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On Stereospecific Labeling of Some $Mn(CO)_5X$ Complexes

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Received January 18, 1971

The virtual equality of the rates of incorporation of labeled CO into the equatorial and axial positions in $Mn(CO)_5X$ (X = Cl, Br, and I) has been conclusively demonstrated.[2,3] More recently it was suggested[4] that this result may be attributed to an intramolecular pathway for equatorial–axial exchange which is rapid relative to the actual introduction of the label into $Mn(CO)_5X$ *via* dissociation. In order to test the validity of the above proposal we undertook the synthesis of stereospecifically labeled $Mn(CO)_5X$ complexes with a view to examining their possible rearrangements. Reported herein are the results of our investigation.

Experimental Section

Materials.—CO (51% ^{13}C enriched) was purchased from Merck Sharpe and Dohme, Ltd., Montreal Canada, whereas 61.2% ^{13}C-enriched $CH_3{}^{13}COONa$ was obtained from Prochem, Ltd., Croyden, England. Hydrogen iodide was prepared from tetrahydronaphthalene and iodine.[5] All solvents and other chemicals used were reagent grade or equivalent. Volatile substances were dried and purified by standard procedures. $Mn(^{12}CO)_5(^{13}COCH_3)$,[6] *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$,[6] $Mn(CO)_5Cl$,[7] $Mn(CO)_5Br$,[7] and $Mn(CO)_5(SO_2CH_3)$[8] were synthesized as described in the literature.

Reactions of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ with Br_2 and I_2.—A solution of 100 mg of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ in pentane was treated with 500 mg of Br_2 in pentane at room temperature and under nitrogen. The resultant mixture was stirred for 30 min and the precipitated $Mn(^{12}CO)_4(^{13}CO)Br$ was collected and washed with pentane. The yield was 102 mg (78%).

Similarly, $Mn(^{12}CO)_4(^{13}CO)I$ was prepared from *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ and I_2.

Reactions of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ with HBr and HI.—Gaseous HBr, dried by passage through a column of $CaSO_4$ and $CaCl_2$, was allowed to flow very slowly over finely powdered *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$, spread thinly to maximize the surface area in a round-bottom flask at room temperature. The passage of HBr was discontinued after the infrared spectrum of the solid showed a virtually complete conversion to $Mn(^{12}CO)_4(^{13}CO)Br$ (*ca.* 16 hr).

By a similar procedure, $Mn(^{12}CO)_4(^{13}CO)I$ was obtained from solid *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ and gaseous HI.

Exchange Reactions of Solid $Mn(CO)_5X$ (X = Cl and Br) with ^{13}CO.—Finely powdered $Mn(CO)_5X$ was spread thinly in a two-neck, 10-ml round bottom flask. The vessel was then evacuated, and ^{13}CO was admitted to a pressure of *ca.* 1 atm from the storage bulb. The bottom part of the flask was heated for 6–10 hr at 40–45°. $Mn(CO)_5X$ slowly sublimed onto the top part of the vessel which was maintained at room temperature. Infrared spectra of both the sublimate and the residue were recorded.

Reaction of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ with Liquid SO_2.—The reaction was carried out at reflux (−10°), as reported previously[8] for the unlabeled $Mn(CO)_5CH_3$.

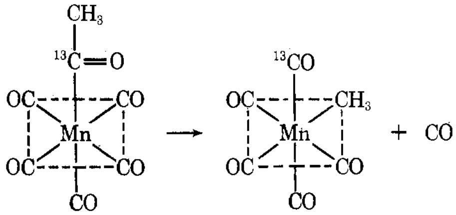
Infrared Spectra.—All spectra were recorded on a Beckman Model IR-9 spectrophotometer using spectroscopic grade carbon tetrachloride, hexane, or cyclohexane for solutions and Nujol for the mulls. A pair of matched 0.1-mm NaCl cells was employed for solution measurements. In recording the spectra of the sparingly soluble $Mn(CO)_5(SO_2CH_3)$ in CCl_4, the vertical-scale expansion mechanism of the instrument was used to obtain approximately a fourfold enlargement.

Results and Discussion

In considering the synthesis of *cis*-$Mn(^{12}CO)_4(^{13}CO)X$ (X = Br or I), we decided to employ the following sequence of reactions. Labeled CO was to be introduced through the interaction of $NaMn(^{12}CO)_5$ with $CH_3{}^{13}COCl$ to give $Mn(^{12}CO)_5(^{13}COCH_3)$ (eq 1).

$$NaMn(^{12}CO)_5 + CH_3{}^{13}COCl \longrightarrow Mn(^{12}CO)_5(^{13}COCH_3) + NaCl \quad (1)$$

Decarbonylation of this complex, as described by Noack and Calderazzo,[6] would afford almost exclusively the cis isomer of $Mn(^{12}CO)_4(^{13}CO)CH_3$ (eq 2). Electrophilic cleavage of the Mn–CH_3 bond of the latter with X_2 or HX should then yield $Mn(^{12}CO)_4(^{13}CO)X$ (eq 3). Success of the entire scheme hinged on the stereospecificity of reaction 3 which had not been investigated.



(2)

$$cis\text{-}Mn(^{12}CO)_4(^{13}CO)CH_3 + \underset{(HX)}{X_2} \longrightarrow Mn(^{12}CO)_4(^{13}CO)X + \underset{(CH_4)}{CH_3X} \quad (3)$$

The preparation of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ was readily achieved as reported in the literature.[6] Initial attempts at cleavage of the Mn–CH_3 bond were carried out by the addition of Br_2 or I_2 in pentane to a solution of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ in the same solvent. The resultant $Mn(^{12}CO)_4(^{13}CO)X$ (X = Br or I) precipitated from solution, thereby reducing any possibility of intramolecular rearrangement which would lead to positional scrambling of the labeled CO.

The infrared spectrum in the 2000-cm^{-1} region of the isolated $Mn(^{12}CO)_4(^{13}CO)Br$ in hexane solution is shown for reference in Figure 1. The Nujol mull spectrum is qualitatively similar but of much lower resolution. The assignment of bands follows that reported earlier by Kaesz, *et al.*[2] Absorption b is due entirely to *cis*-$Mn(^{12}CO)_4(^{13}CO)Br$ (A′ mode) and corresponds to the symmetric stretching of the equatorial CO groups in unlabeled $Mn(CO)_5Br$, whereas absorption g derives from the stretching of the axial carbonyl in *trans*-$Mn(^{12}CO)_4(^{13}CO)Br$ (A_1 mode). To elucidate the relative amounts of the two isomers a solution of unlabeled $Mn(CO)_5Br$ was prepared of such a concentration that the high-frequency A_1 band (a in Figure 1) was of the same intensity as absorption b in the spectrum of the isolated $Mn(^{12}CO)_4(^{13}CO)Br$. When this solution was diluted to one-fourth of its original concentration, the intensity of the low-energy

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[1] NSF summer Undergraduate Research Participant, 1970.

[2] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, **89**, 2844 (1967).

[3] B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *J. Chem. Soc. A*, 522 (1968).

[4] T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).

[5] C. J. Hoffman, *Inorg. Syn.*, **7**, 180 (1963).

[6] K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967); K. Noack, *ibid.*, **12**, 181 (1968).

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

[8] F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1504 (1968).

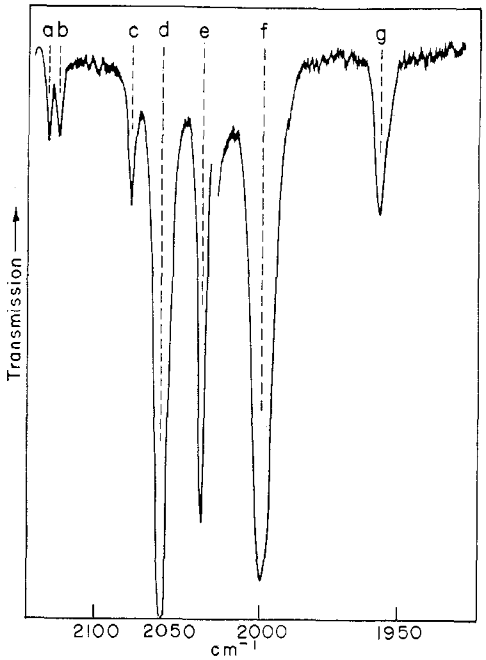

Figure 1.—Infrared spectrum in the carbonyl stretching region of $Mn(^{12}CO)_4(^{13}CO)Br$, obtained from the reaction of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ with Br_2, in hexane solution.

A_1 band (f in Figure 1) was found to be approximately the same as that of absorption g for $Mn(^{12}CO)_4(^{13}CO)Br$. Hence within the approximation that the absolute intensities of the corresponding infrared bands in $Mn(CO)_5X$ and $Mn(^{12}CO)_4(^{13}CO)X$ are equal,[9,10] the distribution of ^{13}CO among the five positions in $Mn(^{12}CO)_4(^{13}CO)Br$ appears to be statistical. A similar result was obtained for $Mn(^{12}CO)_4(^{13}CO)I$.

In an attempt possibly to prevent statistical scrambling of ^{13}CO we synthesized $Mn(^{12}CO)_4(^{13}CO)X$ by the reaction of solid *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ with gaseous HX (X = Br or I). Infrared spectra of these ^{13}CO-enriched pentacarbonyls, measured as Nujol mulls, were again qualitatively similar to the corresponding solution spectra, which showed random distribution of the labeled CO. Hence even in the solid there appears to be no detectable preference as concerns final occupancy of the two nonequivalent sites by ^{13}CO.

Since the above experiments failed to differentiate between the two likely stereochemical processes—(a) CO-randomizing electrophilic cleavage of the $Mn-CH_3$ bond or (b) stereospecific electrophilic cleavage followed by a rapid intramolecular rearrangement—we attempted to prepare *cis*-$Mn(^{12}CO)_4(^{13}CO)X$ (X = Cl or Br) by isotopic exchange of CO groups in powdered $Mn(CO)_5X$. However, no incorporation of ^{13}CO into the pentacarbonyls could be detected in the solid. At temperatures above 40°, statistical exchange occurred either on the surface or in gaseous $Mn(CO)_5X$, as evidenced by the infrared spectra of the sublimates.

In the light of these results the possibility of an intramolecular rearrangement in $Mn(CO)_5X$ remains an open problem. It is certainly not unreasonable to suggest that electrophilic cleavage of the $Mn-CH_3$ bond proceeds *via* a seven-coordinate intermediate, perhaps of the type $Mn(^{12}CO)_4(^{13}CO)(CH_3)H^+X^-$ or $Mn(^{12}CO)_4(^{13}CO)(CH_3)X^+X^-$, in which cis and trans carbonyls lose their positional identity. These species would then rapidly decompose with elimination of CH_4 or CH_3X to yield $Mn(^{12}CO)_4(^{13}CO)X$. The incidence of such a nonstereospecific pathway does not, of course, preclude structural nonrigidity of the resultant $Mn(^{12}CO)_4(^{13}CO)X$. Also noteworthy in this connection is a report[11] that cleavage of the M–C bond in $CH_3{}^*CH(CO_2CH_3)Mn(CO)_5$ with Br_2 proceeds with retention of configuration at the asymmetric carbon.

The ready availability of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ prompted an extension of this investigation to the sulfur dioxide insertion reaction (eq 4). The infrared

$$cis\text{-}Mn(^{12}CO)_4(^{13}CO)CH_3 + SO_2 \longrightarrow Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3) \quad (4)$$

spectrum of $Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$, obtained by using SO_2 at reflux, is shown in Figure 2; that of the unlabeled sulfinate is also reproduced for comparison. The relatively low solubility of $Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$ in CCl_4 may be responsible for a poorer resolution than that achieved with $Mn(^{12}CO)_4(^{13}CO)Br$. Nevertheless, one may with reasonable confidence assign the band at 2132 cm^{-1} (b in Figure 2) to the

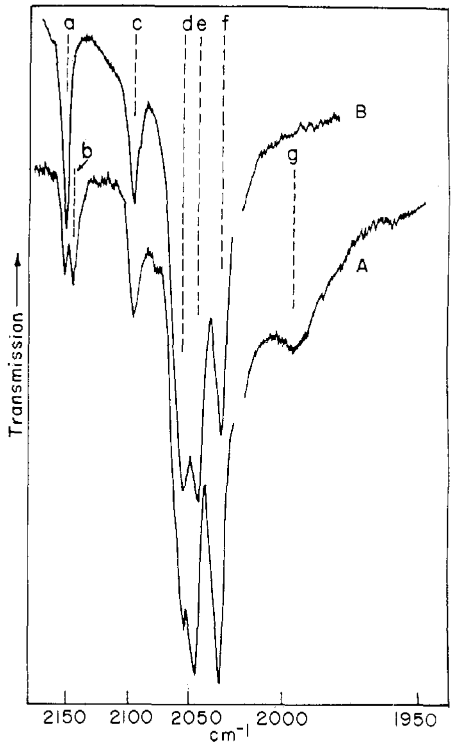

Figure 2.—Infrared spectra in the carbonyl stretching region of (A) $Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$, obtained from the reaction of *cis*-$Mn(^{12}CO)_4(^{13}CO)CH_3$ with liquid SO_2, and (B) $Mn(^{12}CO)_5(SO_2CH_3)$, both in CCl_4 solution.

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(9) Generally such an approximation is not valid, since the relative amounts of axial and equatorial symmetry modes in the two A_1 absorptions vary with ^{13}CO substitution. However, by using the relative intensities calculated by Kaesz, *et al.*[10] (I = 1.00 and 14.80 for the high- and low-energy A_1 bands for $Mn(^{12}CO)_5Br$, I = 1.33 for the highest energy A′ band for *cis*-$Mn(^{12}CO)_4(^{13}CO)Br$, and $I = 14.62 \times 10^4$ l. cm^{-2}/mol for the low-energy A_1 band for *trans*-$Mn(^{12}CO)_4(^{13}CO)Br$), we obtained results which are similar and do not affect our final conclusion. We thank a reviewer for bringing this point to our attention.

(10) P. S. Braterman, R. Bau, and H. D. Kaesz, *Inorg. Chem.*, **6**, 2097 (1967).

(11) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970).

highest energy A′ mode in *cis*-$Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$ and the shoulder at *ca.* 1995 cm^{-1} (g in Figure 2) to the ^{13}CO stretch in *trans*-$Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$. The relative intensities of these absorptions indicate that a substantial amount of *trans*-$Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$ is present in addition to the cis isomer. The Nujol mull spectrum of $Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$ is qualitatively similar to that recorded for the CCl_4 solution.

Again the observation of isotopic scrambling does not permit differentiation between a nonstereospecific mechanism for the insertion, on one hand, and a rapid isomerization following the initial stereospecific sulfonylation, on the other. An attempted exchange between the CO's in $Mn(CO_5)(SO_2CH_3)$ and ^{13}CO in CH_3OH at 27° revealed no detectable incorporation of labeled CO in 24 hr.

The above result stands in sharp contrast to that on the carbonylation of $Mn(CO_5)CH_3$ using ^{13}CO. Only *cis*-$Mn(^{12}CO)_4(^{13}CO)(^{12}COCH_3)$ is obtained in the latter insertion.[6] Also pertinent is the finding[12] that the reaction of SO_2 with optically active π-$C_5H_5Fe(CO)_2$-$^*CH(CH_3)C_6H_5$ proceeds with substantial stereospecificity as concerns the asymmetric carbon.

In conclusion, we infer from these observations that synthesis of stereospecifically labeled complexes of the type $Mn(CO)_5X$ (and perhaps also those of other, related systems)[12a] will present a very formidable and, in some cases, an impossible task. Whether the difficulty is inherent in a structural nonrigidity (in the context of experimental isolation) of at least some of these compounds, cannot be ascertained at present. A recent study on $HMn(CO)_5$ shows[13] that any rearrangement which possibly leads to equivalence of the cis and trans CO groups with respect to isotopic exchange must be a slow process on the nmr time scale. However, the ranges in time scales for nmr spectroscopy and experimental isolation of isomeric species[14] render this finding of limited applicability to preparative studies.

Acknowledgment.—Support of this work through grants from the National Science Foundation (GP-8135 and GP-22544) is gratefully acknowledged.

[12] J. J. Alexander and A. Wojcicki in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, New York, N. Y., 1968, pp 383–384.

[12a] NOTE ADDED IN PROOF.—$Mo(^{12}Co)_4(^{13}CO)NHC_5H_{10}$ preferentially labeled in the equatorial positions has been prepared by ultraviolet irradiation of $Mo(^{12}CO)_5NHC_5H_{10}$ and ^{13}CO in THF solution. See D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971).

[13] G. M. Whitesides and G. Maglio, *ibid.*, **91**, 4980 (1969).

[14] See, for example, E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

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Synthesis of Trifluorophosphazodifluorophosphine from Aminodifluorophosphine

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Received January 20, 1971

Aminodifluorophosphine, PF_2NH_2, has recently been prepared from the reaction of ammonia with difluorohalophosphines.[1] Also, microwave spectral data indicated that the hydrogen atoms attached to the nitrogen exchanged rapidly with deuterium atoms of deuterium oxide to form PF_2ND_2.[1] It has now been found that both hydrogen atoms of the amino group can also be removed when dichlorotrifluorophosphorane, PF_3Cl_2, is used as a substrate and trifluorophosphazodifluorophosphine, $F_3P{=}NPF_2$, chlorodifluorophosphine, and ammonium chloride are the products

$$2PF_2NH_2 + PF_3Cl_2 \longrightarrow F_3P{=}NPF_2 + PF_2Cl + NH_4Cl \quad (1)$$

If, instead, hydrogen chloride or hydrogen difluorodithiophosphate are employed, scission of the P–N bond occurs to yield the amino and difluorophosphine groups

$$PF_2NH_2 + 2HX \longrightarrow PF_2X + NH_4X \quad (2)$$

where X = Cl or $SP(S)F_2$.

Experimental Section

Reagents.—Aminodifluorophosphine[1] and hydrogen difluorodithiophosphate[2] were prepared by the literature methods. Phosphorus trifluoride and chlorine, in lecture bottles, were obtained from the Ozark-Mahoning Co. and the Matheson Co., respectively. The PF_3Cl_2 was prepared by direct combination of Cl_2 with a slight excess of PF_3, was purified by trap-to-trap distillation, and was retained at −126°. Lecture bottles of dimethylamine and hydrogen chloride were procured from the J. T. Baker Co.

Technique and Instrumentation.—All volatile substances were handled within a standard Pyrex-glass vacuum system. The reactor in all syntheses was a 100-ml Pyrex-glass bulb with a stopcock attached. Infrared spectra were obtained with a Perkin-Elmer Model 621 grating spectrometer. A 10-cm path length cell with sodium chloride windows was used for gaseous samples. The spectra of solids were obtained as Nujol mulls between sodium chloride plates. The ^{19}F and ^{31}P nmr spectra were obtained with a Varian Model HA-100 spectrometer, operating at 94.1 and 40.5 HMz, respectively. Fluorotrichloromethane (internal) and 85% orthophosphoric acid (external) were used as standards. Samples were measured in 5-mm o.d. tubes at ambient temperature. A Varian CH-7 mass spectrometer operating at 70 eV was used to obtain the mass spectrum.

Synthesis of $F_3P{=}NPF_2$.—This reaction took place after combining PF_2NH_2 (0.72 mmol) and PF_3Cl_2 (0.40 mmol) at −196° and allowing the reactor to warm slowly and stand 15 min at room temperature. The products were slowly passed through cold traps at −95, −126, and −196°. The −126° trap held the $PF_3{=}NPF_2$ (0.35 mmol, 97% yield based on eq 1) and the −196° trap contained the PF_2Cl, along with trace quantities of POF_3 and PF_3 (0.37 mmol total). Hydrogen chloride also in a small quantity is sometimes observed as a product held in the latter trap. The white solid remaining in the reactor was identified as ammonium chloride by its infrared spectrum.

Properties of $F_3P{=}NPF_2$.—Trifluorophosphazodifluorophosphine is a white solid, mp $-87.2 \pm 0.7°$, and colorless liquid, bp 12.5° (extrapolated). The temperature dependence of the vapor pressure follows the equation $\log P_{mm} = 8.114 - (1494/T)$, determined by least squares, having a "goodness of fit" correlation coefficient equal to 0.998 and the standard error equal to 0.0146. Some measured vapor pressures at specified temperatures are as follows: 8.7 mm, −62°; 22.0 mm, −52.3°; 55.1 mm, −38.0°; 97.2 mm, −28.6°. The latent heat of vaporization is 6837 cal mol^{-1} and entropy of vaporization is 23.9 eu. The equation and thermodynamic constants are valid between −19.7 and −52.3°. Its molecular weight by the method of Regnault using a 208.2-ml bulb was measured to be 170.5 (calcd 170.9).

The following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of $F_3P{=}NPF_2$: 171 ($PF_3NPF_2^+$), 38.7; 152 ($P_2F_4N^+$), 25.8; 102 (F_3PN^+), 54.8; 88 (PF_3^+), trace; 83 (F_3PN^+), 12.9; 69 (PF_2^+), 100; 64 (FPN^+),

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[1] J. E. Smith and K. Cohn, *J. Amer. Chem. Soc.*, **92**, 6185 (1970).

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