report of its preparation has been found.[17] The unusual property of some anhydrous metal nitrates, relatively high volatility,[45,46] was not observed in this research with this compound. The absence of volatility may be due simply to thermal instability. The infrared spectrum of mercury(I) nitrate indicates that the nitrate group is coordinated. The frequencies and assignments are reported in Table III. The assignments are made on the basis of the nitrate group having C_{2v} symmetry which has been found for other nitrato complexes.[47,48]

TABLE III
ASSIGNMENTS OF INFRARED FREQUENCIES OF MERCURY(I) NITRATE (cm^{-1})

ν_2	ν_6	ν_1	ν_4	ν_5	ν_3
1010 s	794 m	1308 sh	1515 w	707 m	748 m
995 s	790 s	1285 vs	1490 vs	700 m	740 s
960 s		1250 vs	1436 vs		732 m

The occurrence of more than one frequency under an assignment may be due to more than one type of nitrate group in the crystal structure[49] or a further lowering of the symmetry of the molecule as a whole.

The compounds of mercury(I) with the perchlorate and hexafluorosilicate anions have been discussed and are believed to be diaquo complexes. Weak complexes between mercury(I) and the nitrate and perchlorate anions in aqueous solution have been described.[7]

The reaction of mercury(I) with the tetraphenylborate anion led to disproportionation. If this mercury(I) compound did exist, it would probably be the diaquo complex and be soluble. Undoubtedly, the mercury(II) compound with this anion is insoluble since this anion is used to precipitate large cations, and hence disproportionation of mercury(I) results.

Conclusions.—The fact has been noted here and by other workers that the chemistry of mercury(I) is governed by the disproportionation reaction which greatly depends on the groups L attached to the ions.[9]

$$Hg + Hg^{II}L_m = Hg^{I}_2L_n + (m - n)L$$
$$K = 88 \pm 4\ (L = H_2O)^7$$

Mercury(I) compounds or complexes exist because the mercury(II) species is soluble, the mercury(I) species has a greater stability than the mercury(II) species, and the mercury(I) species is itself stable toward the heterolytic cleavage of the Hg–Hg bond resulting from the extreme lengthening and weakening of that bond by a strong Hg^{I}–L bond.

In view of the stability of the new mercury(I) complexes of triphenylphosphine oxide, di-*n*-propyl sulfoxide, diphenyl sulfoxide, dimethyl sulfoxide, and pyridine N-oxide, the interaction of such ions as nitrate and sulfate with mercury(I), and the existence of a moderate number of compounds containing mercury(I) and ligands from the lower part of the spectrochemical series, the tendency of mercury(I) to form complex ions is surprisingly favorable.

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The Photochemical Synthesis of Pentacarbonyliron(0) Derivatives

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Complexes of the type $Fe(CO)_4L$ (L = pyridine, α- and γ-picoline, piperidine) have been synthesized photochemically and characterized. CO-stretching frequencies of several other unstable complexes with nitrogen-containing ligands are reported and briefly discussed. Substitution always occurs in the axial position. Acetonitrile and acrylonitrile coordinate with the metal through the nitrogen rather than by π bonding through the CN group or double bond. A new complex di-μ-acrylonitrile-bis(tricarbonyliron(0)) with the formula $[(CO)_3FeCH_2{=}CH{-}CN]_2$ is described.

Introduction

As Hieber and co-workers have already reported,[1] iron pentacarbonyl reacts with various nitrogen-containing bases in a "basic reaction" with disproportionation of the zero-valent metal atom, forming ionic compounds. These ionic species are generally hexacoordinated bivalent cations and polynuclear anions of the general formula $[Fe(B)_6][(A)]$, where A is $[Fe(CO)_4]^{2-}$, $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$, or $[Fe_4(CO)_{13}]^{2-}$, and B is an amine or other nitrogen-containing base. The reaction mixture is heated while the ligand, B, is employed as solvent. Recently, it has been shown that

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[1] W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, **72**, 795 (1960)

the formation of a particular anion is dependent upon the base used[2] and the temperature of the reaction.

In contrast, the experimental work presented below indicates that ultraviolet irradiation of a mixture of pentacarbonyliron(0) with N-bases in a nonpolar solvent such as *n*-hexane gives monosubstituted tetracarbonyliron(0) complexes, of the formula $Fe(CO)_4L$. These observations suggest that the course of the reaction, *i.e.*, whether substitution or disproportionation occurs, depends upon the solvent used. Reactions carried out in polar solvents favor the formation of the ionic complexes, while those carried out in nonpolar solvents give substituted carbonyls. Similar results have been reported with the systems decacarbonyldimanganese–α,α'-dipyridyl and octacarbonyldicobalt–triphenylphosphine.[3,4]

Orgel and co-workers[5] have reported the complex $Fe(CO)_4CH_2{=}CH{-}CN$, in which the ligand is attached to the metal by the double bond. X-Ray studies have shown that the acrylonitrile has replaced the CO group in the equatorial position in pentacarbonyliron(0). Meanwhile, Weiss and co-workers[6] have prepared a large number of substituted tetracarbonyliron(0) complexes of the formula $Fe(CO)_4L$, where L represents an unsaturated ligand in an equatorial position. Using the systematics of the infrared frequencies in the CO-stretching region from the above studies,[5,6] we have strong evidence that in the present work, substitution with nitrogen-containing ligands occurs in an axial position through a coordinate covalent bond.

In reinvestigating the system pentacarbonyliron(0)–acrylonitrile,[5] we have succeeded in obtaining two additional complexes (Table III): (1) a volatile yellow oil in which acrylonitrile is attached to the metal by a coordinate bond through the nitrogen and (2) a bridged species di-μ-acrylonitrile-bis(tricarbonyliron(0)) with the formula $[Fe(CO)_3CH_2{=}CH{-}CN]_2$. It is believed that this compound is the first known metal carbonyl in which two acrylonitrile molecules serve as bridging ligands between two metal carbonyl groups.

Irradiation of a solution of the pentacarbonyliron(0) and thiophene in hexane yielded a very stable yellow compound of the formula $Fe(CO)_3C_4H_4Fe(CO)_3$, in which thiophene has undergone desulfurization. The same complex has already been reported by Hubel[7] and Kaesz[8] using different preparative methods.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 521 and were calibrated against the known peaks of polystyrene. Microanalyses and molecular weight determinations were carried out by Dr. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weights were obtained by vapor pressure measurements in benzene.

Tetracarbonyl(pyridine)iron(0).—In 300 ml of hexane were dissolved 1.5 ml (11.1 mmoles) of pentacarbonyliron(0) and 0.5 ml (6.2 mmoles) of pyridine (spectroscopic purity). Purified nitrogen was bubbled through the reaction mixture for 10 min during which time the residual air was driven out. The solution was then exposed to ultraviolet radiation from a GE AH6 mercury arc lamp for 4 hr. The resulting deep orange solution was filtered, and the solvent was removed by vacuum distillation at room temperature. The brown residue was sublimed twice at 35° yielding 94 mg of orange crystals. The compound is very soluble in organic solvents but insoluble in water. It is relatively stable in the solid state even in air but decomposes rather quickly in solution. It melts with decomposition at 65°.

Anal. Calcd for $Fe(CO)_4C_5H_5N$: Fe, 22.62; N, 5.67; C, 43.75; H, 2.02; mol wt, 246.85. Found: Fe, 22.57; N, 5.45; C, 43.85; H, 2.24; mol wt, 247.

The procedures for synthesizing the complexes $Fe(CO)_4$(α-picoline), $Fe(CO)_4$(γ-picoline), and $Fe(CO)_4$(piperidine) are essentially the same as that described above. The resulting air-stable yellow compounds have properties and infrared spectra in the CO-stretching region similar to the pyridine complex. This strongly suggests that the structures are the same, and elemental analysis was considered unnecessary.

In the case of the unstable complexes $Fe(CO)_4L$ (L = acetonitrile, benzonitrile, piperazine, lutidine, and pyrrolidine), only infrared spectra in the carbonyl-stretching region were recorded. Generally, solutions in *n*-hexane were made approximately 0.004 *M* in $Fe(CO)_5$ and 0.6 *M* in ligands and were irradiated for a suitable length of time in a water-cooled Pyrex-glass flask fitted with a bubbler. Infrared spectra were taken immediately in the CO-stretching region. This procedure allowed separation of the bands of unreacted $Fe(CO)_5$.

Di-μ-acrylonitrile-bis(tricarbonyliron(0)).—In 200 ml of hexane were dissolved 1.2 ml (9 mmoles) of pentacarbonyliron(0) and 0.7 ml (10.5 mmoles) of acrylonitrile. Purified nitrogen was bubbled through the solution for several minutes before it was exposed to ultraviolet radiation from a GE AH6 mercury arc lamp. After 45 min of irradiation, the reaction mixture was filtered to remove a considerable amount of brown precipitate which appeared during the irradiation. The solvent was removed by vacuum distillation at 30° leaving a yellow-brown residue. This was extracted with 10 ml of chloroform and sublimed twice under high vacuum at 40–45°. After the first 10 min a yellow oil appeared on the cooled finger and was removed before sublimation was continued. This oil consisted of a mixture of σ- and π-bonded tetracarbonyl(acrylonitrile)iron(0). The yellow crystals obtained from the yellow oil are stable in the solid state but decompose rather quickly in solution. The compound is soluble in organic solvents and decomposes without melting at 96°.

Anal. Calcd for $[Fe(CO)_3CH_2{=}CH{-}CN]_2$: Fe, 28.9; N, 7.26; C, 37.4; H, 1.6; mol wt, 385. Found: Fe, 28.4; N, 7.12; C, 38.1; H, 2.1; mol wt, 370.

The presence of acrylonitrile in the compound was proven by gas chromatography as follows: 20 mg of the substance was dissolved in acetone and chromatographed after exposing to sunlight for 1 hr. The observed peak corresponded to that of a known sample of acrylonitrile.

σ-(Acrylonitrile)tetracarbonyliron(0).—A solution of 0.5 ml of pentacarbonyliron(0) (3.5 mmoles) and 0.4 ml of freshly distilled acrylonitrile (16 mmoles) in 50 ml of hexane was saturated with purified nitrogen and cooled to −5°. After the irradiation with a GE AH6 lamp, the solvent was removed slowly at −10° under high vacuum. A yellow oil was sublimed from the brown residue onto the cold finger, which was cooled at −78° with methanol–Dry Ice. The oil was rather unstable and soluble in organic solvents. The infrared spectra recorded indicated no trace of the π-bonded complex.

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TABLE I

ISOLATED SUBSTITUTION PRODUCTS OF PENTACARBONYLIRON(0)

Compound	Yield, %	Decompn temp, °C	Color
$Fe(CO)_4$(pyridine)	7	65	Orange
$Fe(CO)_4$(α-picoline)	5	44	Orange
$Fe(CO)_4$(γ-picoline)	2	40	Yellow
$Fe(CO)_4$(piperidine)	3	39	Brown
$[Fe(CO)_3(\text{acrylonitrile})]_2$	11	96	Yellow
$Fe(CO)_4$(σ-acrylonitrile)	2	oil	Yellow

TABLE II

CARBONYL-STRETCHING FREQUENCIES FOR $Fe(CO)_4L$ MOLECULES

Ligand (L)	Medium	CO-stretching frequencies, cm^{-1}		
Triphenylphosphine[9]	Chloroform	2059 m	1978 m	1938 s
Methylisonitrile[9]	Chloroform	2072 m	1996 m	1967 s
Pyridine	n-Hexane	2055 m	1968 m	1942 s
α-Picoline	n-Hexane	2056 m	1966 m	1940 s
β-Picoline	n-Hexane	2055 m	1967 m	1941 s
γ-Picoline	n-Hexane	2057 m	1969 m	1941 s
Acetonitrile	n-Hexane	2064 m	1976 m	1959 s
Benzonitrile	n-Hexane	2064 m	1978 m	1960 s
2,6-Lutidine	n-Hexane	2056 m	1968 m	1942 s
Piperidine	n-Hexane	2049 m	1959 m	1930 s
Pyrrolidine	n-Hexane	2054 m	1964 m	1933 s
Quinoline	n-Hexane	2054 m	1964 m	1941 s

TABLE III

CARBONYL- AND CYANIDE-STRETCHING FREQUENCIES OF IRON CARBONYL COMPLEXES WITH ACRYLONITRILE

Compound	Medium	CO-stretching frequencies, cm^{-1}			
$Fe(CO)_4CH_2{=}CH{-}CN$	n-Hexane	2107 m	2046 m	2031 m	2010 m
$Fe(CO)_4NC{-}CH{=}CH_2$	n-Hexane	2063 m	1979 m	1961 s	
$[Fe(CO)_3CH_2{=}CH{-}CN]_2$	n-Hexane	2057 m	1994 s	1985 s	
	Potassium bromide	2054 m	1990 s	1954 s	
		CN-stretching frequencies cm^{-1}			
	Potassium bromide	2244 m	2218 m		

Discussion

It is generally accepted that the zero-valent oxidation state of the transition metals is stabilized by ligands capable of back-acceptance of some of the charge accumulated by the coordinative covalent metal–ligand bond into vacant p or d orbitals. As has been reported earlier, triphenylphosphine and the isocyanides with low-lying π orbitals are capable of accepting back some charge, forming rather stable mono- and disubstituted compounds. Since nitrogen has no available low-lying π orbitals, the stability of the resulting monosubstituted complexes $Fe(CO)_4L$ is decreased considerably. In fact, even at low temperatures, the complexes formed from the amines, *i.e.*, aniline and formamide, rapidly decompose to $Fe_3(CO)_{12}$ after a short period of irradiation. However, if one chooses pyridine or its derivatives as ligands, where the nitrogen atom is in an aromatic ring system with delocalized π orbitals, there is a possibility of transmission of some electron density through the donor atom to the system. The products isolated in this research (Table I) were indeed fairly stable even in air. In the case of benzonitrile and acetonitrile, infrared spectra of the complexes could be obtained, but it was impossible to isolate pure samples.

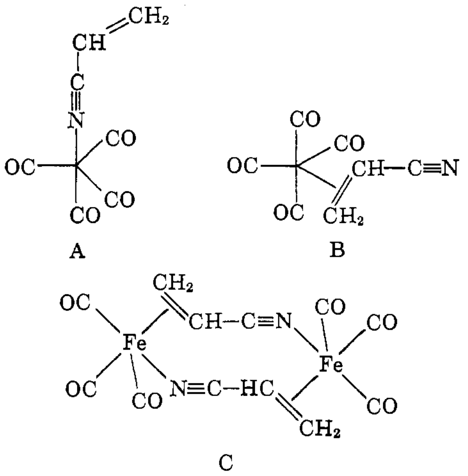

Figure 1.

As can be seen from Table II, infrared spectra in the CO-stretching region in n-hexane show three absorption bands similar to the spectra of $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_4CNR$ reported by Cotton and co-workers.[9] Assuming that no band has gone unresolved, this is strong evidence for C_{3v} symmetry which should result if the ligand replaces one CO group in an axial position of $Fe(CO)_5$. The frequencies for all these σ-bonded complexes in Table II are lower than those in the π-complexes with four infrared-active CO-stretching bands. Substantial evidence that acrylonitrile is bonded to the metal through the nitrogen by a coordinative covalent bond is shown by the excellent agreement with the frequencies of the complex with acetonitrile (Table III).

If one irradiates the system pentacarbonyliron–acrylonitrile for a considerably longer period of time and sublimes the residue at room temperature under high vacuum, infrared spectra taken in n-hexane show seven CO-stretching frequencies due to a mixture of σ- and π-(acrylonitrile)tetracarbonyliron(0) (Figure 1A and B). Finally, raising the sublimation temperature to 40°, we obtained the very stable complex di-μ-acrylonitrile-bis(tricarbonyliron(0)). We assume that in this compound two acrylonitrile molecules serve as bridging ligands between two $Fe(CO)_3$ groups, in which each acrylonitrile molecule is bonded to one Fe atom by a σ bond through the nitrogen and to the other Fe atom by a π bond through the double bond (Figure 1C). This structure is supported by the infrared spectrum in the CO-stretching region and also by nmr

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

spectra. If one of the Fe atoms were assumed to be coordinated with both σ-bonded nitrogens and the other with both π-bonding systems of the two acrylonitrile molecules, the observed infrared frequencies would be too high in the former case and too low in the latter case (Table III). The observed three CO-stretching frequencies are in fact just intermediate as expected for the suggested structure.

The nmr spectrum also supports the proposed structure showing a system of bands with a strong band 2.3 ppm downfield from $Si(CH_3)_4$. Detailed considerations of this molecule must await a more thorough structural investigation by X-ray analysis.

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The Crystal Structure of Trisilver Dinitrate Tris(acetylacetonato)nickelate(II) Monohydrate[1]

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The structure of trisilver dinitrate tris(acetylacetonato)nickelate(II) monohydrate, $AgNi(C_5H_7O_2)_3 \cdot 2AgNO_3 \cdot H_2O$, was determined by three-dimensional, single-crystal X-ray diffraction techniques. There are four molecules per unit cell of symmetry $P4_1$ with dimensions $a = b = 15.053 \pm 0.005$ A and $c = 10.800 \pm 0.007$ A. The compound may be considered to be a complex of silver with the tris(acetylacetonato)nickelate(II) ion. The silver ions are apparently bonded to the central carbon atom (the "active methylene") of one chelate ring and to the oxygen atom of an adjacent ring. The average distances for the interactions of the three nonequivalent silver ions are Ag–C = 2.34 ± 0.09 A and Ag–O = 2.46 ± 0.07 A. The nickel ion is octahedrally surrounded by oxygen atoms at an average distance of 2.04 ± 0.06 A and an average O–Ni–O bond angle of 90 ± 3°. Tris(acetylacetonato)nickelate(II) ions are held together by one of the silver ions in spiral chains parallel to the z axis. These spiral chains are in turn held together by the remaining silver ions through connecting nitrate groups. The magnetic moment of the nickel ion is 3.13 BM.

Introduction

A number of reports concerning the crystal structure of metal acetylacetonates and structures involving metal–olefin bonding have appeared in the literature. We have been interested in the various possible configurations of silver ions in metal–olefin complexes and assumed that $AgNi(acac)_3 \cdot 2AgNO_3 \cdot H_2O$ would be of this type. The silver ion appears to be directly bonded to the electron pair of the "active methylene" carbon, Ag–C = 2.34 A, and not to the adjacent carbon atoms, Ag–C = 2.81 A. This geometry suggests a situation similar to the platinum interactions with the "active methylene" carbon[2] of β-diketones. The silver–carbon interaction is probably predominantly ionic. The synthesis and physical properties of this compound and disilver perchlorate bis(acetylacetonato)copper(II) were brought to our attention by Professor Kline.[3] The structure of the copper complex will be described in a later article.

Experimental Section

Crystal.—Bis(acetylacetonato)nickel(II) was prepared by the addition of a solution of nickel(II) chloride to a mixture of water and 2,4-pentanedione containing enough ammonium hydroxide to make them miscible. The resulting crystals were then purified by recrystallization from hot toluene. The crystal structure of bis(acetylacetonato)nickel(II) has been reported[4] and shows that the molecules exist as trimers.

Trisilver dinitrate tris(acetylacetonato)nickelate(II) monohydrate was prepared by the addition of bis(acetylacetonato)nickel(II) to a 1.5 N aqueous solution of silver nitrate. The blue-green crystals of $AgNi(acac)_3 \cdot 2AgNO_3 \cdot H_2O$ were then recovered by filtration and appeared as elongated parallelepipeds. Crystals suitable for X-ray diffraction studies were difficult to obtain since the compound could not be recrystallized.

Anal. Calcd for blue-green complex: Ag, 39.43; Ni, 7.14; acac, 36.14. Found:[3] Ag, 39.08; Ni, 7.25; acac, 36.3.

A second compound of proposed formula $AgNi(acac)_3 \cdot AgNO_3 \cdot H_2O$ was obtained if 0.5 N aqueous solutions of silver nitrate was used. The crystals were blue.

Anal. Calcd for blue complex: Ag, 33.10; Ni, 9.01; acac, 45.61. Found:[3] Ag, 32.9; Ni, 9.11; acac, 46.7.

A single crystal of the blue-green di(silver nitrate) complex, with dimensions of 0.25 × 0.25 × 1.35 mm, $\mu R = 0.58$, was selected for X-ray measurements. The crystal was sealed in a Pyrex capillary to retard decomposition. Upon repeated exposure to light and X-rays, the crystal turned brown around the edges indicating some decomposition. Single crystals of the blue complex decomposed rapidly at room temperature upon exposure to X-rays, and no reliable intensity data were collected.

X-Ray Data.—All data used for intensity measurements were obtained at room temperature with the multiple film (three films) equiinclination Weissenberg technique. Reflections ($hk0$) to ($hk6$) were recorded using filtered copper radiation, $\lambda_{CuK\alpha}$ 1.54180. The intensities were visually estimated by comparison

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[1] This work was supported by a grant from the Robert A. Welch Foundation.

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