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THE INFRARED SPECTRA OF ISOTOPICALLY SUBSTITUTED METAL CARBONYLS

II*. SOME ^{13}CO- AND C^{18}O-SUBSTITUTED π-CYCLOPENTADIENYLMETAL CARBONYL COMPLEXES

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SUMMARY

All of the IR-active CO stretching absorptions present during the reactions of CpMn(CO)$_3$, CpMn(CO)$_2$(C$_8$H$_{14}$), CpMn(CO)$_2$CS, CpMn(CO)(CS)(C$_8$H$_{14}$), CpV(CO)$_4$, and CpCo(CO)$_2$ with ^{13}C- and/or ^{18}O-enriched CO in n-hexane solution have been assigned to modes of the all-^{12}C^{16}O molecules and the various isotopically enriched species produced in the reactions. The proposed vibrational assignments are supported by force constant calculations for the energy factored CO stretching blocks of the (FG) matrices. The chief product of the reaction of CpMn(CO)$_2$(C$_8$H$_{14}$) with 90% ^{18}O-enriched CO is CpMn(CO)$_2$(C^{18}O); the relative intensities of the three CO stretching absorptions for this species are approximately in the ratio 1/1/1, in agreement with a previous theoretical prediction. The CS group in CpMn(CO)$_2$CS is not replaced by carbon monoxide whereas both CO groups are exchanged. This observation suggests that CS is more strongly bonded to the manganese atom than are the CO groups.

INTRODUCTION

The vibrational spectra of π-cyclopentadienylmetal carbonyl complexes have been the subject of a number of investigations in recent years[2–6]. However, as yet, there have been no detailed studies on the spectra of ^{13}CO- or C^{18}O-enriched species. Moreover, what little work that has been done in this area has only provided conflicting results[3,4].

We now report the results of an IR spectroscopic study of the reactions of CpMn(CO)$_3$ (Cp=π-C$_5$H$_5$), CpMn(CO)$_2$(*cis*-cyclooctene), CpMn(CO)$_2$CS, CpMn(CO)(CS)(*cis*-cyclooctene), CpV(CO)$_4$, and CpCo(CO)$_2$ with ^{13}C- and/or ^{18}O-

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enriched CO. Apart from the intrinsic value of the spectra of the isotopically enriched molecules themselves, we were interested in determining the relative lability of the CO groups and the other ligands in these π-cyclopentadienylmetal carbonyl complexes. In addition, we hoped to validate the method of "local symmetry"[7] for the metal carbonyl moieties of the complexes by comparing the number of observed and calculated CO frequencies for the various isotopically substituted species.

EXPERIMENTAL

The following chemicals were obtained from the sources indicated: $CpMn(CO)_3$ (a gift from Ethyl Corporation); $CpV(CO)_4$ and $CpCo(CO)_2$ (Strem Chemicals); 50% ^{13}C-enriched CO (Merck, Sharpe, and Dohme of Canada Ltd.); 90% ^{18}O-enriched CO (Miles Laboratories Inc.); *cis*-cyclooctene (C_8H_{14}) (Eastman Kodak Chemical Co.).

The literature methods were used to prepare $CpMn(CO)_2(C_8H_{14})$[8], $CpMn(CO)_2CS$[9], and $CpMn(CO)(CS)(C_8H_{14})$[9].

The purity of all the π-cyclopentadienylmetal carbonyl complexes was established by the absence of any impurity peaks in their IR spectra; whenever necessary, the complexes were purified by vacuum sublimation (25°/0.01 mmHg).

^{13}C- and ^{18}O-enriched π-cyclopentadienylmetal carbonyl complexes

Under thermal conditions, the CO groups in π-cyclopentadienylmetal carbonyls are known to be relatively inert towards substitution[10]. Consequently, the ^{13}C- and ^{18}O-enriched species were prepared by UV light induced exchange of the carbonyl complexes with isotopically enriched CO at room temperature in freshly distilled spectrograde n-hexane or CS_2 solutions. The UV source was a Rayonet circular photochemical reactor equipped with up to 16 low-pressure mercury lamps emitting at 2537 Å. Cooling was provided by a fan mounted on the reactor. UV irradiation was unnecessary for the reactions of the *cis*-cyclooctene complexes, these reactions were carried out thermally. The general method used in all cases was similar to that described previously[1] except that for the UV light induced exchanges, the reaction vessel was constructed from quartz and was not blackened.

IR spectra

All spectra were recorded on a special slow-scanning Perkin-Elmer 337 grating IR spectrophotometer equipped with a Texas Instruments Servo/Riter model II expanded scale recorder. The spectra were calibrated against the 2143.2 cm^{-1} band of CO and the 1601.4 and 1583.1 cm^{-1} bands of polystyrene. The frequencies presented in Tables 1–5 are the mean values obtained from the spectra of at least 5 samples taken from the reaction mixtures during the reactions. The reproducibility of the frequencies is about ± 0.5 cm^{-1}, while their absolute precision is ± 1 cm^{-1}. The intensities quoted in the Tables are relative to the most intense band in the spectral region being considered: w, weak; m, medium; s, strong; v, very; (sh), shoulder.

Calculations

The idealized geometries and definition of the "approximate" force constants for the CO groups of $CpMn(CO)_3$, $CpMn(CO)_2CS$, $CpV(CO)_4$, and $CpCo(CO)_2$

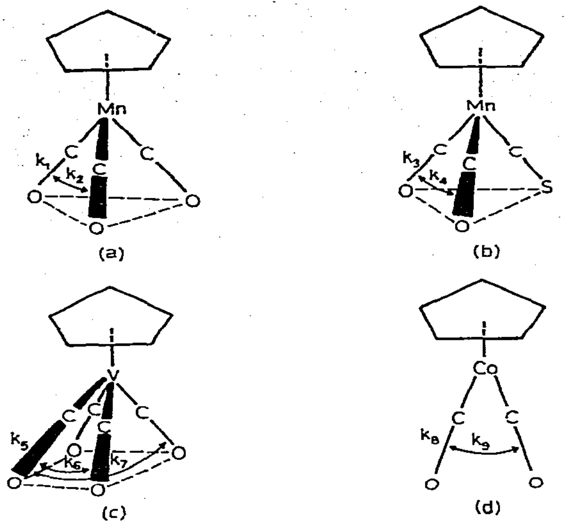

Fig. 1. Idealized geometries and definition of "approximate" force constants for (a) $CpMn(CO)_3$, (b) $CpMn(CO)_2CS$, (c) $CpV(CO)_4$, and (d) $CpCo(CO)_2$.

are shown in Fig. 1. The local symmetries and the internal C–O bond stretching symmetry coordinates for the all-$^{12}C^{16}O$ and the various isotopically substituted carbonyl-containing moieties are sketched in Fig. 2.

Optimum values of the CO force constants were calculated from the available data using the iterative computer program originally written by Schachtschneider and Snyder[11] and modified for use on an IBM 360/75 computer. In general, the observed CO stretching frequencies which were not used as input were predicted to within 4 cm^{-1} *i.e.*, within the error range expected when using frequencies uncorrected for anharmonicity[12] and the CO-factored force field[13].

RESULTS AND DISCUSSION

Assignment of the CO stretching frequencies observed during the reactions of the π-cyclopentadienylmetal carbonyl complexes with ^{13}CO and/or $C^{18}O$

(*a*). *$CpMn(CO)_3$ and $CpMn(CO)_2(C_8H_{14})$*. The $Mn(CO)_3$ moiety in $CpMn(CO)_3$ possesses C_{3v} local symmetry for which two IR-active CO stretching modes (A_1 and E) are expected (Fig. 2a). Substitution of one or two ^{13}CO (or $C^{18}O$) groups into the $Mn(CO)_3$ moiety lowers the symmetry to C_s for which three IR-active CO stretching modes ($2A'$ and A'') should be observed in both cases. The tri-substituted species has the same symmetry as the all-$^{12}C^{16}O$ moiety and so two IR-active CO stretching modes (A_1 and E) are expected for this species. It should be noted that the A'' vibration of mono-substituted species is identical to one component of the E mode of the all-$^{12}C^{16}O$ species; consequently, these should absorb at the same frequency. Similarly, the A'' mode of the di-substituted species and one component of the E mode of the tri-substituted species are expected to be degenerate.

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* The mathematical form of these symmetry coordinates and the associated secular equations are available from the authors on request.

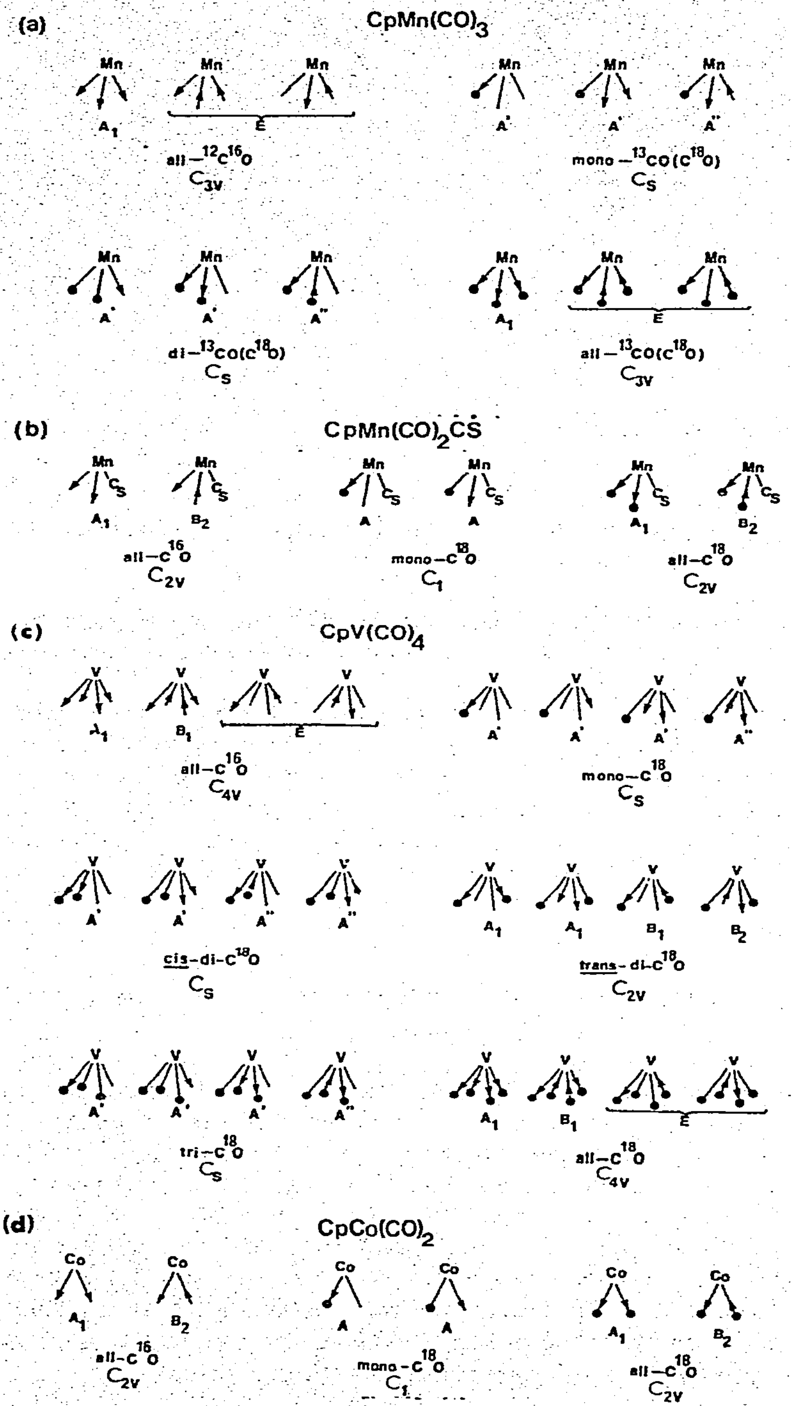

Fig. 2. Internal symmetry coordinates for the all-$^{12}C^{16}O$- and the ^{13}CO- and/or $C^{18}O$-substituted carbonyl-containing moieties of (a) CpMn(CO)$_3$, (b) CpMn(CO)$_2$CS, (c) CpV(CO)$_4$, and (d) CpCo(CO)$_2$. The position of ^{13}CO or $C^{18}O$ is indicated by a heavy dot.

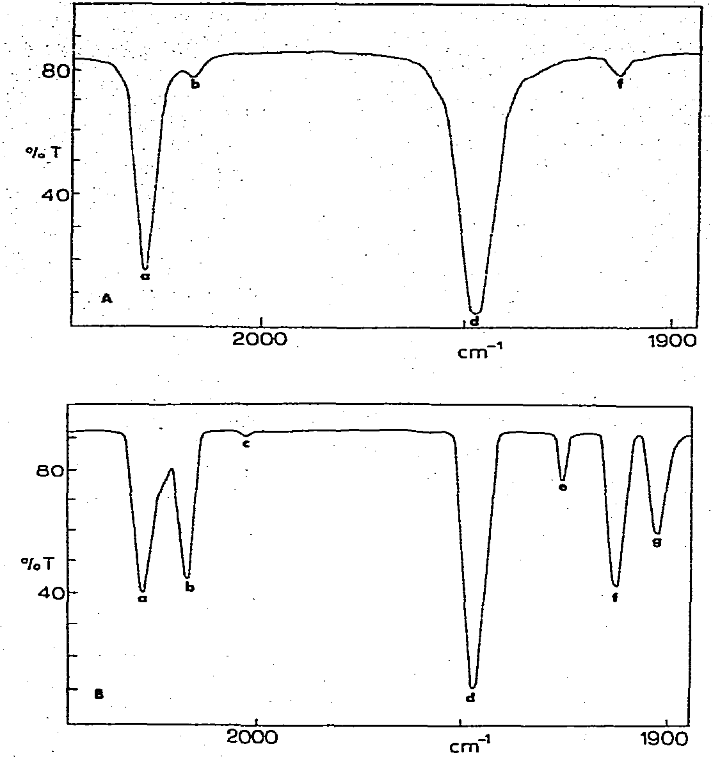

Fig. 3. IR spectrum in the CO stretching region of $CpMn(CO)_3$: (A) before and (B) after 15 min UV light (16 2537 Å lamps) induced exchange with 50% ^{13}C-enriched CO (n-hexane solution).

The CO stretching absorptions of $CpMn(CO)_3$ in n-hexane solution before and after UV light induced exchange with 50% ^{13}C-enriched CO are shown in Fig. 3. There is disagreement in the literature regarding the assignment of bands b and f. Haas and Sheline[3] have assigned them without any direct experimental proof to the two *A'* modes of the mono-substituted species present in natural abundance (3%) whereas Hyams *et al.*[4] prefer to assign them to overtone and/or combination vibrations. It is immediately evident from Fig. 3 that Haas and Sheline are correct in their assignment because bands b and f are greatly enhanced during the exchange with ^{13}CO. In addition, three new bands (c, e, and g) attributable to modes of the di-^{13}CO substituted species have appeared. The actual frequencies and the proposed vibrational assignments are given in Table 1.

Since a band at ca. 1983 cm^{-1} is not observed, it appears that little or none of the all-^{13}CO species is formed during the exchange reaction. This is not unexpected in view of the relatively low percent enrichment of the ^{13}CO used and the photochemical instability of $CpMn(CO)_3$ itself.

It may be mentioned in passing that the frequencies predicted for the di-^{13}CO substituted species, $CpMn(^{12}CO)(^{13}CO)_2$, by Haas and Sheline[3] are in excellent agreement (± 1 cm^{-1}) with those observed directly in the present work. This observation lends some credence to their method of calcuating approximate force constants for metal carbonyl complexes.

TABLE 1

COMPARISON OF CALCULATED AND OBSERVED CO STRETCHING FREQUENCIES (cm^{-1}) FOR ^{13}CO AND C^{18}O-SUBSTITUTED CpMn(CO)$_3$

Molecule and local symmetry	*Vib. species*	*Input*	*^{13}CO-Substituted*				*C^{18}O-Substituted*		
			Calcd.[a]	*Observed from*			*Calcd.*[a]	*Observed from CpMn(CO)$_2$(C$_8$H$_{14}$)*[d]	
				UV-induced exchange[b]		*CpMn(CO)$_2$(C$_8$H$_{14}$)*[c]			
All-^{12}C^{16}O	A_1	2028.4	2028.4	2028.$_4$ s	(a)	2028.$_4$ s	2028.4	2027.$_1$ vvw	(h)
C_{3v}	E	1947.2	1947.2	1947.$_2$ vs	(d)	[e]	1947.2	[e]	
Mono-	A'		2017.7	2017.$_5$ s	(b)	2017.$_6$ ms	2017.1	2018.$_1$ s	(i)
substitution	A'		1914.0	1912.$_4$ s	(f)	1912.$_8$ ms	1910.9	1913.$_6$ s	(n)
C_s	A''		1947.2	[f]		1947.$_2$ vs	1947.2	1946.$_8$ s	(l)
Di-substi-	A'		2004.4	2003.$_3$ w	(c)	2003.$_3$ vvw	2003.0	2004.$_7$ vvw	(j)
tution	A'		1926.7	1925.$_6$ m	(e)	1925.$_6$ vvw	1924.4	1923.$_9$ vw	(m)
C_s	A''		1903.9	1902.$_2$ ms	(g)	[g]	1900.3	[g]	
Tri-substitu-	A_1		1983.3				1979.5		
tion C_{3v}	E		1903.9				1900.3		

[a] Calculated force constants: $k_1 = 15.744$, $k_2 = 0.434$ mdyn/Å. [b] After 15 min with 50% ^{13}C-enriched CO in n-hexane solution. Band designation in parentheses refer to Fig.3. [c] After reaction for 1 week with 50% ^{13}C-enriched CO in n-hexane solution. [d] After reaction for 9 days with 90% ^{18}O-enriched CO in n-hexane solution. Band designations in parenthese refer to Fig.4. [e] Degenerate with A'' mode of mono-substituted molecule. [f] Degenerate with E mode of all-^{12}C^{16}O molecule. [g] Hidden beneath the very weak band (o) due to the B_2 mode of the small amount of unreacted CpMn(CO)$_2$(C$_8$H$_{14}$) remaining. The A_1 and B_2 modes of CpMn(CO)$_2$(C$_8$H$_{14}$) are at 1964.$_3$ (k) and 1905.$_2$ cm^{-1} (o), respectively; the modes associated with the mono-^{13}CO species present in natural abundance are at 1949.$_4$ and 1876.$_8$ cm^{-1} (Fig. 4A).

Angelici and Loewen[7] have shown that under kinetic conditions CpMn(CO)$_2$(C$_8$H$_{14}$) readily undergoes *cis*-cyclooctene substitution with PPh$_3$ in methylcyclohexane solution to form CpMn(CO)$_2$PPh$_3$. Consequently, it is reasonable to expect that CO might substitute into this olefin complex to give CpMn(CO)$_3$. To this end, the reactions of CpMn(CO)$_2$(C$_8$H$_{14}$) with ^{13}C- and ^{18}O-enriched CO in n-hexane solution at 40° were investigated. The CO stretching frequencies observed in these reactions and the proposed assignments are also presented in Table 1. The spectra before and after reaction with 90% ^{18}O-enriched CO are shown in Fig. 4. The data clearly indicate that CO at atmospheric pressure does indeed replace *cis*-cyclooctene in CpMn(CO)$_2$(C$_8$H$_{14}$) to form CpMn(CO)$_3$.

The CO stretching frequencies for ^{13}C- and ^{18}O-enriched CpMn(CO)$_3$ are almost identical (to within 2 cm^{-1}). Similar results have been obtained previously for a number of other ^{13}C- and ^{18}O-enriched metal carbonyl complexes, *e.g.*, *cis*-Fe(CO)$_4$I$_2$[1], Mn(CO)$_5$Br[14,15], and CoCl$_2$(CO)(PEt$_3$)$_2$[16]. This phenomenon is chiefly a consequence of the similarity of the reduced masses of ^{13}CO and C^{18}O but it is also due in part to coupling of the CO stretching modes with the low frequency metal–carbon stretching modes[16]. In any event, it now appears that C^{18}O can be used to verify the assignments of the modes of naturally-occurring ^{13}CO-substituted molecules with reasonable certainty. This is a useful piece of information because, at

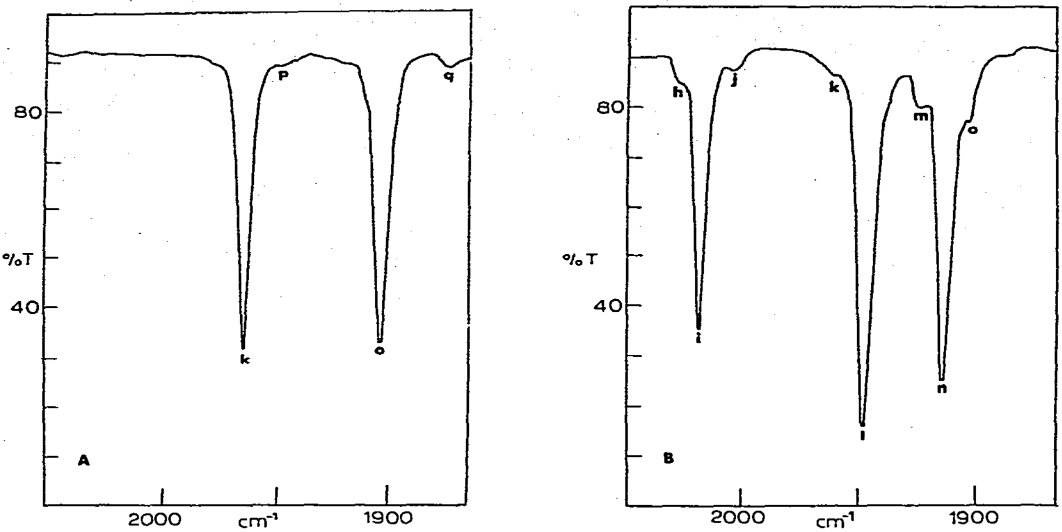

Fig. 4. IR spectrum in the CO stretching region of $CpMn(CO)_2(C_8H_{14})$: (A) before and (B) after reaction for 9 days with 90% ^{18}O-enriched CO at 40° (n-hexane solution).

present, $C^{18}O$ can be obtained commercially in a much higher percent enrichment than ^{13}CO thus enabling more definitive spectra to be recorded.

As expected, owing to the inertness of the CO groups in $CpMn(CO)_3$ towards exchange except under the influence of UV light, the product of the thermal reaction of $CpMn(CO)_2(C_8H_{14})$ with 90% ^{18}O-enriched CO is almost solely $CpMn(CO)_2(C^{18}O)$. There are also small amounts of $CpMn(CO)_3$, $CpMn(CO)(C^{18}O)_2$, and unreacted $CpMn(CO)_2(C_8H_{14})$ present. Some $CpMn(CO)_3$ is expected because the CO used was only 90% ^{18}O-enriched. It is also possible that part of the $CpMn(CO)_3$ was produced by the thermal decomposition of $CpMn(CO)_2(C_8H_{14})$*. Presumably, the di-$CO^{18}O$ substituted species is formed because of some slight enrichment of $CpMn(CO)_2(C_8H_{14})$ prior to replacement of the olefin by $C^{18}O$.

It is of interest to note that, in every $C^{18}O$ (or ^{13}CO) study on a metal carbonyl complex containing more than one CO group reported to date, it has not been possible to obtain the complete IR spectrum in the CO stretching region of a uniquely labelled species. For instance, in CO exchange reactions at least two CO groups are always

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* This complex decomposes in solution to form $CpMn(CO)_3$ and an unidentified brown precipitate. Our attempts to determine the mechanism of the reaction in methylcyclohexane solution were unsuccessful because the thermal decomposition does not proceed according to a simple rate law. Nevertheless, the reaction goes to completion and the yield of $CpMn(CO)_3$ (calculated from a Beer's law plot for its CO stretching band at 1946 cm^{-1}) represents about 50% of the concentration of the original $CpMn(CO)_2(C_8H_{14})$. Moreover, in view of the known mechanism for *cis*-cyclooctene replacement in the olefin complex by PPh_3[7], it seems likely that the mechanism of the thermal decomposition reaction involves steps such as:

$$CpMn(CO)_2(C_8H_{14}) \xrightarrow{slow} CpMn(CO)_2 + C_8H_{14}$$

$$CpMn(CO)_2 + CpMn(CO)_2(C_8H_{14}) \xrightarrow{fast} CpMn(CO)_3 + ?$$

Similar steps have been proposed for the thermal decomposition reactions of $Mo(CO)_5(C_5H_{10}NH)$ and *trans*-$Mn(CO)_3(PPh_3)_2X$ (X=halogen) to form $Mo(CO)_6$ and *cis*-$Mn(CO)_4(PPh_3)X$, respectively[17,18].

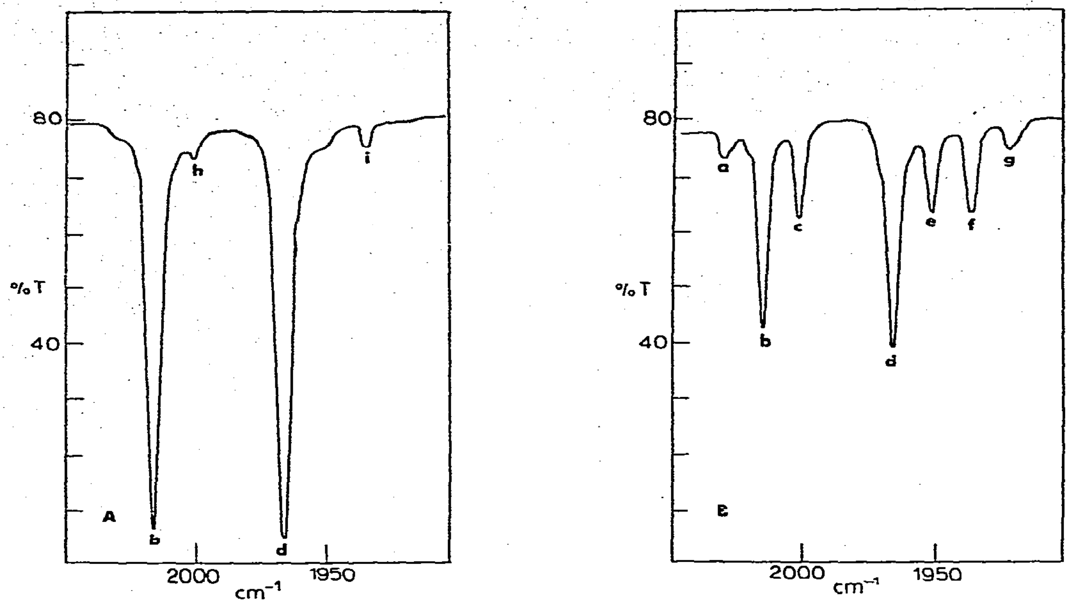

Fig. 5. IR spectrum in the CO stretching region of $CpMn(CO)_2CS$: (A) before and (B) after 5 min UV light (4 2537 Å lamps) induced reaction with 90% ^{18}O-enriched CO (n-hexane solution).

replaced and the resulting IR spectra consist of the spectra of various isotopically substituted species superimposed on the spectra of the parent molecules. In the present case, however, all three of the predicted CO stretching frequencies for $CpMn(CO)_2(C^{18}O)$ are observable directly (Fig. 4B). Moreover, bearing in mind that the intensity of the A'' mode (band l) is enhanced slightly because of degeneracy with the E mode of the small amount of $CpMn(CO)_3$ present, the relative intensities of bands i, l, and n are approximately in the ratio 1/1/1, as predicted theoretically by Haas and Sheline[3,*]. This is the first time that it has been possible to verify, even qualitatively, the calculated intensities of all the CO stretching modes of an isotopically substituted metal carbonyl species by direct experiment.

(*b*). *CpMn(CO)$_2$CS and CpMn(CO)$_2$(CS)(C$_8$H$_{14}$)*. Recently, we reported[9] the synthesis of the first thiocarbonyl complex of manganese, $CpMn(CO)_2CS$. The CS group in this complex is believed to be bonded to the manganese atom through the carbon atom in much the same way as are the CO groups. Furthermore, on the basis of a molecular orbital calculation for the CS molecule, Richards[19] considers that CS should be more strongly attached to a transition metal than is CO. Consequently, we felt that it would be of interest to study the reaction of $CpMn(CO)_2CS$ with ^{18}O-enriched CO to determine whether or not CO is replaced preferentially to CS.

The $Mn(CO)_2$ moiety in $CpMn(CO)_2CS$ has C_{2v} symmetry for which two IR-active CO stretching modes (A_1 and B_2) are expected. Substitution of one of the CO groups by $C^{18}O$ reduces the symmetry to C_1 for which two IR-active CO stretching

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[*] Strictly, their calculation was for the mono-^{13}CO substituted species. However, because the reduced masses of ^{13}CO and $C^{18}O$ are virtually identical and because the same force constants apply, the results of the calculation are also valid for the mono-$C^{18}O$ substituted species.

modes (2*A*) should be observed. Complete substitution by $C^{18}O$ returns the symmetry to C_1 for which two IR-active CO stretching modes (2 *A*) should be observed. Complete substitution by $C^{18}O$ returns the symmetry to C_{2v} and again two IR-active CO stretching modes (A_1 and B_2) are expected (see Fig. 2b).

As with most other π-cyclopentadienylmetal carbonyl complexes, $CpMn(CO)_2CS$ is inert towards thermal substitution. The CO stretching absorptions present before and after the UV light induced reaction of $CpMn(CO)_2CS$ with 90% ^{18}O-enriched CO in n-hexane solution are shown in Fig. 5. Continuation of the reaction for more than 5 min results in complete decomposition of the complexes present in the reaction mixture, despite the fact that 4 lamps, instead of the usual 16 [*c.f.* $CpMn(CO)_3$], were used to induce the reaction. The measured CO stretching frequencies and the proposed vibrational assignments are given in Table 2.

Bands c and f are attributable to $CpMn(CO)(C^{18}O)CS$. The actual frequencies are in excellent agreement (±1 cm^{-1}) with those for bands h and i which are assigned to the corresponding ^{13}CO modes of $CpMn(CO)(^{13}CO)CS$ present in natural abundance (2%). The formation of $CpMn(CO)_3$ (bands a and e) is the result of photochemical decomposition of $CpMn(CO)_2CS$ rather than replacement of CS by $C^{16}O$ present in the 90% ^{18}O-enriched CO. This was demonstrated by irradiating $CpMn(CO)_2CS$ by itself in n-hexane solution; the amount of $CpMn(CO)_3$ formed was approximately the same as that in the reaction with ^{18}O-enriched CO.

At first sight, it seems impossible to say whether or not $CpMn(CO)_2(C^{18}O)$ and $CpMn(C^{18}O)_2CS$ are present. The former should exhibit CO absorptions at 2018, 1947, and 1914 cm^{-1} (Table 1), these could be associated with bands b, e, and g, respectively. The thiocarbonyl species, $CpMn(C^{18}O)_2CS$, is expected to absorb at about 1964 and 1915 cm^{-1}, these bands could possibly be associated with bands d and g. The solution to the problem hinges on whether or not it should be possible under the experimental conditions employed to differentiate between the *A'* mode of

TABLE 2

ASSIGNMENT OF THE CO STRETCHING FREQUENCIES OBSERVED AFTER REACTION OF $CpMn(CO)_2CS$ WITH 90% ^{18}O-ENRICHED CO IN n-HEXANE SOLUTION

ν(CO) (cm⁻¹)			*Assignment*	
Obs.[a]	*Band designation (Fig 5)*	*Calcd.*[b]	*Molecule*	*Vib. species and local symmetry*
2027.$_7$ w	(a)	2028.$_4$[c]	$CpMn\ (CO)_3$	$A_1\ (C_{3v})$
2012.$_5$ s	(b)	2012.5	$CpMn(CO)_2CS$	$A_1\ (C_{2v})$
1998.$_5$ m[d]	(c)	1997.9	$CpMn(CO)\ (C^{18}O)\ CS$	$A\ (C_1)$
1962.$_3$ s	(d)	1962.3	$CpMn(CO)_2CS$	$B_2\ (C_{2v})$
		1964.0	$CpMn(C^{18}O)_2CS$	$A_1\ (C_{2v})$
1946.$_7$ m	(e)	1947.$_2$[c]	$CpMn(CO)_3$	$E\ (C_{3v})$
1931.$_1$ m[d]	(f)	1929.0	$CpMn(CO)\ (C^{18}O)CS$	$A\ (C_1)$
1917.$_8$ w	(g)	1915.0	$CpMn(C^{18}O)_2CS$	$B_2(C_{2v})$

[a] After 5 min UV light induced reaction. [b] The frequencies for the $C^{18}O$ derivatives of $CpMn(CO)_2CS$ were calculated using the frequencies of the parent complex at 2012.5 and 1962.3 cm^{-1} as input; the calculated force constants are: $k_3 = 15.951$, $k_4 = 0.403$ mdyn/Å. [c] Observed frequencies (see Table 1). [d] The corresponding ^{13}CO modes (bands h and i in Fig. 5A) are at 1997.$_9$ and 1930.$_5$ cm^{-1}, respectively.

$CpMn(CO)_2(C^{18}O)$ at 2018 cm^{-1} and the A_1 mode of $CpMn(CO)_2CS$ at 2013 cm^{-1}. Fortunately, as it will be shown shortly, the absorptions due to these modes can be resolved in the reaction of $CpMn(CO)(CS)(C_8H_{14})$ with ^{18}O-enriched CO. This means that $CpMn(CO)_2(C^{18}O)$ is *not* formed in the reaction of $CpMn(CO)_2CS$ with $C^{18}O$. Moreover, the presence of band g indicates that the di-$C^{18}O$ substituted species, $CpMn(C^{18}O)_2CS$, is formed.

The observed shift in the B_2 modes of $CpMn(CO)_2CS$ and $CpMn(C^{18}O)_2CS$ is 44.5 cm^{-1} *i.e.*, very close to the expected value of 47.2 cm^{-1}. That the exact shift expected is not observed for vibrations of totally ^{13}CO- or $C^{18}O$-substituted species has been explained by coupling of the CO stretching modes with the low frequency metal–carbon stretching modes[16].

The fact that both $CpMn(CO)(C^{18}O)CS$ and $CpMn(C^{18}O)_2CS$ are produced whereas $CpMn(CO)_2(C^{18}O)$ is not implies that, under the influence of UV light, rupture of the Mn–CO bonds in $CpMn(CO)_2CS$ is favoured over the rupture of the Mn–CS bond. This result can be taken as being in accord with Richards' prediction[19] mentioned earlier.

The reaction of $CpMn(CO)(CS)(C_8H_{14})$ with ^{18}O-enriched CO has also been investigated. The CO stretching frequencies observed after the thermal reaction at 45° in n-hexane solution together with the proposed vibrational assignments are presented in Table 3. This reaction is much more complex than the analogous reaction of $CpMn(CO)_2(C_8H_{14})$ with ^{18}O-enriched CO discussed in section (*a*) above.

Since $CpMn(CO)(CS)(C_8H_{14})$ is known to react with PPh_3 in methylcyclohexane solution to form $CpMn(CO)(CS)PPh_3$[20], the chief product expected from the reaction with ^{18}O-enriched CO is $CpMn(CO)(C^{18}O)CS$. A little $CpMn(CO)_2CS$

TABLE 3

ASSIGNMENT OF THE CO STRETCHING FREQUENCIES OBSERVED AFTER REACTION OF $CpMn(CO)(CS)(C_8H_{14})$ WITH 90% ^{18}O-ENRICHED CO IN n-HEXANE SOLUTION

ν(CO) (cm^{-1})	*Assignment*		
Obs.[a]	*Molecule*	*Vib. species and local symmetry*	*Previously obs. freq. (cm^{-1})*[b,c]
$2027._8$ w	$CpMn(CO)_3$	$A_1(C_{3v})$	$2028._4$
$2017._5$ ms	$CpMn(CO)_2(C^{18}O)$	$A'(C_s)$	$2018._1$
$2011._9$ m	$CpMn(CO)_2CS$	$A_1(C_{2v})$	$2012._5$
$1997._9$ s	$CpMn(CO)(C^{18}O)CS$	$A\ (C_1)$	$1998._5$
$1961._3$ ms	$CpMn(CO)_2CS$	$B_2(C_{2v})$	$1962._3$
	$CpMn(CO)_2(C_8H_{14})$	$A_1(C_{2v})$	$1964._3$
$1946._3$ vs	$CpMn(CO)_3$	$E(C_{3v})$	$1947._2$
	$CpMn(CO)_2(C^{18}O)$	$A''(C_s)$	$1946._8$
$1932._3$s	$CpMn(CO)(C^{18}O)CS$	$A\ (C_1)$	$1931._1$
$1913._8$ ms	$CpMn(CO)_2(C^{18}O)$	$A'(C_s)$	$1913._6$
$1904._0$ vw	$CpMn(CO)_2(C_8H_{14})$	$B_2(C_{2v})$	$1905._2$

[a] After reaction for 19 h at 45°. [b] See Tables 1 and 2. [c] The single mode (*A*) associated with $CpMn(CO)(CS)(C_8H_{14})$ occurs at $1957._9$ cm^{-1}.

should also be produced. However, in addition to these products, the following species can be identified from their IR-active CO stretching absorptions: $CpMn(CO)_3$ (bands a and f), $CpMn(CO)_2(C^{18}O)$ (bands b, f, and h), a small amount of $CpMn(CO)_2(C_8H_{14})$ (band i ; the other absorption expected is hidden beneath band e). Extensive decomposition also occurs during the reaction, as evidenced by the copious amount of brown precipitate formed. These results emphasize that $CpMn(CO)(CS)(C_8H_{14})$ is much more thermally unstable than $CpMn(CO)_2(C_8H_{14})$*. Presumably, the amount of $C^{18}O$ present in the n-hexane solution is insufficient to stabilize all of the highly reactive intermediate, CpMn(CO)(CS), which is formed by the slow dissociation of C_8H_{14} from $CpMn(CO)(CS)(C_8H_{14})$[20]. Similar results are obtained for the reaction of $CpMn(CO)(CS)(C_8H_{14})$ with PPh_3 when the latter is not in excess; extensive decomposition occurs with $CpMn(CO)_3$, $CpMn(CO)_2CS$, $CpMn(CO)_2PPh_3$, and a brown precipitate being formed as well as the expected product, $CpMn(CO)(CS)PPh_3$.

(*c*). *$CpV(CO)_4$*. Recently, Durig *et al.*[5] have proposed vibrational assignments for the IR and Raman spectra of $CpV(CO)_4$ in terms of the local symmetries of the Cp and $V(CO)_4$ moieties. Of particular interest to the work being discussed here is the fact that these authors were able to assign unequivocally the two IR-active (A_1 and E) and the solitary Raman-active (B_1) CO stretching modes of the C_{4v} $V(CO)_4$ moiety. Substitution of one of the four equivalent CO groups in the $V(CO)_4$ moiety by $C^{18}O$ will lower the symmetry to C_s for which four IR-active CO stretching modes ($3A'$ and A'') are expected. The next $C^{18}O$ molecule can substitute either *cis* or *trans* to the first. The local symmetry of the *cis* species is C_s; four IR-active CO stretching modes ($2A'$ and $2A''$) should be observed for this species. The *trans* species possesses C_{2v} symmetry and should also have four IR-active CO stretching modes ($2A_1$, B_1 and B_2). Tri-substitution by $C^{18}O$ gives a species of symmetry C_s for which four IR-active CO stretching modes ($3A'$ and A'') are expected. Finally, total substitution returns the symmetry to the original C_{4v} for which two IR-active (A_1 and E) and one Raman-active (B_1) CO stretching modes should be observed (see Fig. 2c). It should be noted that the A'' vibrations of the mono- and tri-$C^{18}O$ substituted species will be degenerate with one component of the E vibrations of the all-$C^{16}O$ and all-$C^{18}O$ molecules, respectively.

The IR spectral changes occurring in the CO stretching region during the UV light induced exchange of $CpV(CO)_4$ in n-hexane solution with 90% ^{18}O-enriched CO are shown in Fig. 6. It is evident from the high frequency region in Figs. 6B and 6C (bands a, c, f, l, and n) that the four CO groups in $CpV(CO)_4$ are exchanged extremely rapidly; the half-life for the exchange of one CO group being less than 1 min. The reaction reaches equilibrium after 30 min. However, the A_1 and E modes of $CpV(C^{18}O)_4$ are easily identified as the absorptions at 1985.2 (band n) and 1886.4 cm^{-1} (band o), respectively, from the observed shifts (ca. 45 cm^{-1}) from the modes of the same symmetry for $CpV(C^{16}O)_4$. All the frequencies observed during the exchange and the proposed vibrational assignments are given in Table 4. The data clearly indicate that all of the possible $C^{18}O$-substituted species are formed during the reaction.

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* In methylcyclohexane solution at 70°, the rate for the thermal decomposition of $CpMn(CO)(CS)(C_8H_{14})$ [to form $CpMn(CO)_3$, $CpMn(CO)_2CS$, and a brown precipitate] is approximately four times faster than that for the thermal decomposition of $CpMn(CO)_2(C_8H_{14})$ [to form $CpMn(CO)_3$ and a brown precipitate].

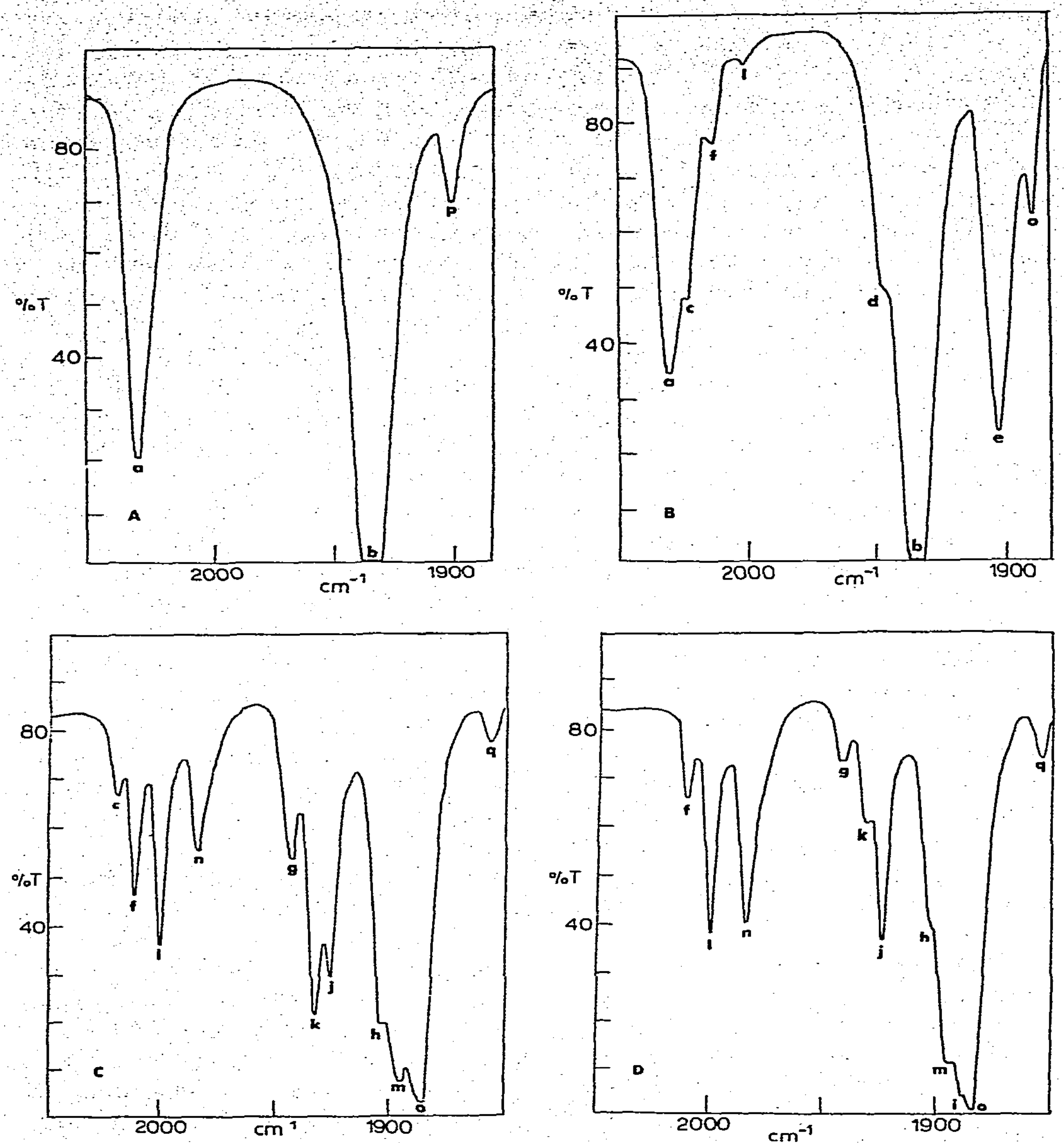

Fig. 6. IR spectrum in the CO stretching region of CpV(CO)$_4$: (A) before, (B) after 1 min, (C) after 10 min, and (D) after 30 min UV light (16 2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (n-hexane solution).

In their study of CpV(CO)$_4$, Durig *et al.*[5] assigned a weak absorption in the solid-state Raman spectrum at 1960 cm^{-1} to the A_1 CO stretching mode of CpV-(^{13}CO)$_4$. However, this assignment must be incorrect because only the mono-^{13}CO substituted species will be present in any significant amount (4% natural abundance). It is possible that the 1960 cm^{-1} band is due to the A' mode of CpV(CO)$_3$(^{13}CO) which is expected at ca. 1950 cm^{-1}. Alternatively, it could be a combination of the A_1

TABLE 4

COMPARISON OF OBSERVED AND CALCULATED CO STRETCHING FREQUENCIES FOR $C^{18}O$-SUBSTITUTED $CpV(CO)_4$

Molecule and local symmetry	*Vib. species*	$\nu(CO)$ (cm^{-1})			
		Obs.[a]	*Band designation (Figs. 6A–6D)*	*Input*	*Calcd.*[b]
All–$C^{16}O$	A_1	$2028._4$	(a)	2028.4	2028.4
C_{4v}	B_1	[c,d]			1959.2
	E	$1932._2$	(b)	1932.2	1932.6
Mono-$C^{18}O$	A'	$2021._9$	(c)		2020.0
substitution	A'	~1946 (sh)	(d)		1953.2
C_s	A'	$1900._9$[e]	(e)		1899.6
	A''	[f]			1932.6
Di-$C^{18}O$	A'	$2012._6$	(f)		2009.6
cis-substitution	A'	$1944._0$	(g)		1949.3
C_s	A''	$1904._9$	(h)		1903.6
	A''	~1891 (sh)	(i)		1895.6
Di-$C^{18}O$	A_1	[g]			2011.7
trans-substitution	A_1	$1926._5$	(j)		1928.0
C_{2v}	B_1	[h]			1886.0
	B_2	$1933._4$	(k)		1932.7
Tri-$C^{18}O$	A'	$2001._3$	(l)		1998.2
substitution	A'	[i]			1928.9
C_s	A'	$1895._7$	(m)		1897.8
	A''	[h]			1886.0
All-$C^{18}O$	A_1	$1985._2$	(n)		1979.5
C_{4v}	B_1	[c]			1912.0
	E	$1886._4$	(o)	1886.4	1886.0

[a] From spectra taken over a 30 min period after UV light initiation of the reaction in n-hexane solution. [b] Calculated force constants: $k_5 = 15.569$, $k_6 = 0.279$, $k_7 = 0.488$ mdyn/Å. [c] Raman-active only. [d] Observed at 1954 cm^{-1} in cyclohexane solution[5]. [e] The corresponding ^{13}CO mode (band p in Fig. 6A) occurs at $1899._5$ cm^{-1}. [f] Degenerate with the E mode of the all-$C^{16}O$ molecule. [g] Coincident with the highest frequency A' mode of the *cis*-di-$C^{18}O$ molecule. [h] Degenerate with the E mode of the all-$C^{18}O$ molecule. [i] Coincident with the lower frequency A_1 mode of the *trans*-di-$C^{18}O$ molecule.

ring breathing mode at 1117 cm^{-1} with the A_1 out-of-plane C–H deformation at 838 cm^{-1}.

The calculated frequency for the B_1 CO stretching mode of $CpV(CO)_4$ is 1959.2 cm^{-1} (Table 4), in good agreement with that observed by Durig *et al.*[5] at 1954 cm^{-1} in the Raman spectrum in cyclohexane solution. This supports Bor's claim[20] as to the utility of force constant calculations employing IR data from ^{13}CO and $C^{18}O$ exchange reactions in predicting the frequencies of IR-inactive fundamentals of a parent molecule.

A new band (q) appears at 1857 cm^{-1} after the exchange reaction has proceeded for 10 min (Fig. 6C). This band is still present when the exchange reaction has reached equilibrium (Fig. 6D). It cannot be due to a $C^{18}O$-substituted $CpV(CO)_4$ species because the lowest frequency expected (and observed) is ca. 1886 cm^{-1}. Most probably this 1857 cm^{-1} band is due to a combination vibration that was previously hidden in the case of the all-$C^{16}O$ molecule but, because of the isotopic shift associated with $C^{18}O$, has now become observable.

(*d*). *$CpCo(CO)_2$*. The local symmetry of the $Co(CO)_2$ moiety in $CpCo(CO)_2$ is C_{2v} *i.e.*, the same as that for the $Mn(CO)_2$ moiety in $CpMn(CO)_2CS$. Consequently, the spectra expected for these two molecules and their $C^{18}O$ substituted derivatives should be very similar. The various modes expected for the $Co(CO)_2$ moiety are illustrated in Fig. 2d.

The CO stretching frequencies observed before and after 10 min UV light induced exchange of $CpCo(CO)_2$ with 90% ^{18}O-enriched CO in n-hexane solution are listed in Table 5 together with the proposed vibrational assignments. Both $C^{16}O$ groups are replaced by $C^{18}O$.

TABLE 5

COMPARISON OF OBSERVED AND CALCULATED CO STRETCHING FREQUENCIES FOR $C^{18}O$-SUBSTITUTED $CpCo(CO)_2$

Molecule and local symmetry	*Vib. species*	*$\nu(CO)(cm^{-1})$*			
		Obs.[a,b]	*Band designation*	*Input*	*Calcd.*[c]
All-$C^{16}O$	A_1	$2029._8$	(a)	2029.8	2029.8
C_{2v}	B_2	$1970._4$	(b)	1970.4	1970.4
Mono-$C^{18}O$ substitution[d]	A	$2015._7$ m	(c)		2014.0
C_1	A	$1941._2$ m	(d)		1938.0
All-$C^{18}O$	A_1	$1987._0$ s	(e)		1980.9
C_{2v}	B_2	$1927._7$s	(f)		1922.9

[a] After 10 min UV light induced reaction with 90% ^{18}O-enriched CO in n-hexane solution; bands a and b no longer present. [b] The corresponding modes after 30 min UV light induced reaction with 90% ^{18}O-enriched CO in CS_2 solution are at: $2024._5$ (a), $1963._2$ (b), $2009._5$ (c), $1934._8$ (d), $1981._2$ (e), and $1919._9$ (f) cm^{-1}, respectively. [c] Calculated force constants: $k_8 = 16.157$, $k_9 = 0.480$ mdyn/Å. *d* The corresponding ^{13}CO modes are at $2014._7$ and $1938._9$ cm^{-1}, respectively.

The extent of the exchange reaction is affected by the nature of the solvent. In n-hexane solution, the reaction had reached equilibrium after 10 min; however, in CS_2 solution, the reaction has still not reached equilibrium after 30 min despite the fact that identical experimental conditions were employed. Moreover, in the case of the latter reaction, the absorptions due to the parent species are still present. The reason for carrying out the exchange reaction in CS_2 as well as in n-hexane solution was to see if there were any noticable changes in the low frequency region (below 700 cm^{-1}) of the IR spectrum. However, no significant changes could be detected. In retrospect, this is not unreasonable in view of the small shifts (< 5 cm^{-1}) found recently[21] for the low frequency modes of $Ni(C^{16}O)_4$ and $Ni(C^{18}O)_4$.

CONCLUSION

It has been demonstrated that the method of local symmetry[7] can be used successfully to predict the IR spectra of the various isotopically substituted derivatives of $CpMn(CO)_3$, $CpMn(CO)_2CS$, $CpV(CO)_4$, and $CpCo(CO)_2$. The stereochemical equivalence of the CO groups in each of these complexes has been confirmed by these spectra. Under the influence of 2537 Å UV irradiation, the CS group in $CpMn(CO)_2CS$ appears to be more strongly bonded to the manganese atom than are the two CO groups. Finally, as has been noted previously[22], the CO-factored force field employing data from isotopic substitution can be used to accurately predict the vibrational frequencies of ^{13}CO- and $C^{18}O$-substituted metal carbonyl complexes.

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