THE VIBRATIONAL SPECTRA OF ISOTOPICALLY SUBSTITUTED METAL CARBONYLS

V*. C¹⁸O-SUBSTITUTED *cis*-Mn(CO)₄LBr (L = PPh₃, AsPh₃, SbPh₃)**

I.S. BUTLER* and H.K. SPENDJIAN

Department of Chemistry, McGill University, P.O. Box 6070, Station A, Montreal, Quebec (Canada) H3C 3G1

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Summary

The reactions of *cis*-Mn(CO)₄LBr (L = PPh₃, AsPh₃, SbPh₃) with 96% ¹⁸O-enriched CO in cyclohexane solution at 35°C have been investigated by IR spectroscopy in the ν(CO) region and the vibrational modes of the parent molecules and the various C¹⁸O-substituted species produced have been assigned with the aid of approximate force field calculations for the energy-factored CO stretching blocks of the (*FG*) matrices. The IR data for the reaction of the triphenylphosphine complex indicate that, while all four carbonyl groups are eventually replaced by C¹⁸O, there is initially a stereochemical preference for axial CO substitution. For the other two complexes, both carbonyl and L substitution take place.

Introduction

In recent years, IR spectra have been reported for the CO stretching modes of complexes of the type *cis*-Mn(CO)₄LX (L = monodentate ligand; X = Cl, Br, I) [2-5]. As expected for C_s symmetry, four IR-active ν(CO) modes ($3a' + a''$) are usually observed for these complexes. The proposed assignments are exemplified by those given by Angelici [4] for *cis*-Mn(CO)₄(PPh₃)I: 2084 (a', axial CO groups); 2021 (a', equatorial CO group *trans* to PPh₃); 2006 (a'', axial CO groups); and 1962 cm⁻¹ (a', equatorial CO group *trans* to I) (CCl₄ solution)***. More recently, from both IR and Raman evidence, Bigorgne et al. [6] have proposed similar assignments for *cis*-Mn(CO)₄(PH₃)I in terms of C_{2v} local symmetry. How-

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* Part IV, see ref. 1.
** Taken in part from the Ph.D. thesis of H.K.S., McGill University, 1970.
*** The terms "axial" and "equatorial" refer to the CO groups in positions 1 and 2, and 3 and 4, respectively, in Fig. 1.

ever, from our own studies, solution Raman data are exceedingly difficult to obtain for other cis-Mn(CO)$_4$LX derivatives owing to their decomposition upon subjection to laser excitation.

Another approach that has proven useful in verifying the assignments of the ν(CO) modes of metal carbonyls is the study of the IR spectra of isotopically enriched species. For example, the CO exchange reactions of Mn(CO)$_5$Br [7,8] and cis-Fe(CO)$_4$I$_2$ [9,10] with ^{13}CO and C^{18}O have been monitored by IR spectroscopy and all the ν(CO) bands observed have been assigned with the aid of approximate force field calculations.

We now report the results of such an IR spectroscopic study in the CO stretching region of the thermal reactions of cis-Mn(CO)$_4$LBr (L = PPh$_3$, AsPh$_3$, SbPh$_3$) with 96% ^{18}O-enriched CO in cyclohexane solution. Apart from the intrinsic value of the spectra of the isotopically enriched species themselves and their use in assigning the fundamentals of the parent molecules, we were also interested in seeing if there was any evidence for stereospecific carbonyl substitution such as that reported recently for Cr(CO)$_4$(o-Phen) (o-Phen = o-phenanthroline) [11], Mn(CO)$_5$Br [12,13] and Re(CO)$_5$Br [13].

Experimental

The cis-Mn(CO)$_4$LBr complexes were prepared and purified by the literature method [2]. The IR spectra were recorded on a Perkin—Elmer Model 337 spectrophotometer coupled to a Texas Instruments Servo/Riter Model II expanded scale recorder and were calibrated with CO gas and polystyrene film (accuracy ±1 cm^{-1}).

^{18}O-Enriched samples of cis-Mn(CO)$_4$LBr were prepared by exchange in spectrograde cyclohexane solution at 35°C with 96% ^{18}O-enriched CO (Miles Laboratories, Elkhart, Indiana, U.S.A.). The experimental procedure for the exchange reactions has been described previously [10].

Calculations

The cis-Mn(CO)$_4$LBr complexes possess the C_s geometry shown in Fig. 1. Using the Cotton—Kraihanzel approximation [14], seven independent force constants are required to construct the force field; these force constants are also defined in Fig. 1. A normal coordinate treatment provides the following symmetrized F matrices (eqns. 1 and 2) which are used in the secular equation. The force constant calculations were carried out as described previously [10].

$$F_{a'} = \begin{vmatrix} k_1 + k_t & \sqrt{2}k_c & \sqrt{2}k_{c'} \\ & k_2 & k_{c''} \\ & & k_3 \end{vmatrix} \tag{1}$$

$$F_{a''} = k_1 - k_t \tag{2}$$

Results and discussion

cis-Mn(CO)$_4$(PPh$_3$)Br

The exchange reaction of cis-Mn(CO)$_4$(PPh$_3$)Br with C^{18}O proceeded to
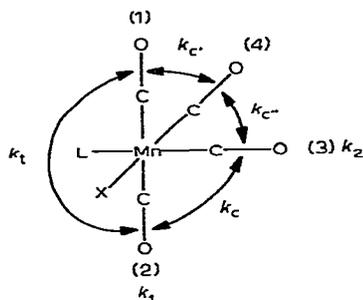
Fig. 1. Idealized geometry and definition of the Cotton—Kraihanzel force constants for cis-Mn(CO)₄LX molecules (L = monodentate ligand, X = halogen).

equilibrium much faster than did the reactions for the other two complexes. The IR-active CO stretching frequencies observed for the reaction mixture at various times are given in Table 1 together with their relative intensities. Some typical spectra are shown in Fig. 2. A number of conclusions are immediately evident from these data.

(1) The bands appearing between 2080 and 2040 cm^{-1} (bands b-f) must all be isotopic vibrations associated with the parent fundamental at 2089.2 cm^{-1} (band a) because no other parent fundamentals are observed above 2023.6 cm^{-1} (band g).

(2) The band at 1919.3 cm^{-1} (band k) must be a derivative of the parent fundamental at 1960.2 cm^{-1} (band j) since this gives an isotopic shift of 41.1 cm^{-1}, while for the next closest fundamental at 2006.0 cm^{-1} (band h), the shift would be 87.7 cm^{-1}. This latter shift is far too great because the maximum shift predicted by the Teller—Redlich product rule for bands ca. 2000 cm^{-1} is ~45 cm^{-1} [8].

(3) The band at 1979.4 cm^{-1} (band i) must arise from either band g or h, the respective isotopic shifts being 44.2 and 22.6 cm^{-1}. Both of these shifts are

TABLE 1

OBSERVED IR SPECTRA IN THE CO STRETCHING REGION AND RELATIVE INTENSITIES FOR THE REACTION OF cis-Mn(CO)₄(PPh₃)Br WITH 96% ^{18}O-ENRICHED CO IN CYCLOHEXANE SOLUTION AT 35°C

ν(CO) (cm^{-1})	Time (min)											Band designation
	0	3	11	20	28	39	55	74	122	180	260	
2089.2	vs	vs	m	mw	w	w	w	w	vw	vw	vvw	a
2077.0		w	m	m	m	m	m	m	m	mw	mw	b
2063.0			w	m	m	m	m	m	m	mw	mw	c
2053.6					vvw	mw	m	m	m	m	mw	d
2048.7										vw	w	e
2042.6										vw	w	f
2023.6	vs	vs	vs	s	s	ms	ms	ms	ms	m	m	g
2006.0	vvs	vs	vs	s	s	ms	ms	ms	ms	ms	ms	h
1979.4		m	s	s	s	s	s	s	s	s	s	i
1960.2	vs	vs	vs	vs	vs	vs	vs	vs	vs	s	s	j
1919.3		vw	w	m	m	ms	ms	ms	ms	ms	ms	k

TABLE 2

ASSIGNMENT OF THE CO STRETCHING FREQUENCIES OBSERVED DURING THE REACTION OF cis-Mn(CO)$_4$(PPh$_3$)Br WITH 96% ^{18}O-ENRICHED CO IN CYCLOHEXANE SOLUTION AT 35°C

| ν(CO) (cm^{-1}) | | | Assignment | |
Obsd.	Calcd.[a]	Band design.[b]	Posn. of C^{18}O substn.[c]	Vib. species and local symmetry
2089.2	2089.1	a	All-C^{16}O	a' (C_s)
	2084.8		3	a' (C_s)
	2082.5		4	a' (C_s)
	2078.2		3,4	a' (C_s)
2077.0	2077.1	b	1	a (C_1)
	2071.2		1,3	a (C_1)
	2069.7		1,4	a (C_1)
	2063.4		1,3,4	a (C_1)
2063.0	2062.2	c	1,2	a' (C_s)
2053.6	2053.5	d	1,2,4	a' (C_s)
2048.7	2050.8	e	1,2,3	a' (C_s)
2042.6	2038.7	f	1,2,3,4	a' (C_s)
2023.6	2023.6	g	All-C^{16}O; 4	a' (C_s)
	2021.7		1 and 1,4	a (C_1)
	2010.7		1,2	a' (C_s)
	2007.8		1,2,4	a' (C_s)
2006.0	2006.0	h	All-C^{16}O; 3; 4; 3,4	a'' (C_s)
	1989.9		1,3	a (C_1)
	1985.5		1,3,4	a (C_1)
	1984.2		3	a' (C_s)
	1980.7		3,4	a' (C_s)
1979.4	1979.4	i	1	a (C_1)
	1974.9		1,2,3	a' (C_s)
	1974.8		1,2,3,4	a' (C_s)
	1974.6		1,4	a (C_1)
	1970.1		1,3	a (C_1)
	1969.6		1,3,4	a (C_1)
1960.2	1960.5	j	All-C^{16}O	a' (C_s)
	1957.7		1,2; 1,2,3; 1,2,4; 1,2,3,4	a'' (C_s)
	1955.2		3	a' (C_s)
	1952.0		1	a (C_1)
	1950.6		1,2	a' (C_s)
	1950.1		1,3	a (C_1)
	1948.9		1,2,3	a' (C_s)
1919.3	1919.3	k	4	a' (C_s)
	1917.6		3,4	a' (C_s)
	1916.3		1,4	a (C_1)
	1915.0		1,3,4	a (C_1)
	1914.4		1,2,4	a' (C_s)
	1913.3		1,2,3,4	a' (C_s)

[a] Associated force constants: $k_1 = 16.698$, $k_2 = 16.646$, $k_3 = 15.882$, $k_t = 0.450$, $k_c = 0.189$, $k_c' = 0.501$, $k_c'' = 0.356$ mdyn/A^{-1}. [b] See Table 1. All but bands d, e and f were used as input for the force constant calculation. [c] See Fig. 1.

acceptable and so we cannot at this stage make any decision as to the origin of band i.

(4) Bands b, i and k are most probably all due to mono-C^{18}O substituted species as they are the first new bands to appear.

From previous studies on the IR spectra of metal carbonyls [15], the highest
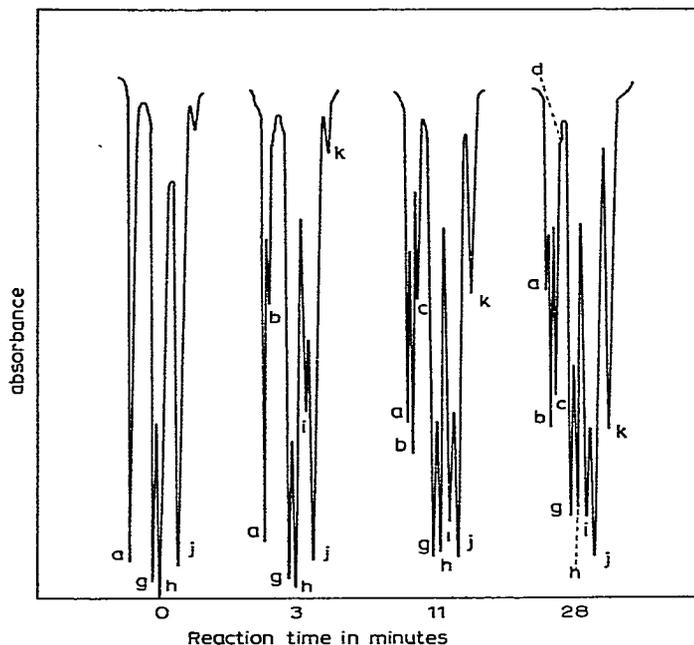
Fig. 2. IR spectrum in the CO stretching region of *cis*-Mn(CO)$_4$ (PPh$_3$)Br at various times during the CO exchange with 96% ^{18}O-enriched CO at 35°C (cyclohexane solution). The frequencies of the labelled bands are given in Table 1.

frequency band (band a) can be assigned to the a' in-phase stretching of the axial CO groups. That this is an a' vibration is supported by the appearence of a strong-ly polarized band at 2090 cm^{-1} in the CHCl$_3$ solution Ramah spectrum of the complex*.

The pattern of increase and decrease in absorbance of bands a, b and c with respect to one another clearly suggests that a sequence of substitution re-actions was taking place. While band a is the a' fundamental associated with the two axial CO groups, bands b and c are presumably the fundamentals associated with the corresponding in-phase CO stretchings of the mono-C^{18}O and di-C^{18}O derivatives, respectively. The isotopic frequency shifts, viz., 12.2 and 26.2 cm^{-1}, respectively, would be in accord with this suggestion [8].

An examination of the relative intensities of bands g and h during the ex-change reaction also leads to some qualitative conclusions concerning the assign-ment of the parent fundamentals. Initially, band h is more intense than band g, but after only 11 min, band g is slightly more intense and this situation persists until, in the spectrum taken after 39 min, the intensities are approximately equal and from then on the original intensity order is restored. Band i increases in in-tensity at a very fast rate which is not matched by the decrease in intensity of band g; therefore, band i is believed to be derived from the fundamental at 2006.0 cm^{-1} (band h). From a qualitative comparison of the very fast initial rates of disappearence of bands a and h and the rates of appearence of their iso-

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* Owing to extensive sample decomposition, this was the only distinct Raman band of *cis*-Mn(CO)$_4$-(PPh$_3$)Br which could be observed (Coherent Radiation Ltd., Kr$^+$ laser, 647.1 nm excitation ($\sim$30 mW); Jarrell—Ash model 25-300 laser Raman spectrometer).

topic bands b and i, it seems that all of these bands are associated with carbonyl groups in equivalent positions, viz., the two axial ones. Therefore, we assign band h to the a'' fundamental of the parent carbonyl complex. Even when band a has virtually disappeared, band h still has an appreciable intensity. This is most probably due to the fact that certain of the isotopic vibrations associated with the fundamental at 2023.6 cm^{-1} (band g) are accidentally degenerate with the a'' mode. This suggestion will be confirmed later by the approximate force field calculation.

The assignment of band h to the a'' parent fundamental also explains the intensity variations discussed above. The initial higher intensity of band h compared to that of band g is reversed when the two axial CO groups exchange faster than the two equatorial CO groups. When exchange equilibrium is reached for the two axial CO groups band h stops decreasing in intensity, while band g continues to decrease in intensity until the exchange of the carbonyl group giving rise to it also reaches equilibrium, thus accounting for the restoration of the original intensity order.

By elimination, bands g and j must therefore be the a' modes of the CO groups *trans* to either PPh$_3$ or Br. Unfortunately, no distinction can be made on the basis of the isotopic exchange data, and it is necessary to invoke the argument (e.g., ref. 14) that the CO group *trans* to a halogen is expected to have the lowest force constant in order to differentiate between the two assignments. On this basis, band g is attributed to the a' vibration of the CO group *trans* to PPh$_3$, while band j is assigned to the a' vibration of the CO group *trans* to Br. That the intensity of band j remains virtually unchanged until well into the reaction can be explained by two factors: (*i*) the rate of disappearance of this band is expected to be slower than that of the other parent bands because the CO group *trans* to Br is more strongly attached to the central metal than are the other CO groups; (*ii*) modes of some of the C^{18}O substituted species may be accidentally degenerate with it.

In conclusion, the assignments proposed here for the CO stretching fundamentals of *cis*-Mn(CO)$_4$(PPh$_3$)Br are 2089.2 (a', axial CO groups), 2023.6 (a', equatorial CO group *trans* to PPh$_3$), 2006.0 (a'', axial CO groups) and 1960.2 cm^{-1} (a', equatorial CO group *trans* to Br). These assignments also provide support for those mentioned earlier for the closely related molecule, *cis*-Mn(CO)$_4$-(PPh$_3$)I [4].

An approximate force field calculation was carried out to verify the assignments proposed for the parent CO stretching fundamentals and those of the C^{18}O-substituted derivatives (Table 2). Eight of the observed frequencies were used as input to calculate the seven force constants; the eight frequencies chosen were those which could be assigned with the greatest confidence, viz., bands a, b, c, g, h, i, j and k. Those frequencies which were not used as input were predicted to within 3.9 cm^{-1}. This is quite reasonable in view of the fact the observed frequencies were not corrected for anharmonicity and that a CO-factored force field was employed. The calculation also confirms that, as suggested earlier, the 1,2-di-C^{18}O and 1,2,4-tri-C^{18}O substituted species should have absorptions close to the parent fundamental at 2006.0 cm^{-1} (band h) (at 2010.7 and 2007.8 cm^{-1}, respectively) thus accounting for its lack of intensity change during the later stages of the CO exchange reaction.

TABLE 3

OBSERVED AND CALCULATED IR SPECTRA IN THE CO STRETCHING REGION OF cis-Mn(CO)$_4$-LBr (L = AsPh$_3$, SbPh$_3$) AND SOME OF THEIR C^{18}O-SUBSTITUTED DERIVATIVES PRODUCED BY CO EXCHANGE WITH 96% ^{18}O-ENRICHED CO IN CYCLOHEXANE SOLUTION AT 35°C

Molecule and Symmetry	Vib. assign.	ν(CO) (cm^{-1})			
		cis-Mn(CO)$_4$(AsPh$_3$)Br^{a,b}		cis-Mn(CO)$_4$(SbPh$_3$)Br^{b,c}	
		Obsd.	Calcd.	Obsd.	Calcd.
Unsubstituted	a'	2088.3	2088.2	2084.7	2084.7
C_s	a'	2019.3	2019.3	2018.3	2018.3
	a'	1959.6	1959.6	1957.5	1957.5
	a''	2008.3	2008.3	2006.7	2006.7
Mono-C^{18}O	a	2075.7	2075.8	2072.8	2072.8
in posn. 1	a		2017.8		2016.5
C_1	a	1978.3	1978.3	1975.2	1975.2
	a		1954.4		1953.8
Mono-C^{18}O	a'		2083.9		2079.0
in posn. 3	a'		1985.1	1984.4	1984.4
	a'		1949.4	1948.4	1948.3
C_s	a''		2008.3		2006.7
Mono-C^{18}O	a'		2082.9		2080.6
in posn. 4	a'		2018.6		2017.7
	a'	1917.9	1917.9	1914.6	1914.6
C_s	a''		2008.3		2006.7

^{a} Calculated force constants using all observed bands as input: k_1 = 16.715, k_2 = 16.540, k_3 = 15.823, k_t = 0.465, k_c = 0.201, k_c' = 0.426, k_c'' = 0.423 mdyn A^{-1}. Also observed and used as input was a band at 2060.0 cm^{-1} attributed to the 1,2-di-C^{18}O substituted molecule (C_s symmetry); this a' mode was calculated at 2059.9 cm^{-1}. ^{b} Mn(C^{16}O)$_4$(C^{18}O)Br modes observed at 2050.3 and 1996.2 cm^{-1}. ^{c} Calculated force constants using all observed bands except 1948.4 cm^{-1} as input: k_1 = 16.718, k_2 = 16.572, k_3 = 15.720, k_t = 0.458, k_c = 0.237, k_c' = 0.360, k_c'' = 0.415 mdyn A^{-1}.

One important result of the reaction of the triphenylphosphine derivative with C^{18}O is that since band a disappears much faster than band g, while band appears appreciably faster than band k, it seems that there is most probably a stereochemical preference for substitution in the axial positions*. Somewhat similar stereochemical preferences have been described previously for the thermal CO exchange reactions of Cr(CO)$_4$(o-Phen) [11], Mn(CO)$_5$Br [12,13] and Re-(CO)$_5$Br [13] with labelled CO.

cis-Mn(CO)$_4$(AsPh$_3$)Br and cis-Mn(CO)$_4$(SbPh$_3$)Br

In the reactions of the triphenylarsine and triphenylstibine derivatives with ^{18}O-enriched CO, the IR spectra of the reaction mixtures indicated that another

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* In the IR spectrum of a concentrated solution of the parent complex, the ratio of the absorbances of the satellite bands at 2077.1 and 1919.3 cm^{-1} due to the axially and equatorially (position 4) mono-^{13}CO substituted species (present in natural abundance), respectively, is approximately 0.2. Owing to the similarity of the reduced masses of ^{13}CO and C^{18}O, and the fact that the interoscillator angles θ and the calculated dipole moment derivatives μ_i' from the two independent CO exchange studies on Mn(CO)$_5$Br by Kaesz et al. (^{13}CO) [7] and Johnson et al. (C^{18}O) [8] are virtually identical, the same absorbance ratio would be expected for bands b and k of the corresponding mono-C^{18}O substituted species. However, after, for example, 11 min, the observed ratio is 2.0 indicating a greater percent enrichment in the axial positions.

reaction apart from the expected CO exchanges was taking place. A careful exam·ination of the new $\nu(CO)$ bands revealed that this reaction was the formation of isotopically labelled $Mn(CO)_5Br$ by replacement of the $AsPh_3$ and $SbPh_3$ ligands with carbon monoxide (e.g., see eqn. 3)*. Fortunately, Johnson et al. [8] have assigned the IR spectra in the $\nu(CO)$ region of ^{18}O-enriched $Mn(CO)_5Br$ so that

$$cis\text{-}Mn(C^{16}O)_4LBr + C^{18}O \begin{cases} \rightarrow Mn(C^{16}O)_3(C^{18}O)LBr + CO \\ \rightarrow Mn(C^{16}O)_4(C^{18}O)Br + L \end{cases} \tag{3}$$
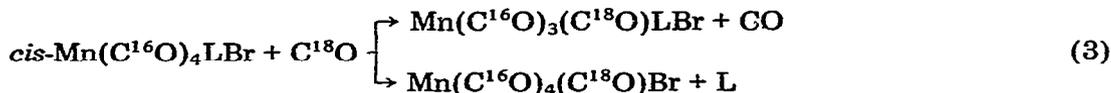
we could readily identify those frequencies belonging to the ^{18}O-enriched cis-$Mn(CO)_4LBr$ species produced during the exchange reactions**. These frequencies and the proposed assignments based on approximate force field calculations are shown in Table 3. The assignments exactly parallel those given earlier for the triphenylphosphine derivative except that fewer data were obtained owing to the slower CO exchange rates of the triphenylarsine and triphenylstibine complexes.

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* A brief kinetic study of the reaction of cis-$Mn(CO)_4(SbPh_3)Br$ with CO to form $Mn(CO)_5Br$ was carried out under pseudo-first-order conditions in cyclohexane solution at 35°C by monitoring the rate of appearance of the product band at 2051 cm^{-1} in the IR spectra of the reaction mixtures. Assuming that the rates are independent of CO concentration, as is usually true of the substitution reactions of most first-row transition metal carbonyl complexes [16,17], the rate of dissociation of the $SbPh_3$ ligand is 1.6×10^{-4} sec^{-1} ($t_{1/2} \simeq 72$ min). At 40°C in s-tetrachloroethane solution, the rate of dissociation of one CO group in the reaction with $P(n\text{-}OBu)_3$ is 5.1×10^{-5} sec^{-1} ($t_{1/2} \simeq 225$ min) [2].

** In one case, a larger scale reaction of cis-$Mn(CO)_4(SbPh_3)Br$ (50 mg) with $C^{18}O$ was stopped after 1 h and, following solvent removal in a stream of N_2, the volatile metal carbonyl material in the residue was sublimed (30°C/0.05 Torr) on to a cold-finger. The IR spectrum of the sublimate in cyclohexane solution exhibited $\nu(CO)$ bands characteristic of mono-$C^{18}O$ substituted $Mn(CO)_5Br$, viz., 2070, 2051, 2019, 1996 and 1957 cm^{-1}. The values predicted by Johnson et al. [8] are 2075.3, 2051.8, 2021.2, 1998.4 and 1959.1 cm^{-1}, respectively. Unfortunately, the limited amount of sample precluded us from observing the weak bands predicted at 2131.5 and 2127.6 cm^{-1}. During the actual CO exchange reactions, only the bands at 2051 and 1996 cm^{-1} were clearly discernible because all the others were buried beneath the much stronger $\nu(CO)$ bands of the parent cis-$Mn(CO)_4$-LBr derivatives.

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