demand more than ten bands in the low-frequency region, while configuration III (having a group symmetry C_{3v}) demands only seven bands in the same region.

In our studies we find seven well-defined bands in the spectra of the monosubstituted iron carbonyl complexes $Fe(CO)_4 \cdot L$, other than the normal ligand vibrations (Table I). The comparison of the number of bands in the low-frequency region with the number of expected ν(M–C) and δ(M–C–O) bands from simple group theoretical methods has been used as a basis for the molecular structure determination of metal carbonyls by several authors.[7–9] The possibility of accidental degeneracy and ν(M–C)–δ(M–C–O) coupling may exist but is ignored as a first approximation. If the bands observed are assumed to be due to ν(M–C) and δ(M–C–O) vibrations alone, then on the basis of the number of infrared-active bands expected for different configurations, $Fe(CO)_4 \cdot L$ seems to exist in configuration III. Therefore in Table I, we have given assignments for $Fe(CO)_4 \cdot L$ complexes taking for granted a trigonal-bipyramidal configuration (III) having a C_{3v} symmetry with the ligand L occupying one of the axial positions. The lower frequency bands are usually[10] assigned to the Fe–C stretching vibrations and the higher frequency bands to the Fe–C–O bending vibrations. The positions of the ν(Fe–C) and δ(Fe–C–O) bands have been found to change little with the change of the ligands LP, LA, and LS.

The disubstituted iron carbonyl complex $Fe(CO)_3 \cdot 2LP$ has been established[1] as having configuration V.

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(7) A. Loutellier and M. Bigorgne, *Bull. Soc. Chim. France*, 3186 (1965).
(8) G Bouquet and M. Bigorgne, *ibid.*, 433 (1963).
(9) M. A. Bannett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).
(10) D. M. Adams, *ibid.*, 1771 (1964).

For a symmetry of D_{3h}, there should be three ν(Fe–C) and δ(Fe–C–O) infrared-active bands (Table II). In Table I, the position of these three bands has been given. No extra band has been found for the Fe–P stretching mode.

The $Mo(CO)_5 \cdot L$ complexes with a C_{4v} symmetry are expected[3] to have seven bands due to the Mo–C stretching and the Mo–C–O bending vibrations (Table II). As can be seen from Table I, seven such bands have been located experimentally.

Metal–Ligand Vibrations.—In both of the cases of iron and molybdenum carbonyl complexes no metal–ligand vibrations have been observed in the region studied. Other authors[11–13] have reported metal–P and metal–As vibrations in the R_3P and R_3As–metal halide complexes in the region 200–550 cm^{-1} (R stands for alkyl or aryl groups). In these cases there is no definite relationship between the vibrational frequency and the atomic mass of the metal. The only information available to the best of the authors' knowledge in the literature about the metal–P or metal–As vibrations in the R_3P- or R_3As-substituted metal carbonyl complexes is that of ν(Ni–P) at ~192 cm^{-1} in $Ni(CO)_3 \cdot LP$[14] and at 262 cm^{-1} in $Ni(CO)_3 \cdot PF_3$[7] complexes and of ν(Ni–As) at 207 cm^{-1} in $Ni(CO)_3 \cdot LA$[8] complexes. No explanation has been given for the apparent lowering of the Ni–P and Ni–As frequencies when the nickel carbonyl complexes are compared with the nickel halide complexes. A complete absence of the metal–N vibration in $M(CO)_5 \cdot CH_3CN$ complexes has recently been reported by Farona, *et al.*[15] No Mo–P vibration has been reported in $Mo(CO)_5R_3P$ complexes in earlier studies.[16]

Various reasons can be suggested for the absence of the metal–ligand bands in the infrared region studied for the metal carbonyl complexes, $M(CO)_xL_y$. Although a possibility, it seems highly improbable that both the M–P and M–As bands might be accidentally degenerate with the ν(M–C), δ(M–C–O), or the ligand vibrations in both the iron and molybdenum carbonyl complexes. The surrounding carbonyls also would not seem to decrease the M–L force constants so as to lower the energy of the vibration below 200 cm^{-1}; on the other hand, because of the strongly polarizing nature of the carbonyls, the metal–ligand force constant must be greater for metal carbonyls than for the metal halide complexes. We therefore believe that the absence of the metal–ligand vibrations in the substituted iron and molybdenum carbonyl complexes is probably due to the ν(M–L)–ν(M–C) coupling which renders ν(M–L) unobservable in the infrared region studied.

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[11] G. E. Coates and C. Parkin, *J. Chem Soc.*, 421 (1963).

[12] A. D. Westland and L. Westland, *Can. J. Chem.*, **43**, 426 (1965).

[13] R. Rivest, S. Singh, and C. Abraham, *ibid.*, **45**, 3137, (1967).

[14] W. F. Edgell and M. P. Dunkle, *Inorg. Chem.*, **4**, 1629 (1965).

[15] N. F. Farona, J. G. Grasselli, and B. L. Ross, *Spectrochim. Acta*, **23A**, 1875 (1967).

[16] R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

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Polarographic Characterization of Monocyano- and Monothiocyanatochromium(III) Complexes

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Both sulfur- and nitrogen-bonded thiocyanate complexes of chromium(III) have been reported[1] in connection with inner-sphere reduction of $Co(en)_2(NCS)X^+$ and $FeNCS^{2+}$ by Cr^{2+}. Linkage isomers of cyanochromium(III) have been proposed[2] as intermediate and product of the reaction of $Co(NH_3)_5CN^{2+}$ with Cr^{2+}. We have studied the polarographic properties of $CrNCS^{2+}$, $CrSCN^{2+}$, and $CrCN^{2+}$. Experiments designed to detect $CrNC^{2+}$ were not successful.

Experimental Section

Analytical grade reagents and water triply distilled from quartz were employed. $CrSCN^{2+}$ was prepared by reduction of $FeNCS^{2+}$ with Cr^{2+} in cooled solution and separated from other chromium species (except for $CrNCS^{2+}$) on a Dowex 50W-X8 column as described by Haim and Sutin.[1] The stock solution was kept frozen. Fresh solutions were prepared for each set of experiments. Solutions of $CrSCN^{2+}$ always contained about 30% $CrNCS^{2+}$.

$CrNCS^{2+}$ was prepared by heating stoichiometric amounts of $Cr(ClO_4)_3$ and NaSCN in solution and separating Cr^{3+} products on a Dowex 50W-X8 column.[3] Another method employed for preparation of $CrNCS^{2+}$ was the Cr^{2+}-catalyzed reaction of $Cr(ClO_4)_3$ with NaSCN.[4] Each species was analyzed for chromium after oxidation by hydrogen peroxide in alkaline solution. Thiocyanate was determined polarographically[5] after hydrolysis of the complex in alkaline solution. $[Co(NH_3)_5CN](ClO_4)_2 \cdot 0.5H_2O$ was prepared by the method of Siebert.[6]

$CrCN^{2+}$ was prepared by reduction of $Co(NH_3)_5CN^{2+}$ by Cr^{2+} in acidic solution and separated from Cr^{3+} and Co^{2+} by slow elution from Dowex 50W-X8 by 0.01 *M* $HClO_4$ in 1 *M* $NaClO_4$.[1] The species separated has a visible spectrum identical with that reported by Espenson and Birk[2] for $CrCN^{2+}$. A band of intensity similar to that of the first visible band (527 mμ) was observed at approximately 265 mμ, immediately followed by a very intense charge-transfer band.

Spectrophotometric measurements were made using the Cary 14. A Sargent XV polarograph was used for recording current–voltage curves. The capillary employed had a drop time of 3.4 sec and flow rate of 2.05 mg/sec (in short circuit with sce and 64-cm Hg column). A modified Kalousek polarographic cell was used. Potentials are listed in volts *vs.* the saturated calomel electrode. For investigation of positive anodic waves, however, the mercurous sulfate reference electrode was used. Ionic strength was adjusted to 1 *M* with $NaClO_4$.

Results

$CrNCS^{2+}$.—In acidic solutions this complex exhibits a polarographic wave corresponding to the reduction

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[1] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).

[2] J. H. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965); J. P. Birk and J. H. Espenson, 154th Meeting National of the American Chemical Society, Chicago, Ill., Sept 1967, paper V18.

[3] E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952).

[4] J. H. Walsh and J. E. Earley, *Inorg. Chem.*, **3**, 343 (1964).

[5] SCN^- exhibits an anodic wave corresponding to formation of a complex with Hg^{2+}: I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, **63**, 1405 (1941).

[6] H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).