Succinonitrile Derivatives of Halogenopentacarbonylmanganese(I)[1]

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Abstract: The compounds $Mn(CO)_3(NCCH_2CH_2CN)X$ (X = Cl, Br, I) have been prepared by the direct reaction of succinonitrile with the manganese pentacarbonyl halides in refluxing chloroform. The derivatives, which are nonelectrolytes in nitromethane, decompose slowly on standing, even under nitrogen and in the cold. Infrared spectral data in acetone solution are consistent with the C_s symmetry of these molecules. In addition to three strong carbonyl bands, a CN stretching frequency is observed at about 2070 cm^{-1} for each of these complexes. This shift to lower frequencies of about 185 cm^{-1} from free succinonitrile is indicative of the novel attachment of succinonitrile to the metal through the CN π systems. An estimation of the amount of participation in π bonding is made by comparing the carbonyl stretching frequencies with those of analogous complexes. Nmr data are also presented and interpreted with regard to the infrared spectral data. Succinonitrile may be replaced in these derivatives by 2,2′-bipyridine and 1,2-bis(diphenylphosphino)ethane. These derivatives appear to represent the first example of coordination of an organonitrile to a metal through the CN triple bond.

An organonitrile possesses two theoretical sites for coordination to a metal, namely, the lone pair of electrons on nitrogen and the CN triple bond. Whereas coordination through the CN π system has been predicted to occur,[2] all transition metal–nitrile complexes reported thus far exhibit metal–nitrogen attachments.[3] Dinitriles also show the same tendency to coordinate through the nitrogen ends, and they act as bridging molecules between two metal complexes.[3]

A common feature exhibited by N-bonded nitrile complexes is a characteristic increase in the CN stretching frequency 30–110 cm^{-1} above that found for the free nitrile.[3] This increase is due primarily to an increase in the CN force constant upon coordination.[4] If coordination through the CN triple bond were to occur, a large decrease in the CN vibrational frequency would be expected. This type of coordination should be analogous to acetylenes coordinated through CC triple bonds, which show CC absorptions 50–250-cm^{-1} lower than those of the uncoordinated acetylenes.[5]

It has recently been shown that an organic isocyanate[6] and dialkylcyanamides[7] can have their CN π systems involved in bonding to transition metals. The coordinated ligands exhibit CN absorptions 150 and 200 cm^{-1} lower, respectively, than those of the uncoordinated ligands.

One approach to preparing a complex in which a nitrile is coordinated to a metal through the CN triple bond is to choose a dinitrile in which the carbon chain is short enough to prevent σ bonding from occurring through the two nitrogen ends to the same metal. Therefore, if chelation should take place, it must occur through the CN triple bonds. The alternative of bridging between two metals would be easily distinguishable from chelation by infrared and molecular weight measurements. Therefore, succinonitrile was chosen because it fits the requirements mentioned above. Manganese pentacarbonyl halides were selected because they readily undergo substitution by various chelates.

Experimental Section

Materials. $Mn(CO)_5Cl$,[8] $Mn(CO)_5Br$,[8] and $Mn(CO)_5I$[9] were prepared by methods described elsewhere. $Mn(CO)_3(bipy)X$ (X = Cl, Br, I) was prepared according to the method reported by Hieber and Schropp.[10] $Mn(CO)_3(Ph_2PCH_2CH_2PPh_2)X$ was prepared in a manner similar to the bipyridine derivatives. Succinonitrile was purchased from the K and K Laboratories, Inc., and recrystallized from ether before used.

Elemental Analyses and Molecular Weights. Carbon, hydrogen, and nitrogen analyses were carried out by the authors using analytical facilities kindly made available by Pittsburgh Plate Glass Co., Research Division, Barberton, Ohio. The manganese determinations were carried out by the authors by the periodate method.[11]

Molecular weights were determined cryoscopically in sulfolane, according to the method reported by Cotton and Mague.[12]

Preparation of Chlorosuccinonitriletricarbonylmanganese(I). $Mn(CO)_5Cl$ (0.20 g, 0.87 mmole) and 0.28 g (3.5 mmoles) of $NCCH_2CH_2CN$ were allowed to react in 50 ml of refluxing chloroform under a nitrogen atmosphere for 6 hr. The product precipitates as an oil, and the solvent gradually becomes essentially colorless after that time. The solvent was decanted and the oil was washed twice with 30 ml of CH_2Cl_2 to remove any unreacted starting materials. The last traces of solvent were removed in a stream of nitrogen, and the oil was induced to solidify by scratching with a glass rod. Except for mechanical losses, the yield is essentially quantitative.

Anal. Calcd for $Mn(CO)_3(NCCH_2CH_2CN)Cl$: C, 33.04; H, 1.58; N, 11.01; Mn, 21.59; mol wt, 254.5. Found: C, 32.28; H, 1.74; N, 11.09; Mn, 21.1; mol wt, 226.

Preparation of Bromosuccinonitriletricarbonylmanganese(I). This compound was prepared in a manner similar to that described for the chloro derivative, except that the reaction time was 8 hr. Except for mechanical losses, the yield was essentially quantitative.

Anal. Calcd for $Mn(CO)_3(NCCH_2CH_2CN)Br$: C, 28.12; H, 1.35; N, 9.37; Mn, 18.38; mol wt, 299. Found: C, 28.37; H, 1.50; N, 9.20; Mn, 17.80; mol wt, 285.

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(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966.

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(3) R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965).

(4) K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 919 (1966).

(5) G. E. Coates and F. Glockling in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 461.

(6) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).

(7) H. Bock and H. tom Dieck, *Ber.*, **99**, 213 (1966).

(8) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(9) From the reaction of $NaMn(CO)_5$ and I_2 as reported in W. Schropp, Jr., Doctoral Thesis, Technische Hochschule Munchen, 1960.

(10) W. Hieber and W. Schropp, *Z. Naturforsch.*, **14b**, 460 (1959).

(11) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1950, p 430.

(12) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1402 (1964).

Preparation of Iodosuccinonitriletricarbonylmanganese(I). This compound was prepared in a manner similar to that described for the chloro derivative, except that the reaction time was 12 hr. The yield was about 85%.

Anal. Calcd for $Mn(CO)_3(NCCH_2CH_2CN)I$: C, 24.30; H, 1.17; N, 8.1; Mn, 15.88. Found: C, 22.89; H, 1.55; N, 8.22; Mn, 15.99.

Reaction between $Mn(CO)_3(NCCH_2CH_2CN)Br$ and 2,2′-Bipyridine. $Mn(CO)_3(NCCH_2CH_2CN)Br$ (0.1 g, 0.33 mmole) and 2,2′-bipyridine (0.11 g, 0.70 mmole) were heated in 50 ml of 1,2-dichloroethane at 40° under nitrogen for 1 hr. A decomposition product of unknown structure precipitated from solution. From the 1,2-dichloroethane solution, $Mn(CO)_3(bipy)Br$ (identified by infrared spectrum) and free succinonitrile were isolated.

Reaction between $Mn(CO)_3(NCCH_2CH_2CN)Cl$ and 1,2-Bis(diphenylphosphino)ethane. The reaction was carried out in a manner similar to that described above for bipyridine, except that reaction temperature was 60°. From the solvent were isolated $Mn(CO)_3(diphos)Cl$ (identified by infrared spectrum) and free succinonitrile.

Reaction between Succinonitrile and Decacarbonyldimanganese. The reaction of $Mn_2(CO)_{10}$ (0.2 g, 0.5 mmole) with $NCCH_2CH_2CN$ (0.16 g, 2 mmoles) was allowed to proceed in both diglyme and *p*-xylene solutions, under a nitrogen atmosphere, at temperatures ranging from 85 to 120° for 1 hr. In all cases a yellow compound precipitated from solution, but upon removal of the solvent, the new products decomposed rapidly to a dark brown to black material, even under nitrogen. The nature of the dark decomposition products was not investigated further.

Infrared and Nmr Spectra. Infrared spectra were obtained with a Perkin-Elmer Model 337 grating infrared spectrophotometer. All spectra reported herein were taken in acetone solution using a 0.5-mm cell and a matching reference cell. The instrument was calibrated with a polystyrene standard.

Nmr spectra were obtained on a Varian DP-60 spectrometer, kindly made available by Pittsburgh Plate Glass Co. Spectra were obtained in deuterated dimethyl sulfoxide. Tetramethylsilane and benzene were used as internal standards for these measurements.

Electrical Conductivity. Measurements were made with an Industrial Instruments Model RCM15 conductivity bridge and a cell with platinum electrodes in nitromethane and acetone solutions.

Results

Properties of the Complexes. The halogenosuccinonitrile derivatives range in color from pale yellow for the chloride, yellow for the bromide, and dark yellow to orange for the iodide. They are insoluble in all but the very polar organic solvents. Thus, they are moderately soluble in acetone and nitromethane, soluble in dimethyl sulfoxide and sulfolane. They decompose slowly on standing, even under nitrogen and in the cold. This decomposition was observed by attaching a flask containing a sample of the iodide derivative, under nitrogen, to a gas buret. An amount of CO was evolved in 15 hr representing 10–15% decomposition. Therefore all analytical and spectral measurements were carried out within a few hours of preparation of the complexes. The derivatives decompose more rapidly in solution than in the solid state. The decomposition in solution is particularly marked for the iodide derivative; hence molecular weight measurements in sulfolane were not successful for this derivative.

The compounds are nonelectrolytes in acetone and nitromethane solutions, but the conductivity values increase slowly during the measurements, presumably due to decomposition in these solutions.

Infrared Spectra. The infrared spectra obtained for the $Mn(CO)_3(NCCH_2CH_2CN)X$ compounds in the 1900–2200-cm^{-1} region are reported in Table I. The table also shows the CO stretching frequencies of some analogous compounds belonging to the symmetry point group C_s. Included for comparison with the succinonitrile derivatives are $Mn(CO)_3(bipy)X$ and $Mn(CO)_3(diphos)X$. The CN stretching frequency of succinonitrile is also included for comparison.

Table I. CN and CO Stretching Frequencies (cm^{-1}) of $Mn(CO)_3(LL)X$ Complexes[a]

Compound	CN	CO (2A′ + A″)		
$NCCH_2CH_2CN$	2257 ms			
$Mn(CO)_3(succin)Cl$	2068 ms	2024 s	1977 s	1927 s
$Mn(CO)_3(succin)Br$	2068 ms	2021 s	1977 s	1932 s
$Mn(CO)_3(succin)I$	2074 ms	2002 s	1978 s	1935 s
$Mn(CO)_3(bipy)Cl$		2030 s	1932 s	1919 s
$Mn(CO)_3(bipy)Br$		2029 s	1932 s	1921 s
$Mn(CO)_3(bipy)I$		2022 s	1931 s	1922 s
$Mn(CO)_3(diphos)Cl$		2023 s	1951 s	1925 s
$Mn(CO)_3(diphos)Br$		2022 s	1952 s	1926 s
$Mn(CO)_3(diphos)I$		2019 s	1949 s	1925 s

[a] Abbreviations: succin, succinonitile; bipy, 2,2′-bipyridine; diphos, 1,2-bis(diphenylphosphino)ethane; m, medium; s, strong.

Nmr Spectra. The nmr spectra obtained for the three derivatives are similar in that they all exhibit a single proton signal shifted upfield by about τ 0.3 from the single signal received for free succinonitrile. The signals obtained for the bromide derivative were relatively sharp; however, those obtained for the chloride and iodide derivatives were broader than the bromide signals, presumably due to some decomposition in solution leading to the formation of a paramagnetic species.

Discussion

The infrared spectra of $Mn(CO)_3(NCCH_2CH_2CN)X$ complexes exhibit three strong carbonyl bands, which is in accord with simple group theoretical predictions for a *cis* tricarbonyl species of molecular C_s symmetry. In addition to the CO bands, a CN stretching frequency is observed for each of these derivatives around 2070 cm^{-1}. This represents a decrease in the CN stretching frequency by some 185 cm^{-1} from that observed for free succinonitrile. This decrease is about the magnitude expected if coordination occurs through the CN triple bond (by analogy to CC triple bond coordination) and observed for the other molecules containing a CN π system involved in coordination to a metal (*vide supra*). There is no trace of CN absorption either above 2257 cm^{-1} or around 2257 cm^{-1}, ruling out, respectively, coordination through nitrogen or the presence of an uncoordinated nitrile. Therefore, on the basis of elemental analyses, molecular weight data, electrical conductivities, and infrared measurements, the structure shown in Figure 1 is proposed for the three succinonitrile derivatives.

An alternate structure in which the succinonitrile molecule is attached to manganese through the nitrile carbons may be ruled out on the basis of the value of the CN stretching frequency. For this structure, the nitrile carbon would assume sp^2 hybridization, resulting in a CN double bond. The CN stretching frequency would therefore be expected to occur at a considerably lower frequency than 2070 cm^{-1}, since CN double bonds normally absorb in the 1600–1700-cm^{-1} region. Thus, the succinonitrile derivatives appear to represent the first examples of coordination of an organonitrile to a metal through the CN triple bond.

It is possible to estimate the extent to which the CN participates in π bonding with the metal relative to other chelates in molecules of analogous structure. The CO stretching frequencies of the succinonitrile adducts are higher than those of the corresponding 2,2′-bipyridine or 1,2-bis(diphenylphosphino)ethane derivatives, as can be seen in Table I. This means that the CN π system "back-bonds" to a larger extent than do the other bidentates considered, since higher CO stretching frequencies reflect an increase in the carbon–oxygen and a corresponding decrease in the metal–carbon bond orders.

If a comparison of the CO stretching frequencies of some N-bonded nitrile derivatives of group VI-B hexacarbonyls is made with those of some corresponding organophosphine derivatives,[13] then it is found that, in general, the organophosphine derivatives exhibit higher CO stretching frequencies than those of the corresponding acetonitrile derivatives. Group VI-B hexacarbonyl derivatives of olefins coordinated through their π systems exhibit higher CO absorption than do some corresponding organophosphine derivatives.[14] The fact that coordinated succinonitrile affords infrared spectral data more in accord with coordinated olefins rather than N-bonded nitriles further supports the assignment made above that the attachment of succinonitrile to manganese is through the CN triple bonds.

The proton nmr spectra for the three derivatives are similar in that they all exhibit a single signal shifted upfield about τ 0.3 from that observed for free succinonitrile. If one considers bonding through the CN triple bond, then the CN bond order should decrease slightly toward a double bond. The hybridization on the nitrile carbon thus changes slightly from sp toward sp^2. Stewart–Briegleb molecular models show that for an sp^2 nitrile carbon (*i.e.*, a CN double bond), the succinonitrile skeleton lies in the same plane with manganese and the two equatorial CO's. Thus, the four protons are equivalent (and apparently are unaffected by the different axial groups), leading to a single proton signal. However, this argument cannot be regarded as unequivocal and is presented only as a possible explanation.

It has been observed that the complexes $(CH_3CN)M(CO)_5$ (M = Cr and W), in which the acetonitrile molecule is N-bonded to the metal, give rise to a small downfield shift from the normal location of acetonitrile.[15] That an upfield shift is observed for the succinonitrile complexes can be possibly explained by considering that the CN triple bond attachment is involved in π acceptance from the metal to a relatively large degree. This rather extensive donation of metal electrons to the CN antibonding orbitals would lead to a decrease in the electronegativity of the CN group relative to the methylene carbons. This in turn leads to greater shielding of the methylene protons and a consequent upfield shift.

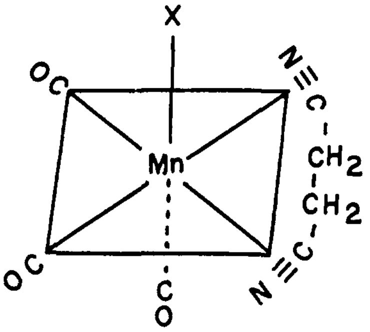

Figure 1. Proposed structure for $Mn(CO)_3(NCCH_2CH_2CN)X$ complexes.

In an attempt to find a system which might exhibit an nmr spectrum analogous to those of the succinonitrile derivatives, the spectrum of $Mn(CO)_3(Ph_2PCH_2CH_2PPh_2)Br$ was obtained and compared with the former ones. However, the nmr spectrum of the diphosphine derivative is very complex, and no direct correlation of the methylene protons of the two systems could be made.

The succinonitrile bidentate may be replaced rather readily by 2,2′-bipyridine and 1,2-bis(diphenylphosphino)ethane leading to the correspondingly more stable products and some decomposition. The important feature of the above reactions is that free succinonitrile is recovered unchanged during the replacement reaction, indicating that no rearrangement of the succinonitrile molecule has occurred upon chelation. The reverse reaction of replacement of bipyridine or diphosphine by succinonitrile does not occur, even after refluxing in chloroform for 6 hr, and the starting materials are recovered unchanged.

Samples of $Mn(CO)_3(NCCH_2CH_2CN)X$ when heated to reflux temperatures in chloroform only decompose, and no evidence has been obtained that the chelating succinonitrile has any tendency to rearrange to some N-bonded form.

All attempts to prepare $Mn_2(CO)_8(NCCH_2CH_2CN)$, analogous to the known compound $Mn_2(CO)_8(Ph_2PCH_2CH_2PPh_2)$,[16] were unsuccessful because the yellow compounds which precipitate from solution decompose immediately to a dark-colored compound upon removal of the solvent, even under nitrogen.

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[13] See F. A. Cotton, *Inorg. Chem.*, 3, 702 (1964), for infrared spectral data of acetonitrile and corresponding phosphine derivatives of group VIb hexacarbonyls.

[14] Compare, *e.g.*, infrared data reported by B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *ibid.*, 2, 1023 (1963), for coordinated acrylonitrile with phosphine derivatives reported in ref 13.

[15] B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *ibid.*, 2, 1023 (1963).

[16] W. Hieber and W. Freyer, *Ber.*, 92, 1765 (1959).