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Preparation, Characterization, and Reactions of the *cis*-Dihalotetracarbonylmanganate(I) Anions

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Compounds of the type $R_4N[cis\text{-}Mn(CO)_4X_2]$, where R = C_2H_5 or C_4H_9 and X = Cl, Br, I, or CN, have been prepared from $Mn(CO)_5X$ and $[R_4N]X$. The formation of the product takes place by way of an SN1 mechanism. The C–O stretching vibrational modes of $[cis\text{-}Mn(CO)_4X_2]^-$ have been assigned to the observed infrared absorptions, and the compounds have been found to react with phosphines (L) to give *cis*-$Mn(CO)_4LX$.

Although the preparation of $K[Mn(CO)_4(CN)_2]$ from $Mn(CO)_5Cl$ and KCN has already been reported,[1] no experimental evidence that would substantiate this formulation was given. It was stated that the compound had properties very similar to those of $K[Re(CO)_4(CN)_2]$,[2] which had been obtained earlier in an impure state.

While the present manuscript was in preparation, the synthesis of the analogous halide compounds, $[cis\text{-}Mn(CO)_4X_2]^-$, where X = Cl, Br, or I, was reported.[3] The present paper reports their synthesis in somewhat better yields and their mechanism of formation from $Mn(CO)_5X$ and X^-. Detailed assignments of the C–O stretching absorption bands have been made to the appropriate modes of vibration in $[cis\text{-}Mn(CO)_4X_2]^-$, including X = CN, and in *cis*-$Mn(CO)_4[P(C_6H_5)_3]I$.[4] The reactions of $[cis\text{-}Mn(CO)_4X_2]^-$ with $P(C_6H_5)_3$ have also been investigated.

Experimental

Materials.—$Mn(CO)_5Cl$,[5] $Mn(CO)_5Br$,[5] $Mn(CO)_5I$,[6] *cis*-$Mn(CO)_4[P(C_6H_5)_3]Br$,[7] and *cis*-$Mn(CO)_4[P(C_6H_5)_3]I$[7] were prepared by methods already given in the literature. The tetraethylammonium chloride and tetrabutylammonium iodide were purchased from Eastman Kodak Co. and Matheson Coleman and Bell and were used without further purification. The tetraethylammonium bromide was dried in a vacuum desiccator over Drierite.

The halide determinations were made by titration with standard $Hg(NO_3)_2$.[8]

Preparation of $(C_2H_5)_4N[cis\text{-}Mn(CO)_4Cl_2]$.—$Mn(CO)_5Cl$ (0.20 g., 0.87 mmole) and 0.10 g. (0.61 mmole) of $[(C_2H_5)_4N]Cl$ were refluxed in 10 ml. of CH_2Cl_2 for 1 hr. under a nitrogen atmosphere. Upon cooling to room temperature, part of the product crystallized out of solution. Approximately 10 ml. more of CH_2Cl_2 was added to dissolve the crystallized product. The solution was filtered and upon addition of 50 ml. of hexane the product began to crystallize from solution. After 45 min. the yellow product was separated from the solution by filtration, washed with hexane, and dried under vacuum; yield 48%.

Anal. Calcd. for $(C_2H_5)_4N[Mn(CO)_4Cl_2]$: H, 5.48; N, 3.81; Cl, 19.3. Found: H, 5.57; N, 3.81; Cl, 19.7.

The compound in the solid state is very stable to light and air but decomposes slowly in solution. It dissolves readily in methanol, tetrahydrofuran, and acetone, but decomposes rapidly in the latter two solvents. It is moderately soluble in CH_2Cl_2, dichloroethane, and water, but is insoluble in $CHCl_3$, benzene, and hexane.

Preparation of $(C_2H_5)_4N[cis\text{-}Mn(CO)_4Br_2]$.—$Mn(CO)_5Br$ (0.20 g., 0.73 mmole) and 0.14 g. (0.68 mmole) of $[(C_2H_5)_4N]Br$ were warmed in 7 ml. of absolute methanol under a nitrogen atmosphere at 45–50° for 1 hr. The methanol was then evaporated from the orange solution at the above temperature with a water aspirator. The remaining yellow solid was dissolved in 20 ml. of CH_2Cl_2, and the solution was filtered under nitrogen. After adding 100 ml. of hexane to the filtrate, the cloudy solution was allowed to stand for 2 hr. The yellow crystals were separated by filtration, washed with hexane, and dried under vacuum; yield 0.25 g. (84%).

Anal. Calcd. for $(C_2H_5)_4N[Mn(CO)_4Br_2]$: H, 4.41; N, 3.06; Br, 35.0. Found: H, 4.72; N, 2.89; Br, 35.8.

The solid is very stable and in solution is more stable to oxidation than the analogous chloride. It has solubility properties very similar to those of the chloride but is somewhat more soluble in CH_2Cl_2, dichloroethane, and $CHCl_3$. It decomposes readily in acetone.

Preparation of $(C_4H_9)_4N[cis\text{-}Mn(CO)_4I_2]$.—$Mn(CO)_5I$ (0.20 g., 0.62 mmole) and 0.21 g. (0.57 mmole) of $[(C_4H_9)_4N]I$ in 9 ml. of absolute methanol were warmed at 50–60° for 1 hr. under a nitrogen atmosphere. The methanol was evaporated off under vacuum leaving a red-brown oil. This oil was dissolved in 10 ml. of $CHCl_3$. The product was obtained as an oil from the filtered solution by adding 100 ml. of hexane. After allowing the solution to stand overnight the solvents were poured off. The remaining oil was covered with hexane and allowed to stand overnight. The slightly solidified oil could be induced to form an orange solid by scratching. The hexane was decanted, and the compound was dried under vacuum. It was identified only by comparing its infrared spectrum with those of the analogous chloride and bromide complexes. This compound is far more soluble in organic solvents than the bromide, and its solutions are more stable toward air as well.

Preparation of $(C_2H_5)_4N[cis\text{-}Mn(CO)_4(CN)_2]$.—$Mn(CO)_5Br$ (0.20 g., 0.73 mmole), 0.095 g. (1.46 mmoles) of KCN, and 0.12 g. (0.73 mmole) of $[(C_2H_5)_4N]Cl$ were warmed at 50–55° in 10 ml. of absolute methanol for 1 hr. under a nitrogen atmosphere. After evaporation of the methanol, the residue was dissolved in 10 ml. of CH_2Cl_2, and the resulting solution was filtered under nitrogen and treated with 150 ml. of hexane. After allowing the cloudy solution to stand for 20 hr. in the dark, the solvent was decanted and the residual yellow oil was dissolved in 7 ml. of CH_2Cl_2. After filtration and treatment with 150 ml. of hexane, the solution was again allowed to stand overnight. The solvents were poured off, and the yellow oil was induced to solidify

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TABLE I

INFRARED SPECTRA OF $R_4N[cis\text{-}Mn(CO)_4X_2]$ IN 1,2-DICHLOROETHANE IN THE C–O STRETCHING REGION

Compound	Frequencies (cm.$^{-1}$)^a of C–O stretching modes			
	A_1^a	B_1	A_1^b	B_2
$(C_2H_5)_4N[Mn(CO)_4Cl_2]$	2098 (vw)^b	2026 (s)	1986 (w)	1936 (s)
$(C_2H_5)_4N[Mn(CO)_4Br_2]$	2098 (w)	2026 (s)	1990 (m)	1939 (s)
$(C_4H_9)_4N[Mn(CO)_4I_2]$	2082 (m)	2006 (s)	1986 (s)	1939 (s)
$(C_2H_5)_4N[Mn(CO)_4(CN)_2]$	2103 (w)^c	2029 (s)	2005 (m)	1936 (s, br)

[a] ±2 cm.$^{-1}$. [b] vw, very weak; w, weak; m, medium; s, strong; br, broad. [c] Bands at 2146 (w) and 2087 (vw) cm.$^{-1}$ attributed to C–N stretching modes.

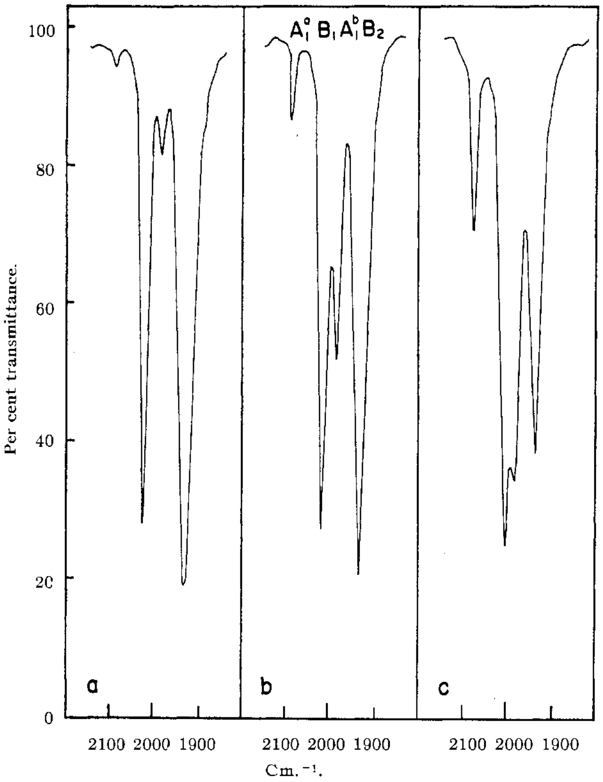

Fig. 1.—Infrared spectra of: (a) $(C_2H_5)_4N[cis\text{-}Mn(CO)_4Cl_2]$; (b) $(C_2H_5)_4N[cis\text{-}Mn(CO)_4Br_2]$; and (c) $(C_4H_9)_4N[cis\text{-}Mn(CO)_4I_2]$ in 1,2-dichloroethane in the C–O stretching region.

by allowing it to stand in hexane overnight. The hexane was decanted, and the pale yellow crystals of the product were obtained by drying under vacuum; yield 0.175 g. (70%).

Anal. Calcd. for $(C_2H_5)N[Mn(CO)_4(CN)_2]$: C, 48.12; H, 5.78; N, 12.04. Found: C, 46.84; H, 6.03; N, 11.67.

The compound has solubility properties close to those of $(C_2H_5)_4N[Mn(CO)_4Br_2]$, but its solutions are considerably more stable to oxidation.

Infrared Spectra.—The frequencies recorded in Table I were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer equipped with NaCl optics using 0.5-mm. cells. The instrument was calibrated with a polystyrene standard. To check for further splitting of bands the spectra of $(C_2H_5)_4N[cis\text{-}Mn(CO)_4Cl_2]$ and $(C_2H_5)_4N[cis\text{-}Mn(CO)_4(CN)_2]$ were also obtained with a Beckman IR-7 spectrophotometer.[9]

Determination of Rates of Reaction.—The rate of reaction of $Mn(CO)_5I$ with $[(C_4H_9)_4N]I$ was determined by noting the rate of disappearance of the most intense C–O stretching absorption of $Mn(CO)_5I$. The rate constants were evaluated from first-order plots that were linear to at least 85% completion of the reaction. The general treatment of the data was the same as that reported earlier.[4] Qualitative observations of other rates were estimated from the rates of disappearance or appearance of prominent C–O stretching bands in the reactant or product. All species involved in the reactions were readily identified from their infrared spectra.

Results

The infrared spectra taken in the C–O stretching region of 1,2-dichloroethane solutions of the $R_4N[cis\text{-}Mn(CO)_4X_2]$ complexes are shown in Fig. 1 and Table I. The spectrum of $(C_2H_5)_4N[cis\text{-}Mn(CO)_4Cl_2]$ showed only four bands even on the higher resolution instrument. The broad absorption of $(C_2H_5)_4N[cis\text{-}Mn(CO)_4(CN)_2]$ at 1936 cm.$^{-1}$ showed some indefinite splitting under higher resolution, and this splitting was dependent upon the concentration of the solution. This suggests that strong ionic interactions in the relatively nonpolar solvent are responsible. The spectrum of this compound pressed into a KBr pellet showed five broad absorptions at 2143 (w), 2104 (m), 2087 (w), 2020 (s), and 1916 (s) cm.$^{-1}$. The broadness of these bands has covered up the 2005 cm.$^{-1}$ absorption, but the symmetry of the molecule has apparently not been altered. In contrast, the spectrum of $(C_2H_5)_4N[cis\text{-}Mn(CO)_4Br_2]$ in KBr shows five bands at 2095 (w), 2007 (s), 1990 (sh), 1932 (s), and 1912 (m) cm.$^{-1}$, which indicates that a change in symmetry has occurred in the crystalline state.

It was also observed that the intensities of the three high-frequency bands of $(C_2H_5)_4N[cis\text{-}Mn(CO)_4Br_2]$ decreased slightly as the solvent was changed from $CHCl_3$ to 1,2-dichloroethane. If this were due to isomerization to the *trans* form, one might expect such a spectral change. This, however, means that the *cis* isomer is favored by the least polar solvent, $CHCl_3$, which is not expected. In a solvent of even higher polarity, β,β'-dichloroethyl ether, the intensities of the bands were very close to those observed in $CHCl_3$. Together with the fact that changing the temperature from 25 to 40° produced no significant changes in intensities, the above observations suggest that specific solvent effects rather than *cis* to *trans* isomerization are responsible for these intensity variations.

Discussion

Infrared Spectra.—A group theoretical treatment of $[cis\text{-}Mn(CO)_4X_2]^-$ indicates that four C–O stretching modes $(2A_1 + B_1 + B_2)$ should be active in the infrared region. The *trans* isomer, on the other hand, would give rise to only one expected absorption. That the compounds do produce four absorptions (Fig. 1

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[9] For these measurements, the author thanks Miss Evelyn Conrad of Ames Laboratory.

and Table I) is very strong evidence supporting the *cis* assignment. The *cis* isomer would also be the expected isomer on the basis of π-bonding arguments, which suggest that a CO bonded *trans* to a poorly π-bonding ligand, such as a halide, would be in a more favorable position for participating in strong Mn–C π-bonding than if it were *trans* to another strongly π-bonding CO. The strong Mn–C bonds *trans* to the halides are apparently sufficient to favor this isomer over the *trans* form in which there is relatively weak Mn–C π-bonding for all the CO groups.

The four C–O stretching modes of [*cis*-$Mn(CO)_4X_2$]$^-$ are the symmetric (A_1^a) and antisymmetric (B_1) modes of the CO groups *trans* to each other and the symmetric (A_1^b) and antisymmetric (B_2) modes of the two CO groups *trans* to the X groups.[10] The two bands of lowest frequency in Fig. 1 have been assigned to the modes involving the CO groups *trans* to the X groups because force constants of CO groups *trans* to halides are considerably smaller than those of CO groups *trans* to each other.[10] This is presumably a result of increased Mn–C π-bonding in positions *trans* to halides. That the lowest frequency absorption has been assigned to the B_2 mode is consistent with the normal assignment of symmetric and antisymmetric vibrations of *cis* CO groups in metal carbonyls.[10,11]

The highest frequency band of lowest intensity can be readily assigned to the A_1^a mode,[11] leaving the B_1 mode for the next highest frequency absorption. The separation between the symmetric and antisymmetric vibrational modes of the *trans* CO groups is relatively constant (72–76 cm.$^{-1}$), as was earlier observed for $Mn(CO)_5X$, the separation being 81–84 cm.$^{-1}$ in that case.[10,12]

The above considerations therefore strongly favor the assignments given in Fig. 1. The high-frequency band of [*cis*-$Mn(CO)_4X_2$]$^-$, corresponding to the symmetric stretching mode (A_1^a) of vibration of the CO groups *trans* to each other, decreases in intensity as X is changed from I to Br to Cl. This phenomenon had been observed previously for the $Mn(CO)_5X$ compounds[13] and was attributed to the size of X. This explanation states that the symmetric vibration of CO groups *trans* to each other does not involve a change in dipole moment, and thus any intensity which this absorption might have is due to coupling with another allowed vibration having the same symmetry. As a result such symmetric modes generally have low intensities. However, if the *trans* CO groups can be bent away from their straight line relationship, there will be an over-all change in dipole moment. This bending can be accomplished by introducing a group on the metal which will repel CO groups *cis* to it. Thus in the case of [*cis*-$Mn(CO)_4X_2$]$^-$ the CO groups *trans* to each other would not lie on the same straight line if a bulky X were to repel them. Increasing the size of X would lead to a greater change of dipole moment and a greater observed intensity for the A_1^a absorption.

Although this explanation is quite reasonable for the A_1^a mode in [*cis*-$Mn(CO)_4X_2$]$^-$, it does not cast any light on why similar intensity changes occur in the A_1^b absorption. Because the A_1^b mode always involves a relatively large change in dipole moment and is thus infrared active, it is not obvious why the intensity of this band decreases with changes in X from I to Br to Cl.

The assignment of the absorption bands of [*cis*-$Mn(CO)_4(CN)_2$]$^-$ was made by comparing the positions and intensities of the observed bands with those of the halide complexes. After the CO frequencies were assigned, the two remaining bands at 2146 and 2087 cm.$^{-1}$ were attributed to the symmetric and antisymmetric stretching modes of the *cis* CN groups. This is consistent with the fact that C–N stretching vibrations generally occur at somewhat higher frequencies than C–O vibrations.[14] It might also be noted that the infrared spectrum of [*cis*-$Mn(CO)_4(CN)_2$]$^-$ does not indicate that Mn–CN bonding is drastically different from Mn–X bonding, as might be expected if CN^- were considered to be an extremely good π-bonding ligand.

It is interesting to compare frequencies of absorption of similar vibrational modes in [*cis*-$Mn(CO)_4I_2$]$^-$ and in *cis*-$Mn(CO)_4[P(C_6H_5)_3]I$. The symmetrical stretching mode (A′) of the CO groups *trans* to each other in the latter compound gives rise to an absorption at 2084 cm.$^{-1}$.[15] The absorption resulting from the analogous vibrational mode (A_1^a) in [*cis*-$Mn(CO)_4I_2$]$^-$ occurs at 2082 cm.$^{-1}$. The replacement of $P(C_6H_5)_3$ by I^- has not altered the frequency of this vibration to any significant extent. This suggests that the over-all charge on the complex has a relatively small influence on the absorption frequencies.

It had been shown previously that the T_{1u} mode of $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$ gave absorptions at 2096, 2000, and 1859cm. $^{-1}$.[16] Since the charge on the complex and the oxidation number of the metal were both changing across this series, it was not clear as to which was causing the rather large C–O stretching shifts. From the above results on [*cis*-$Mn(CO)_4I_2$]$^-$ and *cis*-$Mn(CO)_4[P(C_6H_5)_3]I$, it appears that the charge on the metal is primarily responsible.

If one compares the C–O stretching vibrational frequencies of [*cis*-$Mn(CO)_4I_2$]$^-$ and *cis*-$Fe(CO)_4I_2$ (bands at 2132, 2086, 2081, and 2063 cm.),[17] it can be seen that the $Fe(CO)_4I_2$ absorptions generally occur at higher frequencies. Since the over-all charge on the complex does not appear to exert a very large influence on the frequencies, it is quite likely that the shift to

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higher frequencies in $Fe(CO)_4I_2$ is due to the higher positive charge on Fe. The negative charge contributed by X^- to the complex is apparently not available for metal to CO π-bonding.

One might also expect the separation between the absorption bands, due to the symmetric and antisymmetric stretching modes of CO groups *trans* to each other, to be equal in $[cis\text{-}Mn(CO)_4I_2]^-$ and $cis\text{-}Mn(CO)_4[P(C_6H_5)_3]I$. The separation between the A_1^a and B_1 absorptions in $[cis\text{-}Mn(CO)_4I_2]^-$ is 76 cm.$^{-1}$. Since the four observed bands of $cis\text{-}Mn(CO)_4[P(C_6H_5)_3]I$ are at 2084 (m), 2021 (s), 2006 (s), and 1962 (s) cm.$^{-1}$, the absorption at 2006 (s) cm.$^{-1}$ is very likely that which corresponds to the antisymmetric stretching mode (A''). One can then quite readily assign the low-frequency band to the CO *trans* to I, leaving the 2021 cm.$^{-1}$ band to the CO *trans* to $P(C_6H_5)_3$.

Kinetics of Formation of $[cis\text{-}Mn(CO)_4X_2]^-$.—In order to determine the mechanism by which $[cis\text{-}Mn(CO)_4I_2]^-$ is formed from $Mn(CO)_5I$ and $[(C_4H_9)_4N]I$, the rate of reaction was followed by measuring the decrease of the most intense C–O absorption of $Mn(CO)_5I$. At 39.2°, 0.00746 *M* $Mn(CO)_5I$ and 0.0746 *M* $[(C_4H_9)N]I$ in $CHCl_3$ were found to react with a first-order rate constant of 1.53×10^{-5} sec.$^{-1}$. When the $[(C_4H_9)_4N]I$ concentration was increased to 0.224 *M*, the rate dropped slightly to 1.31×10^{-5} sec.$^{-1}$. Since the rate of formation of $[cis\text{-}Mn(CO)_4I_2]^-$ does not increase with increasing $[(C_4H_9)_4N]I$ concentration, the reaction probably occurs by a dissociative mechanism.

$$Mn(CO)_5I \xrightarrow{\text{slow}} Mn(CO)_4I + CO$$

$$Mn(CO)_4I + I^- \xrightarrow{\text{fast}} [cis\text{-}Mn(CO)_4I_2]^-$$

This is the same mechanism that was proposed for the reaction of $Mn(CO)_5X$ with such differing ligands as CO, PR_3, and aniline, all of which were found to react with $k = 1.71 \times 10^{-5}$ sec.$^{-1}$.[4]

The reaction with I^- is somewhat slower than that with these other ligands, and also the rate of reaction with I^- decreases slightly with increasing $[(C_4H_9)_4N]I$ concentration. These observations are consistent with studies which show that CO dissociates from $Mn(CO)_5X$ more slowly in polar solvents.[4] Thus increasing the concentration of ionic $[(C_4H_9)_4N]I$ increases the effective polarity of the solvent and reduces the rate. If the reaction mixture is allowed to remain at 39.0° for 10 days, there is no evidence that any further substitution of CO occurs. Although no quantitative study was made, $Mn(CO)_5Cl$ and $[(C_2H_5)_4N]Cl$ were found to react in CH_2Cl_2 to form $[cis\text{-}Mn(CO)_4Cl_2]^-$ at approximately the same rate as $Mn(CO)_5Cl$ and phosphines react to yield $cis\text{-}Mn(CO)_4LCl$.[4] It is assumed that all of the manganese pentacarbonyl halides react with halides by way of a dissociative mechanism.

Reactions of $[cis\text{-}Mn(CO)_4X_2]^-$.—The $[cis\text{-}Mn(CO)_4X_2]^-$ complexes in the presence of a very large excess of $P(C_6H_5)_3$ were found to undergo the following sequence of reactions.

$$[cis\text{-}Mn(CO)_4X_2]^- + P(C_6H_5)_3 \longrightarrow cis\text{-}Mn(CO)_4[P(C_6H_5)_3]X + X^- \quad (1)$$

$$cis\text{-}Mn(CO)_4[P(C_6H_5)_3]X + P(C_6H_5)_3 \longrightarrow trans\text{-}Mn(CO)_3[P(C_6H_5)_3]_2X + CO \quad (2)$$

Because reaction 2 was considerably slower than (1), it was possible to identify each product spectroscopically. It was noted in an earlier paper[4] that $cis\text{-}Mn(CO)_4[P(C_6H_5)_3]X$ with a relatively small excess of $P(C_6H_5)_3$ did not form $trans\text{-}Mn(CO)_3[P(C_6H_5)_3]_2X$, in which the $P(C_6H_5)_3$ groups are *cis* to X but *trans* to each other. In the present study this reaction did occur but very slowly. At about 25° in $CHCl_3$, reaction 2 took place with $t_{1/2} \sim 3$ days for X = Br. The huge excess of $P(C_6H_5)_3$ probably accounts for the fact that reaction 2 took place. In contrast to the halo complexes, there was no spectroscopic evidence for the formation of $trans\text{-}Mn(CO)_3[P(C_6H_5)_3]_2(CN)$ even after 4 weeks at the above conditions.

Reaction 1 went to completion in all cases except where X = CN. In $CHCl_3$ at 25° it did go to about 80% completion, however, and absorption bands of the product, $cis\text{-}Mn(CO)_4[P(C_6H_5)_3](CN)$, were distinguishable at 2118 (vw, CN stretch), 2097 (w), 2021 (vs), and 1981 (s) cm.$^{-1}$. No attempt was made to isolate the compound. The reaction took place very slowly ($t_{1/2} \sim 1$ week), while under the same conditions the reaction of $[cis\text{-}Mn(CO)_4I_2]^-$ with $P(C_6H_5)_3$ proceeded at $t_{1/2} \sim 10$ hr. With X = Br the analogous reaction proceeded with a half-life of less than 1 min. Since $(C_2H_5)_4N[Mn(CO)_4Cl_2]$ was insoluble in chloroform, its reaction with $P(C_6H_5)_3$ was carried out in 1,2-dichloroethane and took place with a half-life of about 30 min. One might have expected it to react faster than $[Mn(CO)_4Br_2]^-$, but the difference in solvents may account for this apparent anomaly. If one assumes that the replacement of X^- by $P(C_6H_5)_3$ occurs *via* a dissociative mechanism, one might expect Br^- to dissociate more readily than I^- since this trend has already been observed in the halogen exchange of $Mn(CO)_5Br$ and $Mn(CO)_5I$.[18] This interpretation means that CN^- is bonded much more strongly to Mn than any of the halides.

It had originally been hoped that a phosphine would displace CO from $[cis\text{-}Mn(CO)_4X_2]^-$. Since this was not possible with $P(C_6H_5)_3$, it seemed that a less bulky ligand such as $P(OCH_2)_3CCH_3$[19] might be more suitable for the formation of $[Mn(CO)_3LX_2]^-$. This reaction was attempted with $[cis\text{-}Mn(CO)_4I_2]^-$, but again only replacement of I^- occurred. In a further attempt to prepare $[Mn(CO)_3LX_2]^-$, $Mn(CO)_4[P(C_6H_5)_3]I$ and a large excess of $[(C_4H_9)_4N]I$ were allowed to react in dichloroethane. This resulted in the displacement of $P(C_6H_5)_3$ to form $[cis\text{-}Mn(CO)_4I_2]^-$.

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