of C_2F_6 and an indefinite amount of nitrogen which had to be removed before use.

The fluorocarbon iminosulfur difluorides were prepared from SF_4 and NaSCN or the appropriate fluorocarbon nitriles.[13] Prepurification of SF_4, purchased as technical grade, lead to the need for less drastic conditions in their preparation.

In general the irradiation system was loaded to a given pressure and the amount of material was determined from a knowledge of the volume of the system. The composition of mixtures was determined on the assumption that no associative interactions were occurring at well below an atmosphere of pressure. These are reported in Tables I and II. In almost every instance what appeared to be short—up to 1 hr.—induction times were observed. Whether this was inherent in the photoreaction or a function of the sampling system was never completely ascertained. The residual gas in the reaction system, at the end of certain reactions, was purged of noncondensables and the condensables were separated by semipreparative vapor phase chromatography in order to obtain adequate amounts of pure samples of the various materials for an unambiguous identification.

NF_2SF_5 was identified by its molecular weight and n.m.r. and infrared spectra, which were identical with those previously reported.[8]

$NF_2CF_2CF_2NF_2$ was identified from its molecular weight (203) and its mass spectrum, which was most similar to that previously reported.[10] The structure was confirmed by its n.m.r. spectrum [CF_2 (39.9 p.p.m. triplet) and NF_2 (−92.4 p.p.m. broad band) with peaks of equal area] and its infrared spectrum which (in cm.$^{-1}$) is: 1295 (m), 1235 (vs), 1190 (ms), 1165 (s), 1140 (ms), 1065 (w), 975 (ms), 950 (s), 925 (vs), 865 (s), 765 (s).

NF_2CF_2CN was identified from its molecular weight (130), n.m.r. spectrum [CF_2 (14.9 p.p.m. triplet) and NF_2 (−103 p.p.m. broad band) with peaks of equal area], and its infrared spectrum, which is (in cm.$^{-1}$): 2240 (s), 1220 (vvs), 1130 (s), 990 (vs), 933 (vs), and a weak band at 705–695. *Anal.* Calcd.: C, 18.5; F, 58.4. Found: C, 18.3; F, 58.9. The following vapor pressure data were determined for this compound [T (°K.), p (mm.)]: (193°, 38), (200°, 65), (207°, 110), (214°, 182), (227°, 359), (229°, 392), (237°, 613), (238°, 690). Extrapolation of the log p_m *vs.* $1/T$ plot results in a normal boiling point of 241°K. or −32°C. The straight line relationship fits the equation log $p_{mm} = -1250/T + 8.05$. This relationship gives a heat of vaporization of 5740 cal./mole and a Trouton's constant of 23.4, implying some minor nonideal behavior. The mass spectrum which was obtained after the material was identified had the following characteristics (mass, ion, relative intensity): (76, CF_2CN, 100), (69, CF_3, 30), (23, CF, 23), (50, CF_2, 10), (90, CF_2N_2, 10), (83, CF_2N, 7), (45, CNF, 6), (33, NF, 5), (43, C_2F, 4), (52, NF_2, 4), (57, CFCN, 4).

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π-Complexes of Cyclopentadienylmanganese Tricarbonyl with Acrylonitrile and Butadiene

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When solutions of cyclopentadienylmanganese tricarbonyl and a ligand in pentane, hexane, or cyclohexane are exposed to ultraviolet radiation, both π[2] and σ[3,4] complexes can be synthesized depending on the nature of the ligand utilized.

If a ligand is used which contains two or more π-bonding groups or both σ-[5–8] and π-bonding groups in the same molecule, ambiguity exists about the type(s) of bonding to be expected. If a solution of $C_5H_5Mn(CO)_3$ in hexane is irradiated with ultraviolet light in the presence of acrylonitrile, it is possible to separate a complex with the formula $C_5H_5Mn(CO)_2CH_2{=}CHCN$ from the irradiation mixture by means of adsorption chromatography. The compound is relatively stable in the solid state but decomposes rather quickly in solution. Infrared and n.m.r. measurements show that the bonding to the substituted metal carbonyl utilizes the double bond of the acrylonitrile molecule. This is in interesting contrast to the bonding which occurs between acrylonitrile and manganese decacarbonyl in the complex $Mn_2(CO)_9CH_2CHCN$.[9]

Fischer and co-workers[2a] synthesized the complex $C_5H_5Mn(CO)C_4H_6$ by ultraviolet irradiation of a $C_5H_5Mn(CO)_3$–butadiene mixture. In this complex both π-bonding sites of butadiene are utilized. Indeed, irradiation of the $C_5H_5Mn(CO)_3$–butadiene mixture with a G.E. AH6 lamp for 3 hr. produced the same chelate complex, $C_5H_5Mn(CO)C_4H_6$, observed by Fischer and co-workers.[2a] However, irradiation under the same conditions, but for 30 min. only, yielded exclusively the complex $C_5H_5Mn(CO)_2C_4H_6$, in which only one of the π-bonding sites of butadiene has been utilized. This complex is an orange oil which decomposes slowly even under dry nitrogen into a compound whose formula is $[C_5H_5Mn(CO)_2]_2C_4H_6$. We believe this compound is the first known manganese metal carbonyl complex in which butadiene acts as a bridging ligand. Details of the preparations follow.

Experimental

(A) **$C_5H_5Mn(CO)_2CH_2CHCN$ (I).**—Cyclopentadienylmanganese tricarbonyl (500 mg., 2.56 mmoles) and 5 ml. (75 mmoles) of acrylonitrile were dissolved in 200 ml. of *n*-hexane. The solution was then exposed to ultraviolet radiation from a Hanovia Quartz burner (Type S-100) for 6 hr. in a reaction tube cooled by water. Purified nitrogen was bubbled through the solution before and during the irradiation. After 6 hr. the reaction mixture was filtered through a frit to remove small amounts of solid residue which appeared during the irradiation. The solvent was then removed by vacuum distillation. The residue was dissolved in a minimum amount of methanol (about 3–4 ml.) and adsorbed on an aluminum oxide column 10 cm. long and 1 cm. in diameter. The compounds were eluted with *n*-hexane. Elution time for the starting material, $C_5H_5Mn(CO)_3$, was very short but was approximately 4 hr. for the acrylonitrile derivative.

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[1] This work was supported by the United States Atomic Energy Commission under Contract No. AT-(40-1)-2434 and by the Petroleum Research Fund of the American Chemical Society.

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After the solvent had been removed by vacuum distillation the compound was recrystallized from *n*-hexane. The yield of fine yellow crystals was 10%. The complex is very soluble in polar organic solvents, fairly soluble in hexane and benzene, but insoluble in water. It decomposes at 110° without melting.

Anal. Calcd. for $C_5H_5Mn(CO)_2CH_2CHCN$ (I): C, 52.42; H, 3.52; Mn, 23.98; N, 6.12. Found: C, 51.21; H, 3.62; Mn, 23.59; N, 5.75.

(B) $C_5H_5Mn(CO)_2C_4H_6$ (II) and $[C_5H_5Mn(CO)_2]C_4H_6$ (III). Cyclopentadienylmanganese tricarbonyl (500 mg., 2.46 mmoles) was dissolved in 200 ml. of *n*-hexane into which purified butadiene was continuously bubbled. After 10 min., during which time the residual air was driven out, the solution was irradiated for 30 min. with ultraviolet light from a G.E. AH6 mercury lamp. The solution was then separated from minor solid residue by filtration under dry nitrogen and the solvent removed by vacuum distillation. The oily residue was dissolved in 5 ml. of hexane and adsorbed on an aluminum oxide column 30 cm. long and 2 cm. in diameter. Elution under dry nitrogen with *n*-hexane produced three distinct zones. The fastest moving one contained the starting material. Then came the monosubstituted product and finally a light yellow zone which moved very slowly. This last zone was identified as $[C_5H_5Mn(CO)_2]_2C_4H_6$. The second zone contained the unstable monosubstituted butadiene complex, $C_5H_5Mn(CO)_2C_4H_6$, which was characterized by comparing its infrared spectrum in hexane with those of other monosubstituted complexes (see Table I). Analysis for the more stable complex, $[C_5H_5Mn(CO)_2]_2C_4H_6$, yielded the following results.

Anal. Calcd.: C, 53.22; H, 3.97; Mn, 27.05. Found: C, 53.10; H, 4.20; Mn, 26.77.

Compound II is generally soluble in organic solvents but not in water. Compound II decomposes at 140° without melting; it can be recrystallized either from methanol or benzene as dark yellow plates or light yellow needles.

Discussion

There are four arguments which taken together indicate strongly that the acrylonitrile complex is bonded through the double bond rather than the lone pair of electrons on the nitrogen. These arguments are (1) the stability of the complex, (2) the CO stretching frequencies in the infrared, (3) the CN stretching frequencies in the infrared, and (4) the p.m.r. spectra. Detailed arguments follow.

In speaking of the zerovalent carbonyl derivatives of the transition metal elements, the concept of increased stability resulting from back donation of charge (from a filled metallic d orbital into vacant antibonding π orbitals of the ligand) is generally accepted. Experimental justification of this concept comes from the σ-bonded derivatives of $C_5H_5Mn(CO)_3$ reported by Strohmeier[3,4] relative to the ethylene and the butadiene complexes reported by Fischer.[2] The acrylonitrile derivative (I) reported here is quite stable, suggesting that the bonding is to the double bond with available π orbitals for back donation rather than to the nitrogen whose π orbitals are unavailable.

Quantitative rather than qualitative evidence for the π-bonded acrylonitrile complex structure comes from the infrared spectrum. Assuming C_s symmetry simple group theory predicts that both structures should have two bands, A′ and A″. Presumably the A′ band has the higher frequency (1996 cm.$^{-1}$ in hexane) and the A″ the lower (1939 cm.$^{-1}$). The observed intensities are approximately the same. However, Strohmeier, *et al.*,[10] in comparing the infrared frequencies of several derivatives of $C_5H_5Mn(CO)_3$ with nitrogen donors with the infrared frequencies of $C_5H_5Mn(CO)_3$ itself have noted a frequency decrease of approximately 90 cm.$^{-1}$. This is understandable when one compares the two most prominent structures for the bonding in a metal carbonyl bond shown below.

$$\underset{A}{M—C\equiv O} \leftrightarrow \underset{B}{M=C=O}$$

The nitrogen donor ligands are not able to accept back donation from the metal atom and hence tend to favor structure B with its implied lower CO stretching frequency. π-Bonding donors favor structure A and a higher CO stretching frequency.

The infrared frequencies of $C_5H_5Mn(CO)_3$ and a number of π- and σ-bonded complexes are compared in Table I. The shifts in the infrared frequencies from $C_5H_5Mn(CO)_3$ to the π-bonded ethylene and butadiene complexes are much smaller than for the σ-bonded complexes. This shift is least of all in the case of the acrylonitrile complex reported here and thereby gives strong quantitative evidence for a π-bonded complex. In connection with Table I, it should be noted that Fischer[2b] reported four bands for the ethylene derivative. On rerunning the infrared spectrum, we found that only two bands belong to this ethylene derivative. The other two bands result from the starting material, $C_5H_5Mn(CO)_3$.

TABLE I

CO AND CN STRETCHING FREQUENCIES OF SOME CYCLOPENTADIENYLMANGANESE TRICARBONYL DERIVATIVES

Complexes	CO stretching freq., cm.$^{-1}$	Solvent
$C_5H_5Mn(CO)_3$	2029 vs 1946 s	Hexane
$C_5H_5Mn(CO)_2C_4H_6$ (II)	1976 s A′ 1916 s A″	Hexane
$C_5H_5Mn(CO)_2C_2H_4$	1976 s A′ 1917 s A″	Hexane
$C_5H_5Mn(CO)C_4H_6$	1932 s	Hexane
$[C_5H_5Mn(CO)_2]_2C_4H_6$ (III)	1961 s 1896 s	Acetone
$C_5H_5Mn(CO)_2CH_2CHCN$[a] (1)	1996 s A′ 1940 s A″	Hexane
$C_5H_5Mn(CO)_4CH_3CN$	1933 1859	Hexane

[a] For this compound, the CN stretching frequency is 2205 cm.$^{-1}$ (KBr pellet).

Additional evidence for the bonding through the double bond is obtained from the CN stretching frequency. In π-bonded acrylonitrile carbonyl complexes of nickel,[8] tungsten,[6] and iron,[7] the CN stretching frequency shifts to lower frequencies relative to the free ligand while in σ-bonded $W(CO)_5CN$[6] it shifts to higher frequencies. The CN stretching frequency at 2205 cm.$^{-1}$ (KBr pellet) in compound I is considerably lower than that of the free ligand[8] (2225 cm.$^{-1}$).

Proton resonance measurements lend unequivocal support to the π-bonded structural assignment. The CP protons appear 4.6 p.p.m. downfield from TMS,

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as they do in the unsubstituted $C_5H_5Mn(CO)_3$. The ABC pattern of the olefinic protons in the complex lies between 1.8 and 2.8 p.p.m. downfield (shifted 3.7 p.p.m. upfield from the free ligand). Precisely the same shift was observed in complexes of the type $Fe(CO)_4L$ involving olefinic ligands.[11]

An unequivocal proof of the existence of the monosubstituted complex $C_5H_5Mn(CO)_2C_4H_6$ (II) is difficult because of its instability. The evidence rests almost entirely on the infrared spectrum. Two infrared bands are clearly observed in the CO stretching region (see Table I). This is precisely what is expected assuming C_s symmetry. Even more to the point is the very close agreement between infrared CO stretching frequencies of the butadiene derivative and the previously established mono derivative of ethylene, $C_5H_5Mn(CO)_2C_2H_4$. This comparison, 1976 and 1916 cm.$^{-1}$ for the butadiene derivative and 1976 and 1917 cm.$^{-1}$ for the ethylene derivative, shown in Table I, is strong evidence that compound II is indeed the monosubstituted $C_5H_5(CO)_2C_4H_6$.

Analytical data for compound III are in excellent agreement with the assumption that there is one butadiene molecule for each two $C_5H_5Mn(CO)_2$ groups. No other simple empirical formula fits nearly as well. This strongly suggests that butadiene serves as a bridge between two $C_5H_5Mn(CO)_2$ groups in compound III. Utilizing the method of local symmetry, group theoretic considerations suggest that two infrared bands should be observed for this compound. This is precisely what is observed. Detailed considerations of the structure of this molecule must await a more thorough structural investigation. X-Ray analysis is in process in another laboratory.

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Stabilization of High Oxidation States of Representative Elements by Complexation[1]

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The use of complexing agents for the express purpose of stabilizing high oxidation states of representative elements has received little attention despite the conspicuous success of stabilizing uncommon oxidation states of transition metals by the appropriate choice of ligands. It has been established experimentally that the fluoride ion and oxygen-containing ligands are particularly effective in stabilizing the highest oxidation state of a metal. This stabilizing effect has been accounted for in a satisfactory manner by proposing that in addition to σ-bond formation between the metal ion and the ligand there is an appreciable overlap of p orbitals, and occasionally d orbitals, on the ligand with the metal d orbitals.[2] Ligands which contain lone pairs of electrons in p orbitals and which transfer electron density *onto the metal* through π bonds are effective in stabilizing high oxidation states. At the same time the ligand must be sufficiently electronegative so as not to give up an electron to the metal. This in effect would result in oxidation of the ligand. The fluoride ion and oxygen-containing ligands, such as phosphine oxides, sulfoxides, and phosphate esters, are particularly effective in stabilizing high oxidation states because of their apparent ability to increase the electron density on the metal and their resistance to oxidation. The chloride ion is less desirable as a stabilizing ligand because of its tendency to be oxidized when bound to a strong oxidizing agent.

Stabilization of arsenic pentachloride by complexation was chosen to demonstrate the usefulness of this concept. The nonexistence of free arsenic pentachloride is a well-known fact. Careful vapor pressure measurements of the $AsCl_3$–Cl_2 system have given no evidence for arsenic pentachloride.[3] The negligible chlorine exchange between radioactive chlorine and arsenic trichloride has been interpreted as evidence for the nonexistence of an activated complex equivalent to arsenic pentachloride.[4] The instability of arsenic pentachloride relative to arsenic trichloride and chlorine has been accounted for in terms of unfavorable thermodynamics.[5] The purpose of complexation is, therefore, simply to lower the potential energy of the arsenic(V) species below that of its decomposition products.

Three general methods for the stabilization of arsenic(V) bonded to three or more chloride ions are summarized in eq. 1–3.

$$AsCl_3 + Cl_2 + MCl_n = [AsCl_4^+][MCl_{n+1}^-] \qquad (1)$$

where MCl_n[6] = $AlCl_3$,[7] $GaCl_3$,[7] PCl_5,[8,9] and $SbCl_5$.[9]

$$AsCl_3 + Cl_2 + [Q^+][Cl^-] = [Q^+][AsCl_6^-] \qquad (2)$$

where $[Q^+]$ is any bulky cation such as $[(C_2H_5)_4N^+]$.

$$AsCl_3{\cdot}xD + Cl_2 = AsCl_5{\cdot}yD + (x - y)D \qquad (3)$$

where D is a neutral ligand.

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[1] This work was supported by the National Science Foundation.

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