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Coordination of Organonitriles through CN π Systems[1]

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The compounds $M(CO)_3(NCRCN)X$ (M = Mn, Re; R = $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$; o-C_6H_4; X = Cl, Br) have been prepared by direct reaction of malono-, succino-, glutaro-, and phthalonitrile with the manganese and rhenium pentacarbonyl halides in solution. Also reported are preparations and properties of $M(CO)_3(CH_3CN)_2X$ (M = Mn, Re; X = Cl, Br). Whereas the acetonitrile derivatives coordinate in the usual manner through the lone pair of electrons on N and show the characteristic increase in the CN stretching frequencies upon coordination, the dinitriles all show large decreases in their CN stretching frequencies (about 185 and 230 cm^{-1}, respectively, for the Mn and Re complexes) and therefore appear to be coordinated as bidentates through their CN triple bonds. Infrared bands in both the 1800–2400- and 250–700-cm^{-1} regions support the proposed C_s structures of the molecules. Two of the molecules, $Mn_2(CO)_6[NC(CH_2)_3CN]Cl_2$ and $Mn_2(CO)_6(CH_3CN)_2Cl_2$, are dimeric in nature. Spectral studies indicate their structures to be analogous and to contain the nitrile as N-bonded molecules. The glutaronitrile derivative contains both bridging Cl and dinitrile groups. The π-bonded dinitriles may be replaced by certain solvent and bidentate molecules.

Introduction

In a previous paper[2] it was shown that succinonitrile ($NCCH_2CH_2CN$) is capable of coordinating to a metal as a bidentate through the triple bonds of its two CN groups. The approach in preparing a π-coordinated dinitrile was to choose a dinitrile whose carbon chain is too short to permit σ bonding from occurring to the same metal through the lone pairs on the nitrogen atoms. The transition metal host chosen for the bidentate nitriles was $Mn(CO)_5X$ (X = Cl, Br, I), because it readily undergoes substitution of two *cis* CO groups by a variety of ligands.

This work has now been expanded to include a variety of dinitriles which meet the above requirement, and also extended to the $Re(CO)_5X$ system. This extension allows us to correlate the size of the bidentate and a change in metal with observed physical and chemical properties.

Experimental Section

Starting Materials.—The manganese carbonyl halides $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ were prepared by methods described elsewhere.[3] The corresponding rhenium carbonyl halides were prepared by methods analogous to the above manganese compounds. They were identified by comparing their infrared spectra to those reported for $Re(CO)_5X$ by Abel, *et al.*[4]

Malononitrile, purchased from Aldrich, was purified by chromatography on a basic alumina column using ether as the eluting solvent. Succinonitrile (MC and B) and glutaronitrile (Aldrich) were used as received. Spectroquality acetonitrile was used without further purification. Phthalonitrile (City Chemical) was decolorized with activated charcoal and recrystallized from ether before use.

Elemental Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and/or MHW Laboratories, Garden City, Mich.

Preparation of the Complexes.—Described below is the detailed preparation of one of the complexes, $Mn(CO)_3sucBr$. All complexes were prepared in an analogous manner, with minor variations with respect to reaction solvent and time. Table I presents the conditions for preparations, while Table II gives the elemental analysis of the nitrile complexes.

$Mn(CO)_5Br$ (0.28 g, 1 mmol) and 0.20 g (2.5 mmol) of $NCCH_2CH_2CN$ were allowed to react in 50 ml of refluxing CH_2Cl_2 under a nitrogen atmosphere for 15 hr. The product slowly precipitated as a yellow crystalline solid during that time, and the color of the solution gradually changed from yellow to essentially colorless. The solvent was removed by decantation and the product was washed twice with CH_2Cl_2 to remove any unreacted starting materials. The last traces of solvent were removed in a stream of nitrogen. Except for mechanical losses, the yield was essentially quantitative.

In addition to the mononuclear dinitrile complexes listed in Tables I and II, the dinuclear dinitrile complex $Mn_2(CO)_6gluCl_2$ as well as the σ-bonded acetonitrile derivatives $Mn_2(CO)_2(ace)_2Cl_2$, $Mn(CO)_3(ace)_2Br$, and $Re(CO)_3(ace)_2X$ (ace = acetonitrile; X = Cl, Br) were also prepared. Their methods of preparation and analyses are as follows.

Preparation of $Mn_2(CO)_6(NC(CH_2)_3CN)Cl_2$.—To 0.40 g (1.74 mmol) of $Mn(CO)_5Cl$ in 50 ml of CH_2Cl_2 was added 0.082 g (0.87 mmol) or $NC(CH_2)_3CN$ and the mixture was refluxed under nitrogen for 4 days. At that time an infrared spectrum of the solution showed a complete absence of the starting materials. The solvent was removed on a rotary evaporator, and the resulting solid product was washed with hexane and ether and dried in a stream of nitrogen, to yield 0.31 g, or 80% of theory. *Anal.* Calcd for $Mn_2(CO)_6(NC(CH_2)_3CN)Cl_2$: C, 29.83; H, 1.36; N, 6.32. Found: C, 29.83; H, 1.48; N, 6.45.

If the above reaction is carried out using an excess of glutaronitrile (as in the preparation of the other dinitrile complexes), then the product, after removal of the solvent, is obtained dissolved in the excess dinitrile, which is very difficult to remove. However, evidence for a mononuclear derivative has never been obtained, regardless of the molar ratios of the starting materials.

Preparation of $Mn_2(CO)_6(CH_3CN)_2Cl_2$.—A mixture of 0.2 g (0.87 mmol) of $Mn(CO)_5Cl$, 0.13 ml (0.102 g, 2.49 mmol) of CH_3CN, and 15 ml of hexane was refluxed under nitrogen for 1 hr in the absence of light. The product which precipitated from the hexane solution was filtered and washed with 50 ml of hexane and dried in a stream of nitrogen to yield 0.14 g, 0. 65% of theory. *Anal.* Calcd for $Mn_2(CO)_6(CH_3CN)_2Cl_2$: C, 27.86; H, 1.40; N, 6.49. Found: C, 27.68; H, 1.46; N, 6.47.

Preparation of $Mn(CO)_3(CH_3CN)_2Br$.—A mixture of 0.2 g (0.727 mmol) of $Mn(CO)_5Br$, 0.13 ml (0.102 g, 2.49 mmol) of CH_3CN, and 15 ml of hexane was refluxed under nitrogen for 2 hr in the absence of light. The product which precipitated from the hexane was filtered and washed with 50 ml of hexane and dried in a stream of nitrogen. The yield was 58% of theory.

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[1] Presented in part at the Third International Symposium on Organometallic Chemistry, Munich, Germany, Aug 1967.

[2] M. F. Farona and N. J. Bremer, *J. Amer. Chem. Soc.*, **88**, 3735 (1966).

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

[4] E. W. Abel, G. R. Hargreaves, and G. Wilkinson, *ibid.*, 3149 (1958).

TABLE I

REACTION CONDITIONS FOR PREPARATION OF DINITRILE COMPLEXES

Complex	Solvent	Reaction time	mmol ratio L/M[a]	Yield, %
$Mn(CO)_3malCl$	CH_2Cl_2	10 hr	2.5/1	70
$Mn(CO)_3malBr$	CH_2Cl_2	18 hr	2.5/1	70
$Re(CO)_3malCl$[b]	CH_2Cl_2	5 days	2.5/1	70
$Re(CO)_3malBr$	$CHCl_3$	20 hr	2/1	73
$Mn(CO)_3sucCl$	CH_2Cl_2	10 hr	2.5/1	~100
$Mn(CO)_3sucBr$	CH_2Cl_2	15 hr	2.5/1	~100
$Re(CO)_3sucCl$	$CHCl_3$	15 hr	2/1	82
$Re(CO)_3sucBr$	$CHCl_3$	15 hr	2/1	66
$Mn(CO)_3gluBr$	CH_2Cl_2	15 hr	2.5/1	. . .
$Re(CO)_3gluCl$	CH_2Cl_2	4 days	2/1	87
$Re(CO)_3gluBr$	$CHCl_3$	21 hr	2/1	66
$Mn(CO)_3phthBr$	Hexane	14 days	2.5/1	. . .

[a] L = ligand, M = metal complex, $M(CO)_5X$; mal = malononitrile, suc = succinonitrile, glu = glutaronitrile, phth = phthalonitrile. [b] This complex is very difficult to obtain pure, since its preparation is often (but not always) accompanied by a small amount of unidentified green by-product.

TABLE II

ELEMENTAL ANALYSES FOR DINITRILE COMPLEXES[a]

Complex	Calcd, %			Found, %		
	C	H	N	C	H	N
$Mn(CO)_3(NCCH_2CN)Cl$	29.97	0.84	11.65	29.83	1.02	11.39
$Mn(CO)_3(NCCH_2CN)Br$	25.92	0.70	9.83	25.36	0.76	10.06
$Re(CO)_3(NCCH_2CN)Cl$	19.39	0.54	7.53	19.33	0.50	7.36
$Re(CO)_3(NCCH_2CN)Br$	17.32	0.48	6.73	17.52	0.48	6.91
$Re(CO)_3(NC(CH_2)_2CN)Cl$	21.79	1.04	7.26	21.77	1.07	7.35
$Re(CO)_3(NC(CH_2)_2CN)Br$	19.54	0.94	6.51	19.73	1.11	6.71
$Mn(CO)_3(NC(CH_2)_3CN)Br$	30.70	1.93	8.95	29.55	1.95	8.77
$Re(CO)_3(NC(CH_2)_3CN)Cl$	24.03	1.51	7.01	23.73	1.32	6.83
$Re(CO)_3(NC(CH_2)_3CN)Br$	21.63	1.36	6.30	21.42	1.46	6.07
$Mn(CO)_3(C_6H_4(CN)_2)Br$	38.07	1.16	8.07	38.05	1.30	7.91

[a] The C, H, N, and Mn analyses and molecular weight measurements for the succinonitrile complexes $Mn(CO)_3(NC(CH_2)_2CN)X$ (X = Cl, Br) were given in ref 2. Although their preparative procedures given in this paper are slightly different from those in ref 2, the compounds were identified as authentic from comparison of their infrared spectra and decomposition points.

Anal. Calcd for $Mn(CO)_3(CH_3CN)_2Br$: C, 27.93; H, 2.01; N, 9.31. Found: C, 27.75; H, 1.93; N, 9.24.

Preparation of $Re(CO)_3(CH_3CN)_2Cl$.—To 0.20 g (0.55 mmol) of $Re(CO)_5Cl$ was added 3 ml of acetonitrile and the mixture was refluxed under nitrogen for 3 hr in the absence of light. The excess acetonitrile was removed on a rotary evaporator and the resulting solid product was washed with 50 ml of hexane and dried in a stream of nitrogen. The yield was essentially quantitative. *Anal.* Calcd for $Re(CO)_3(CH_3CN)_2Cl$: C, 21.68; H, 1.56; N, 7.22. Found: C, 21.55, H, 1.40; N, 7.00.

Preparation of $Re(CO)_3(CH_3CN)_2Br$.—This product was prepared in a manner analogous to that given above for the corresponding chloride derivative. The yield was essentially quantitative. *Anal.* Calcd for $Re(CO)_3(CH_3CN)_2Br$: C, 19.45; H, 1.40; N, 6.48. Found: C, 19.26; H, 1.37; N, 6.29.

Infrared Spectra.—Infrared spectra in the 2350–1800-cm^{-1} region were obtained on a Perkin-Elmer Model 337 grating infrared spectrophotometer. The samples were recorded as Nujol mulls between KBr disks. The spectra in the 700–250-cm^{-1} region were obtained on a Perkin-Elmer Model 521 grating infrared spectrophotometer. The samples were recorded as Nujol mulls between CsBr disks in this region.

Mass Spectra.—Mass spectra of the compounds were recorded on an AEI MS-12 mass spectrometer using a direct-insertion probe and an ionizing voltage of 70 eV.

Results and Discussion

Properties of the Complexes.—The colors of the π-coordinated dinitrile derivatives of Mn(I) are various shades of yellow whereas those of the corresponding Re(I) derivatives are white or off-white. They are relatively stable compounds in the solid state when exposed to air; they can be stored under nitrogen and in the cold several months without noticeable decomposition. This observation contrasts with our former report on the succinonitrile derivatives.[2] We noted then that the complexes, particularly the iodide, decompose slowly upon standing. With the methods of preparation reported in this paper, apparently better samples are obtained (*i.e.*, much less decomposition accompanies production of the product), and previously we underestimated the relative stabilities of the complexes. The decomposition points of the complexes are given in Table III.

TABLE III

DECOMPOSITION POINTS OF THE DINITRILE AND ACETONITRILE COMPLEXES

Complex	Dec pt,[a] °C	Complex	Dec pt,[a] °C
$Mn(CO)_3malCl$	100–105	$Re(CO)_3sucBr$	220–223
$Mn(CO)_3malBr$	155–170	$Mn(CO)_3gluBr$	80–85
$Re(CO)_3malCl$	220–225	$Re(CO)_3gluCl$	160–165
$Re(CO)_3malBr$	190[b]	$Re(CO)_3gluBr$	204–206
$Mn(CO)_3sucCl$	155–156	$Mn(CO)_3(ace)_2Br$	86–88
$Mn(CO)_3sucBr$	151–155	$Re(CO)_3(ace)_2Cl$	131–134
$Re(CO)_3sucCl$	190[b]	$Re(CO)_3(ace)_2Br$	149–151

[a] Uncorrected. [b] Begins to darken and decomposes over a wide range.

The π-coordinated nitrile complexes, which are nonvolatile, are generally insoluble in all organic solvents; we have found that solvents which apparently dissolve these samples either react with the coordinated dinitrile or displace it from its position in the coordination sphere. For example, it appears that certain solvents with active hydrogens (*e.g.*, acetone) react with coordinated dinitriles to convert them to Schiff bases. This aspect is currently under investigation and the results will be reported in a subsequent publication. Some coordinating solvents (*e.g.*, acetonitrile) react with the complexes to coordinate two solvent molecules in place of the bidentate dinitrile (*vide infra*). These observations, therefore, limit the use of nmr and molecular weight measurements as structural tools.

Solution studies of infrared and nmr spectra and molecular weights were reported for the succinonitrile derivatives. This dinitrile is also susceptible to attack by certain compounds containing active hydrogen and also undergoes replacement by various solvents. However, the reactions of coordinated succinonitrile proceed much more slowly than those of the other dinitriles; hence, solution studies reported in the previous publication are regarded as accurate.

Infrared Spectra.—Infrared spectra in both the 2400–1800- and 700–250-cm^{-1} regions are most revealing in elucidating the structures of the mononuclear dinitrile complexes. Like acetylenes, which show a decrease in the $C\equiv C$ stretching frequency of 50–250 cm^{-1} upon coordination through their π systems,[5] π-coordinated

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

nitriles should show similar decreases in their CN stretching frequencies when compared to the same stretching frequency of the free nitrile.

Generally, when nitriles coordinate in the normal manner through the lone pair of electrons on nitrogen, an increase in the CN stretching frequency of 30–110 cm^{-1} is observed with respect to the uncoordinated nitrile.[6] However, it has recently been shown that a decrease in the CN stretching frequency can accompany coordination through nitrogen.[7,8] The acetonitrile derivative of Co(I)[7] and benzonitrile and acetonitrile derivatives of Ru(II)[8] show decreases in their CN stretching frequencies of 45 and 31–57 cm^{-1}, respectively, upon coordination. These decreases are considerably less than those observed for the nitrile systems which are believed to coordinate through their π systems. For example, π-coordinated succinonitrile derivatives show decreases in ν(CN) of 180 cm^{-1} from that of the free nitrile,[2] and diethylaminoacetonitrile, which coordinates as a bidentate through the amino nitrogen and the CN triple bond to the group VIb hexacarbonyls, shows decreases of some 100 cm^{-1} in the CN stretching frequency upon coordination.[9] Nevertheless, we have prepared acetonitrile derivatives of Mn(CO)$_5$X and Re(CO)$_5$X (X = Cl, Br) to determine the direction and the magnitude of the shift in ν(CN) upon coordination in these systems.

TABLE IV

INFRARED SPECTRA OF THE COMPLEXES IN THE 2400–1800-CM^{-1} REGION

Compound	ν(CN),[a] cm^{-1}	ν(CO),[a] cm^{-1}		
NCCH$_2$CN (mal)	2778 m[b]			
Mn(CO)$_3$malCl	2066 sh	2045 s	1969 s	1938 s
Mn(CO)$_3$malBr	2062 sh	2049 s	1957 s	1936 s
Re(CO)$_3$malCl	2045 sh	2030 s	1930 s	1910 s
Re(CO)$_3$malBr	2045 sh	2030 s	1934 s	1910 s
NCCH$_2$CH$_2$CN (suc)	2257 m[b]			
Mn(CO)$_3$sucCl	2070 s	2024 s	1982 s	1923 s
Mn(CO)$_3$sucBr	2072 m	2045 s	1957 s	1938 s
Mn(CO)$_3$sucCl[c]	2068 ms	2024 s	1977	1927
Mn(CO)$_3$sucBr[c]	2068 ms	2021 s	1977 s	1932 s
Re(CO)$_3$sucCl	2041 sh	2033 s	1931 s	1905 s
Re(CO)$_3$sucBr	2045 sh	2031 s	1927 s	1901 s
NCCH$_2$CH$_2$CH$_2$CN (glu)	2257 m[b]			
Mn(CO)$_3$gluBr	2062 m	2041 s	1957 s	1931 s
Re(CO)$_3$gluCl	[e]	2037 s	1942 s	1905 s
Re(CO)$_3$gluBr	2045 sh	2028 s	1923 s	1905 s
o-C$_6$H$_4$(CN)$_2$(phth)	2237 m[b]			
Mn(CO)$_3$phthBr	2041 sh	2024 s	1951 s	1923 s
Mn(CO)$_3$phthBr[b]	2049 sh	2039 s	1976 s	1946 s
CH$_3$CN (ace)	2250 s[d]			
Mn(CO)$_3$(ace)$_2$Cl	2300 vw, 2273 w	2035 s	1953 s	1927 s
Mn(CO)$_3$(ace)$_2$Br	2302 vw, 2276 w	2043 s	1957 s	1934 s
Re(CO)$_3$(ace)$_2$Cl	2307 w, 2283 w	2024 s	1932 s	1895 s
Re(CO)$_3$(ace)$_2$Br	2309 w, 2283 w	2039 s	1916 s	1896 s

[a] All bands, except where indicated, recorded as Nujol mulls between KBr disks. Abbreviations: sh, shoulder; s, strong; m, medium; w, weak; v, very. [b] CHCl$_3$ solution. [c] Acetone solution.[2] [d] Neat liquid. [e] Probably covered by 2037-cm^{-1} band.

The infrared spectra of the complexes in the 2400–1800-cm^{-1} region are given in Table IV. Also shown in Table IV are the acetone solution spectra of the Mn(CO)$_3$sucX derivatives for comparison. The CN stretching frequencies of the free ligands are also shown. Table V gives the infrared spectra of the complexes in the 700–250-cm^{-1} region.

The infrared spectra of the dinitriles in the CN and CO stretching region generally show four bands; if one of these is assigned to ν(CN), then the other three bands are ν(CO) (2 A′ + A″), which is in accord with the C$_s$ symmetry of the molecules. The CN stretching bands, while clearly resolved in solution spectra of Mn(CO)$_3$sucX, appear as poorly resolved shoulders on the high-frequency side of the highest frequency CO band in the solid-state spectra. The two lowest frequency bands lie very close together and are poorly resolved in the solid-state spectra; the general appearance is one broad band, but obviously containing more than one component.

The observed shifts in the CN stretching frequency indicate that the dinitriles are coordinated through their CN triple bonds. Among the manganese compounds, the CN stretching frequencies of the malononitrile derivatives decrease by about 215 cm^{-1} upon coordination; the succinonitrile derivatives show decreases of 185 cm^{-1} from the free nitrile. The glutaronitrile and phthalonitrile complexes exhibit decreases in their CN stretching frequency of about 195 cm^{-1} upon coordination. The corresponding rhenium analogs all show decreases in the CN stretching frequencies of about 230 cm^{-1}, considerably lower than those of the manganese complexes. Apparently, the Re–π-CN bond is stronger than the Mn–π-CN attachment since the coordinated CN frequency appears at lower frequencies for Re than Mn, and the lower CN bond strength probably indicates a greater involvement of the CN triple bond with the metal. There are never any bands in the 2250–2350-cm^{-1} region in the spectra of the mononuclear dinitrile complexes; this fact rules out the existence of N-bonded or uncoordinated nitrile groups.[10]

The infrared results of the acetonitrile derivatives lend strong support to the contention that the dinitriles are coordinated through the CN triple bonds. In these systems, the acetonitrile ligands are coordinated in the usual way through the lone pair of electrons on nitrogen. Both the manganese and rhenium derivatives show the characteristic increase in the CN stretching frequency upon coordination; ν(CN) occurs 25–60 cm^{-1} higher than that found for free CH$_3$CN. Two bands are reported in the 2270–2310-cm^{-1} region for ν(CN). Two ν(CN) bands are expected; however, the higher frequency band could possibly be a combination band arising from the symmetric CH$_3$ deformation and symmetric CC stretching modes which appear as very weak bands in the range of 1350–1370 and 930–940 cm^{-1}, respectively.[11]

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[6] R. A. Walton, *Quart. Rev.*, **19**, 126 (1965).

[7] A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *Chem. Commun.*, 208 (1969).

[8] P. C. Ford and R. E. Clark, *ibid.*, 1109 (1968); R. E. Clark and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).

[9] S. C. Jain and R. Rivest, *Inorg. Chim. Acta*, **3**, 249 (1969).

[10] There are two exceptions to this statement. The infrared spectra of Re(CO)$_3$gluX (X = Cl, Br) show very weak CN bands around 2300 cm^{-1}, presumably from some N-bonded nitrile compound. However, all evidence indicates these complexes to be monomeric, and it is likely that these bands arise from small amounts of impurities, which are difficult to remove.

[11] B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963), and references therein.

TABLE V

INFRARED SPECTRA OF THE COMPLEXES IN THE 700–250-CM^{-1} REGION[a]

Compound	ν(MC) + δ(MCO) + ligand, cm^{-1}															ν(MCl), cm^{-1}
$NCCH_2CN$ (mal)[b]				575 w									360 ms		330 w	
Mn(CO)$_3$malCl	680 s	667 sh	624 s	610 sh			510 s	460 sh		451 m	393 w		368 w		315 w	285 m
Mn(CO)$_3$malBr	676 s	661 sh	622 s				520 s	465 sh		460 ms	410 w		378 w		320 w	
Re(CO)$_3$malCl	649 s		623 s	595 w	578 m	558 m	520 s				380 s				330 w	282 m
Re(CO)$_3$malBr	645 s		625 s	610 sh	578 s	568 s	528 s				378 vw		341 vw		300 vw	
$NCCH_2CH_2CN$ (suc)[b]				588 ms						462 m	341 w					
Mn(CO)$_3$sucCl	680 s	667 m	622 s	605 sh			522 ms	500 s		441 ms	400 vw					280 m
Mn(CO)$_3$sucBr	678 s	680 sh	628 s	610 sh			530 sh	518 s	468 sh	458 ms	410 vw					
Re(CO)$_3$sucCl	646 s		628 s	605 sh			540 sh	530 s		485 s						275 ms
Re(CO)$_3$sucBr	644 s		628 s	605 sh			548 sh	530 m		482 s						
$NCCH_2CH_2CH_2CN$ (glu)[c]				577 m					500 vw				370 w		317 m	
Mn(CO)$_3$gluBr	676 s	668 sh	625 sh	612 sh			512 s			460 m	410 w					
Re(CO)$_3$gluCl	648 s		628 s				533 m	521 s		480 s					315 w	280 m
Re(CO)$_3$gluBr	648 s		628 s				533 s	521 s		485 s					315 w	
CH_3CN (ace)[c]												377 s				
Mn(CO)$_3$(ace)$_2$Cl	680 s		628 s				535 sh	510 s		460 ms		410 m	400 m			282 m
Mn(CO)$_3$(ace)$_2$Br	684 s		630 s				530 s	518 sh		471 ms		421 w	401 ms			
Re(CO)$_3$(ace)$_2$Cl	649 s		633 ms				531 s			482 s		415 w	403 m	395 s		286 ms
Re(CO)$_3$(ace)$_2$Br	645 s		631 ms	594 m			533 s	524 s		488 s		415 s	402 m	388 w	342 w	

[a] All bands, except where indicated, recorded as Nujol mulls between CsBr disks. [b] Thin film, neat solid. [c] Neat liquid.

TABLE VI

INFRARED SPECTRA OF THE DINUCLEAR NITRILE COMPLEXES IN THE 2400–1800- AND 700–250-CM^{-1} REGIONS[a]

Complex	ν(CN) + ν(CO), cm^{-1}							
$Mn_2(CO)_6$gluCl$_2$	2300 w		2058 s	2041 s	1967 s	1953 s	1932 s	1917 sh
$Mn_2(CO)_6$(ace)$_2$Cl$_2$	2320 w	2294 w		2049 s	1967 s	1957 s	1936 s	1896 m

	ν(MnC) + δ(MnCO) + ligand, cm^{-1}									ν(MnCl), cm^{-1}	
$Mn_2(CO)_6$gluCl$_2$	680 s	628 s	621 s	510 s	499 sh	468 w	452 m	400 w	395 sh	308 m	265 m
$Mn_2(CO)_6$(ace)$_2$Cl$_2$	680 s	635 s	626 s	512 s	485 m	469 w	453 ms	403 w	399 w	288 m	257 m

[a] All spectra recorded as Nujol mulls.

The low-frequency infrared data are consistent with the proposed C_s symmetry of these complexes. Table V shows that at least nine bands are observed in the MC stretching and MCO bending regions. The metal–chlorine stretching frequency is observed in the 275–285-cm^{-1} region.

The acetonitrile adducts exhibit spectra in the 700–250-cm^{-1} region which are very similar to those of the dinitrile derivatives. In addition, δ(NCC) bands are observed in the 390–420-cm^{-1} region as have been observed and assigned as such in a variety of cases.[12]

We conclude from the evidence presented above that all the mononuclear dinitrile derivatives are coordinated through the CN triple bonds as bidentate ligands. The proposed structures are presented in Figure 1.

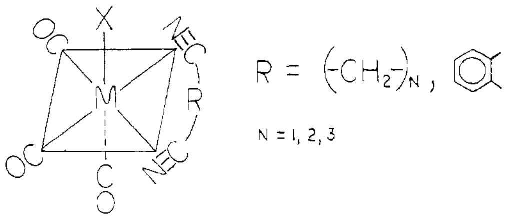

Figure 1.—Proposed structure of the mononuclear dinitrile complexes.

Dinuclear Derivatives.—At least two chloride derivatives are isolated as dimeric products, *viz.*, $Mn_2(CO)_6$gluCl$_2$ and $Mn_2(CO)_6$(ace)$_2$Cl$_2$. Once again, infrared spectra both in the 2400–1800- and 700–250-cm^{-1} regions provide strong evidence as to the structures of these molecules. These data are presented in Table VI.

The spectra of these dinuclear complexes are considerably different from the π-bonded dinitrile complexes in both the 2000-cm^{-1} and the CsBr regions. Both of these complexes exhibit certain bands in clear contrast with those shown by the dinitrile derivatives.

First, ν(CN) bands are observed around 2300 cm^{-1}, an increase of some 40–50 cm^{-1} compared with the bands of the uncoordinated nitrile. In light of the data presented for the acetonitrile complexes, the nitriles in these complexes appear to be N bonded. Furthermore, the spectra of both complexes in the 250–310-cm^{-1} region reveal two Mn–Cl stretching bands, whereas in the spectra of the mononuclear derivatives, only one Mn–Cl stretching band is observed. Clearly, the presence of two Mn–Cl stretches indicates bridging chlorines between two metals; these stretching frequencies appear at about the same frequencies observed for $Mn_2(CO)_8Cl_2$,[13] where the chlorines are known to bridge. Furthermore, mass spectral evidence indicates an *m/e* peak which can be ascribed to $Mn_2Cl_2^+$, and this peak is not found for the dinitrile derivatives. In light of the similarity of the infrared spectra in both the 2000-cm^{-1} and the CsBr regions with respect to number, relative intensities, and positions of the bands, the structures of the acetonitrile and glutaronitrile dimers are most likely analogous. Since the glutaronitrile molecule does not π bond to the metal in the

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dimer and is too short to σ bond as a chelate to the same metal and there is no evidence of the existence of an uncoordinated nitrile, the structure must be one in which the glutaronitrile bridges between the two metal atoms. The proposed structure is shown in Figure 2.

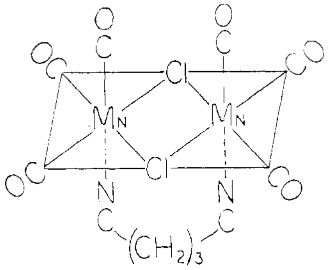

Figure 2.—Proposed structure of $Mn_2(CO)_6gluCl_2$.

The structural formulation of this compound can be shown, with the aid of scale molecular models, to possess no prohibitive amount of strain or steric hindrance in its assemblage.

The bands in the 2000-cm^{-1} and the CsBr regions are in accord with the proposed structure. Both regions show clear differences with those of the mononuclear dinitrile spectra. For the proposed structure, which belongs to the point group C_{2v}, five infrared-active CO stretches are predicted, $2\ A_1 + 2\ B_1 + B_2$, and five main CO bands are observed for each complex. In the CsBr region five MnC stretching ($2\ A_1 + 2\ B_1 + B_2$) and nine MnCO bending ($3\ A_1 + 3\ C_1 + 3\ B_2$) modes are expected to be infrared active. In fact, nine bands are observed in the CsBr region, excluding those already assigned as MnCl stretches.

The structure of the dinuclear derivatives, while unusual for manganese carbonyl compounds, is not without precedence. A similar structure was proposed for Ti_2Cl_8glu, where both bridging Cl and glutaronitrile groups are believed to exist.[14] Whereas a few anionic substitution derivatives of $Mn_2(CO)_8X_2$ are known,[15] to our knowledge, these dimeric derivatives are the only known examples of neutral derivatives of $Mn_2(CO)_8Cl_2$ and are also the first examples of triply bridged derivatives of this system. The observation that this structure occurs only with the manganese chloride derivative and glutaronitrile indicates that the sizes of the metal, chlorine, and glutaronitrile are important in determining the stereochemistry of the complex, although this does not explain why the bromide derivatives do not tend to bridge in the case of the acetonitrile compounds.

Nitrile Replacement Studies.—It was mentioned previously that solvents in which the dinitrile derivatives are soluble either react with or displace the bidentate from its position in the octahedral coordination sphere around the metal. Acetonitrile appears to replace the π-bonded dinitriles more or less rapidly. Regardless of the dinitrile derivative dissolved in CH_3CN, the infrared spectra in the 1900–2200-cm^{-1} region are identical with those of the corresponding acetonitrile derivatives in CH_3CN. The replacement of succinonitrile occurs much more slowly than either malono- or glutaronitrile, which are extremely rapid. This observation has led to the preparation of the monomeric $Mn(CO)_3(ace)_2Cl$, which was not obtained by direct reaction of $Mn(CO)_5Cl$ and CH_3CN. If $Mn(CO)_3malCl$ is dissolved in CH_3CN and the solvent removed, the spectrum of the residue is very similar in the carbonyl region to that of $Mn(CO)_3(ace)_2Br$, and its spectrum is presented in Table IV. Accompanying the carbonyl bands is the CN band of free malononitrile, liberated in the reaction with CH_3CN.

It was reported in the succinonitrile paper[2] that the dinitrile can be replaced by other bidentate molecules such as 2,2′-bipyridine and 1,2-bis(diphenylphosphino)ethane, and the free nitrile could be recovered unchanged from these reactions. Malononitrile and glutaronitrile undergo similar displacements in these complexes. Infrared spectra of the residues reveal not only the spectrum of the new carbonylcompound but the presence of the liberated, uncoordinated nitrile as well.

Besides the chemical indications which show the nitrile is intact in the complexes, mass spectral evidence supports the same conclusion. In the mass spectra of all the chelated dinitrile complexes, the largest m/e peak is always due to the singly charged ligand, again showing that the dinitrile is unaltered in these complexes.

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