

## INFRARED SPECTROSCOPIC STUDIES ON METAL CARBONYL COMPOUNDS

### XIV\*. ASSIGNMENTS IN THE C-O STRETCHING REGION OF THE AUTHENTIC INFRARED SPECTRA OF THE COMPOUNDS $MCo(CO)_9$ ( $M=Mn$ or $Re$ ) AND OF THE MONOSUBSTITUTED DERIVATIVE $MnCo(CO)_8P(C_6H_5)_3$

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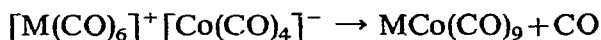
#### SUMMARY

Reported for the first time are the infrared spectra and their assignments in the C-O stretching region for the compounds  $MCo(CO)_9$  ( $M=Mn, Re$ ). We also report the preparation and the IR spectrum of the new monosubstituted compound  $MnCo(CO)_8P(C_6H_5)_3$ . The three compounds have also been characterized by their mass spectra.

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#### INTRODUCTION

The preparation of the mixed manganese cobalt nonacarbonyl compound  $MnCo(CO)_9$  (I) was reported for the first time by Joshi and Pauson<sup>1</sup>, but the C-O stretching frequencies they reported were erroneous. Subsequently the  $MCo(CO)_9$  compounds ( $M=Mn, Re$ ) were obtained by Kruck *et al.*<sup>2,3</sup> as products in the spontaneous redox reaction of the following salt-like complexes:



They reported five C-O stretching frequencies, but Bower<sup>4</sup> later reported the presence of nine bands in the same region, although the main absorptions occurred at nearly the same frequency values in each of the two reports. No assignments are to be found in the literature for such compounds, and Bower explicitly said that "the C-O stretching frequencies defied satisfactory assignment"<sup>4</sup>.

The interpretation of these spectra seemed particularly interesting, since a

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number of anionic complexes of the type  $[MM'(CO)_9]^-$  which have probably the same molecular geometry, have been reported by Ruff<sup>5</sup>. The spectra of these compounds have a striking similarity to that of (I) apart from a general shift towards lower frequencies caused by the negative charge.

## RESULTS

In our experience  $MnCo(CO)_9$ , as normally obtained, always contains small quantities of  $Mn_2(CO)_{10}$ , which do not disappear even on chromatography. Compound (I) is in fact, not very stable in solution, decomposing to give  $Mn_2(CO)_{10}$  and other, unidentified, compounds. From Table 1 it can be seen that, while the spectrum obtained by Pauson<sup>1</sup> certainly refers to a different compound, that reported by Bower has two bands (at 2046.1 and 2015.6  $cm^{-1}$  precisely) which coincide with the two strongest absorptions of  $Mn_2(CO)_{10}$  at 2045.8 and 2014.7  $cm^{-1}$ <sup>6</sup>. On the other hand, the weak shoulder at 2004  $cm^{-1}$  was not resolved by Kruck *et al.*<sup>2</sup>, probably because of the broadening effect of the solvent used.

The careful purification of the compound, using chromatography followed by several crystallizations, led to the complete disappearance of the bands due to  $Mn_2(CO)_{10}$ , and the presence of a genuine shoulder at 2004  $cm^{-1}$  was revealed by high resolution spectra, high concentration measurements being made on several crystallization fractions in order to demonstrate the constancy of its relative intensity (see Fig. 2). On the basis of these results, and keeping in mind the importance of relative intensity, we can say that there are six genuine C-O stretching bands. The spectrum is shown in Fig. 1, and the frequencies are listed in Table 1.

TABLE 1

### C-O STRETCHING FREQUENCIES<sup>a</sup>

Comparison of literature data and of those obtained in the present study for  $MCo(CO)_9$  compounds

<i>M = Mn</i>				<i>M = Re</i>	
<i>Joshi and Pauson</i> <sup>1</sup>	<i>Kruck and Höfler</i> <sup>2</sup>	<i>Bower</i> <sup>4</sup>	<i>This work</i> <sup>b</sup>	<i>Kruck et al.</i> <sup>3</sup>	<i>This work</i> <sup>b</sup>
2070	2117 w	2116.4	2116.5 w	2139 vw	2133.9 w
	2058 vs	2056.3 2046.1	2056.2 s	2064 s-vs	2059.8 s
2035					
2022	2025 vs	2027.2 2024.4 2015.6	2025.8 vs	2035 vs	2032.8 vs
2008		2003.9	2004.0 (sh)		2007.0 w
	1994 m	1995.9	1996.0 m	1990 s-vs	1990.0 s
1988	1981 (sh)	1982.7	1981.0 (br)	1977 (sh)	1971.7 (br)

<sup>a</sup> w = Weak, vw = very weak, m = medium, s = strong, vs = very strong, (sh) = shoulder, (br) = broad. <sup>b</sup> Accuracy:  $\pm 0.3 cm^{-1}$ ; calibration against CO and DCI bands.

In order to have a more complete picture of the characteristics of such compounds, we prepared the analogous  $ReCo(CO)_9$  (II), using a different method from

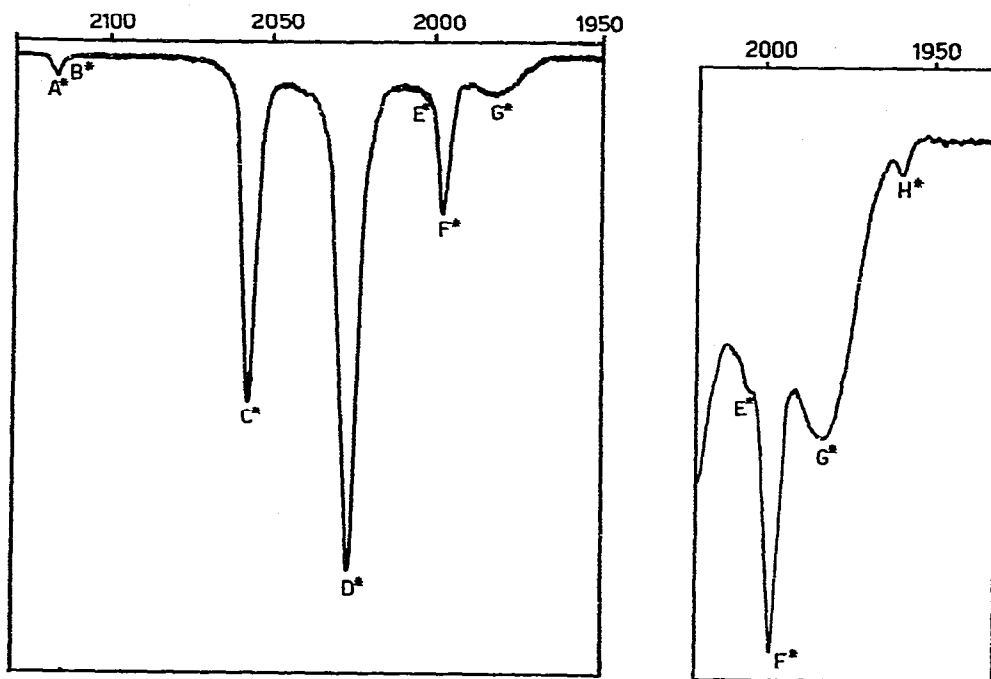


Fig. 1. IR spectrum of  $\text{MnCo}(\text{CO})_9$  in the C-O stretching region.

Fig. 2. High-concentration spectrum of  $\text{MnCo}(\text{CO})_9$  for the identification of the weak band  $\text{E}^*$  ( $2004\text{ cm}^{-1}$ ) and of the natural isotopic satellite  $\text{H}^*$  ( $1956\text{ cm}^{-1}$ ).

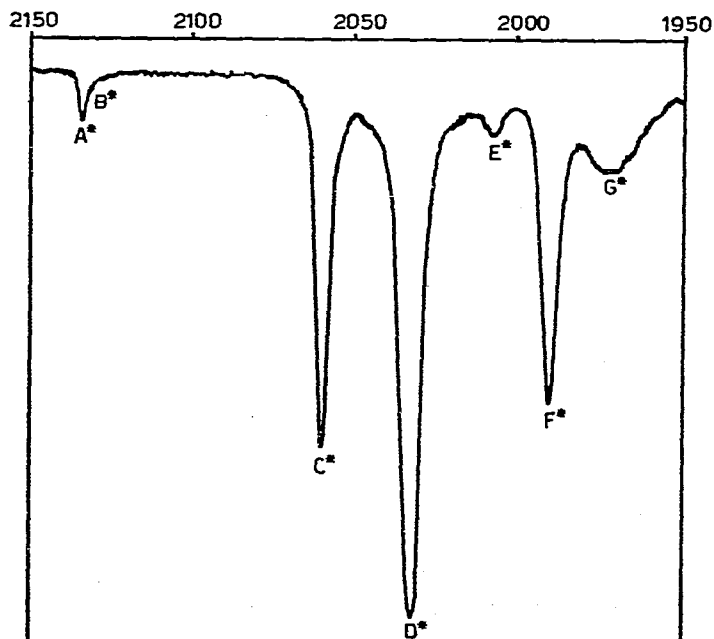


Fig. 3. IR spectrum of  $\text{ReCo}(\text{CO})_9$  in the C-O stretching region.

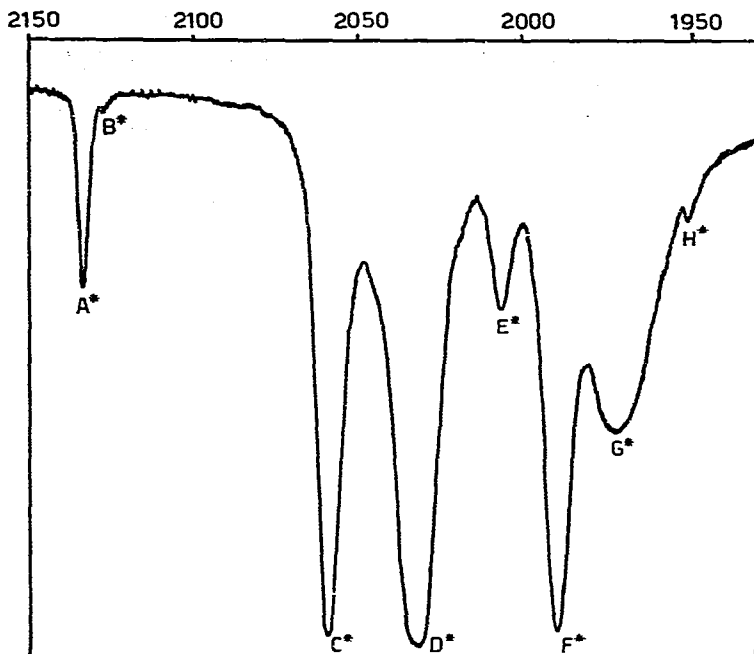
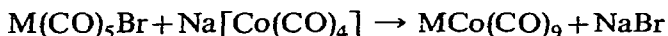


Fig. 4. High-concentration spectrum of  $\text{ReCo}(\text{CO})_9$ .

that described by Kruck *et al.*<sup>3</sup> In view of the close analogy between the IR spectra of (I) and (II), we can assume for  $\text{ReCo}(\text{CO})_9$  a structure similar to that proposed for the manganese compound.

From the spectrum of (II), we had further evidence that the weak shoulder at  $2004\text{ cm}^{-1}$  in the spectrum of (I) was a genuine absorption, since in the spectrum of (II) there is a more intense, clearly separated band at  $2007\text{ cm}^{-1}$  (not reported by Kruck *et al.*<sup>3</sup>) which maintains a constant intensity after chromatography and repeated crystallizations (see Fig. 4). Frequency values and spectra of compound (II) are reported in Table 1 and Fig. 3, respectively.

It is interesting to note that the reaction:



goes to completion at room temperature within one hour when  $\text{M}=\text{Mn}$  but when  $\text{M}=\text{Re}$  two days at a higher temperature ( $40^\circ\text{C}$ ) are needed to complete the formation of the binuclear product. This is probably due to the fact that the  $\text{Re}-\text{Br}$  bond is less polarized than the  $\text{Mn}-\text{Br}$  bond, the difference being related to the difference in the electronegativities of the two metals ( $\text{Mn}=1.5$ ,  $\text{Re}=1.9$ ,  $\text{Br}=2.8$ , on Pauling's scale).

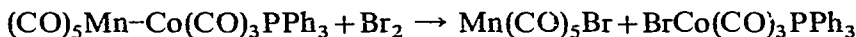
#### SUBSTITUTION REACTION

No evidence for the existence of monosubstituted compounds has been previously presented in the case of dinuclear mixed carbonyls. It thus seemed of interest to prepare a monosubstitution compound with phosphine as a hetero ligand; (a) from the chemical point of view, to see in which moiety of the molecule the substitution

occurs, and (b) from the spectroscopic point of view, to compare its spectrum with those of the known homogeneous dinuclear compounds  $\text{Co}_2(\text{CO})_7\text{L}$  and  $\text{Mn}_2(\text{CO})_9\text{L}$ .

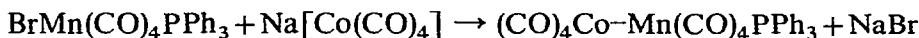
Compound (I) reacts with triphenylphosphine during two days at room temperature (solvent n-hexane) to give  $\text{MnCo}(\text{CO})_8\text{P}(\text{C}_6\text{H}_5)_3$  (III), as an orange oil, which crystallizes from n-hexane. Comparison of the spectra of the reaction mixture with those taken after chromatography and recrystallization gave no evidence of disubstitution or of the formation of other carbonyl compounds under these mild conditions. The mass spectrum confirms the monosubstituted formulation indicated by the IR spectrum. The principal C–O stretching frequencies are at 2092.5 s, 2005.8 vs, 1995.5 s, 1978.1 m, and 1939.0 m  $\text{cm}^{-1}$  (see Fig. 5).

To determine whether the substitution with triphenylphosphine occurred at the manganese or cobalt atom (III) was treated with bromine in carbon tetrachloride. The colour of the solution changed from orange to yellow, and the IR spectrum showed the presence of  $\text{Mn}(\text{CO})_5\text{Br}$  only, and no  $\text{BrMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ . The bromination thus occurred according to the equation:



proving that the substitution took place on the cobalt. The other product of this reaction, tricarbonyl(triphenylphosphine)cobalt bromide, is well known to be very unstable<sup>7</sup>. Further evidence for the substitution at the cobalt was found from the mass spectrum, in which there are clearly present the fragments  $\text{CoP}(\text{C}_6\text{H}_5)_3(\text{CO})_{3-n}^+$  with  $n=0-3$ .

Attempts to prepare the Mn-substituted compound according to the equation:



have been so far unsuccessful.

## DISCUSSION

No X-ray data are available on the structure of  $\text{MnCo}(\text{CO})_9$  or of any other compound of this type. Since the IR spectrum indicates unequivocally the absence of bridging C–O groups, the only structure which seems logical is a combination of a  $\text{Mn}(\text{CO})_5$  and a  $\text{Co}(\text{CO})_4$  radical through a direct metal–metal bond. From what we know of the geometry of  $\text{XMn}(\text{CO})_5$  and  $\text{RCo}(\text{CO})_4$  compounds, respectively, it seems almost certain that the local symmetry of the  $\cdot\text{Mn}(\text{CO})_5$  entity is  $C_{4v}$ , and that of the  $\cdot\text{Co}(\text{CO})_4$  group is  $C_{3v}$ . By combining these two units we have as a maximum a  $C_s$ , or even a  $C_1$  rigid overall molecular symmetry. In both cases, all nine C–O stretching modes should be IR active.

If, on the other hand, the two "local symmetries"<sup>8</sup> governed the selection rules, we would expect  $2A_1 + 1E = 3$  bands for the  $\text{Co}(\text{CO})_4$  part of the molecule, and  $2A_1 + 1E = 3$  bands for the  $\text{Mn}(\text{CO})_5$  moiety, giving altogether a band number of six, which is in agreement with the observations. However, if this application of the selection rules were correct, we should have found two very strong bands (species *E*) in the spectrum with an intensity ratio of ca. 3/4, representing approximately  $\frac{7}{9}$  of all of the C–O stretching intensities (assuming that the dipole moment gradient has the same value for all CO groups present in the molecule). Clearly the observed spectrum does not fulfil these requirements, and it was necessary to find another model which

accounts not only for the observed number of six bands but also for the observed intensity distribution.

#### ASSIGNMENTS

As far as (i) the number of the observed bands, (ii) their fundamental and isotopic frequencies, (iii) the assignment of the bands, and (iv) the intensity distribution are concerned, we found complete agreement with characteristics expected for the "free rotational model"<sup>9</sup>, which postulates free rotation about the metal-metal axis. Moreover, this model allows, in contrast to that based on two "separated" local symmetries, all possible interactions between CO ligands bound to the different metal atoms. Thus both the  $A_1$  and the  $E$  type vibrations of the two halves of the molecule become coupled, and the nine C-O stretching modes are distributed in the following way among the three species:

- (a) four vibrations belong to a species which is totally symmetrical with respect to the free rotational axis of the molecule;
- (b) two vibrations belong to a doubly degenerate ( $E$ ) species; and
- (c) one vibration of species  $B_1$  in point group  $C_{4v}$  remains localized onto the Mn-(CO)<sub>5</sub> moiety, which is IR inactive.

TABLE 2

ASSIGNMENT OF THE C-O STRETCHING FREQUENCIES OF THE COMPOUNDS  $MCo(CO)_9$

Species	$v_i$	$M = Mn$	$M = Re$
<i>Symmetrical</i>	A* $v_1$	2116.5 w	2133.9 w
	E* $v_2$	2004.0 (sh)	2007.0 w
	C* $v_3$	2056.2 s	2059.8 s
	F* $v_4$	1996.0 s	1990.0 s
<i>E</i>	D* $v_5$	2025.8 vs	2032.8 vs
	G* $v_6$	1981.0 m(br)	1971.7 m(br)
<sup>13</sup> C-O	B* $v_7$	2112.5	2127.0
	H* $v_8$	1956.0	1950.0

The assignment of the bands to these species, confirmed by our calculations, is shown in Table 2. The totally symmetric species is divided in two parts, both containing two vibrations. The frequencies  $v_1(A^*)^*$  and  $v_2(E^*)$  are very weak in intensity and they correspond to species  $A_1$  and  $A_{1g}$  in the case of point groups  $D_{4d}$  and  $D_{3d}$ , respectively, i.e., to the inactive vibrations of compounds  $M_2(CO)_{10}$  ( $M = Mn, Tc, Re$ )<sup>10</sup>, and  $HgCo_2(CO)_8$ <sup>11</sup>. The bands assigned to frequencies  $v_3(C^*)$  and  $v_4(F^*)$  show high intensities, and this is in agreement with the fact that vibrations of this type are active also in the case of point groups  $D_{4d}$  and  $D_{3d}$ , corresponding to the species  $B_2$  and  $A_{2u}$  respectively.

The most intense band,  $v_5(D^*)$ , is assigned unequivocally to a vibration of species  $E$ , corresponding to  $E_1$  in point group  $D_{4d}$  and to  $E_u$  in point group  $D_{3d}$ .

\* The symbols with an asterisk refer to the labels of the bands in Figs. 1-4 and in Table 2, whereas symbols of species are in italics without an asterisk.

The other degenerate vibration  $\nu_6$  is assigned to the lowest frequency ( $G^*$ ), by analogy with the inactive vibrations  $E_3(D_{4d})$  and  $E_8(D_{3d})$ .

#### ISOTOPIC FREQUENCIES

The presence of natural  $^{13}\text{C}$  gives rise to four types of isotopically substituted molecules with the ratio 4/3/1/1. The high concentration spectra, show isotopic satellites in the regions where they normally occur, *viz.*  $B^*$  next to the band with highest frequency, and in the lower part of the spectrum ( $H^*$ ) (Fig. 4). Calculations are in progress to confirm the assignment of these bands and the position of other, presumably still weaker absorptions.

#### INTERPRETATION OF THE SPECTRUM OF $\text{MnCo}(\text{CO})_8\text{P}(\text{C}_6\text{H}_5)_3$

The spectrum of compound (III) shows five C–O stretching absorptions (Fig. 5). Also in this case the spectrum can be interpreted on the basis of the "free rotational model" for the same considerations outlined for compounds (I) and (II). In this

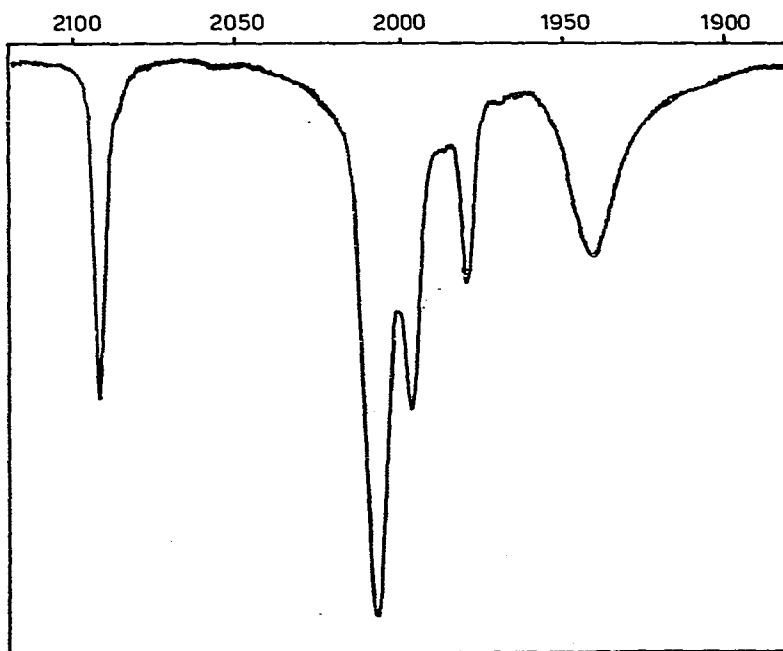


Fig. 5. Spectrum of  $\text{MnCo}(\text{CO})_8\text{P}(\text{C}_6\text{H}_5)_3$ .

molecule there are eight normal modes for C–O stretching; the decrease from nine to eight is due to the substitution of a CO group, which reduces to three the number of different CO-sets, and thus also the order of the symmetrical species. Hence the normal modes are distributed as follows:

- (a) three vibrations belong to the species which is symmetric with respect to the rotational axis of the molecule;

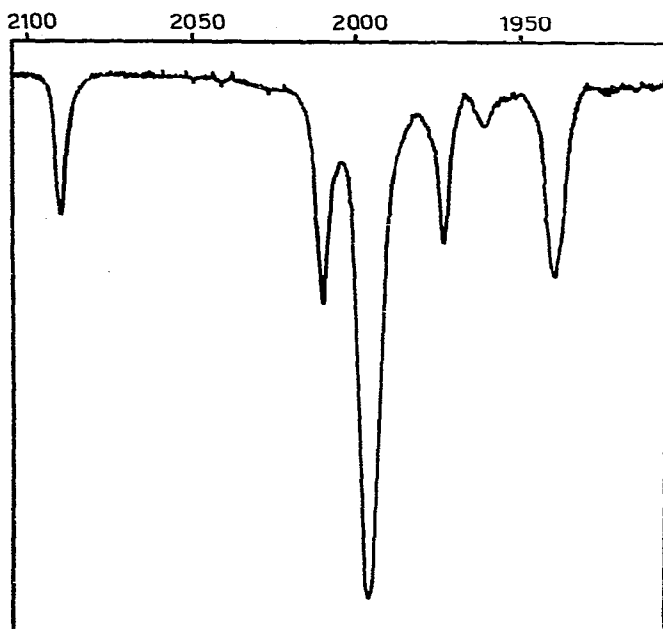


Fig. 6. Spectrum of  $\text{Mn}_2(\text{CO})_9\text{P}(\text{C}_6\text{H}_5)_3$ .

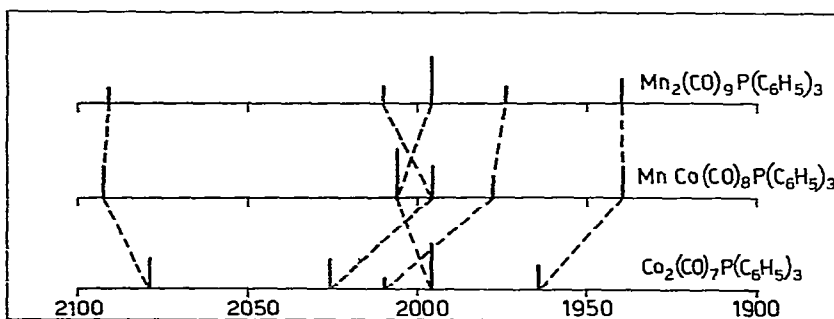


Fig. 7. Graphical comparison of the C-O stretching frequencies of the monosubstituted derivatives  $\text{Mn}_2(\text{CO})_9\text{L}$ ,  $\text{MnCo}(\text{CO})_8\text{L}$ , and  $\text{Co}_2(\text{CO})_7\text{L}$  ( $\text{L} = \text{PPh}_3$ ).

- (b) the doubly degenerate species  $E$  is of second order;  
 (c) there is also here a first order species of the type  $B_1$  in point group  $C_{4v}$ , localized onto the  $\text{Mn}(\text{CO})_5$  moiety, which is IR inactive.

The assignment can be made unequivocally, not only on the basis of the relative band intensities but also by comparison of the spectrum of (III) with those of  $\text{Mn}_2(\text{CO})_9\text{P}(\text{C}_6\text{H}_5)_3$ <sup>12</sup> and  $\text{Co}_2(\text{CO})_7\text{P}(\text{C}_6\text{H}_5)_3$ <sup>13</sup>. For the former the assignment suggested by Ziegler *et al.*<sup>12</sup> has been confirmed by our calculations<sup>14</sup> (we have recorded the following wave numbers for the fundamental bands in *n*-hexane solution: 2090.8, 2010.4, 1996.0, 1973.7, and 1938.4  $\text{cm}^{-1}$ ; see Fig. 6). In the case of  $\text{Co}_2(\text{CO})_7\text{PPh}_3$ , calculations<sup>14</sup> indicated an assignment in which the bands labelled as  $A^*$ ,  $B^*$ , and  $C^*$  in ref. 13 belong to species  $A_1$ , whereas bands  $D^*$  and  $E^*$  refer to species  $E$  of point group  $C_{3v}$ .

The spectra of these three compounds can also be compared directly (Fig. 7)



because of the equal number of the C–O stretching bands and also of their distribution among the species. This is due to the fact that in the case of nonacarbonyl dimanganese triphenylphosphine there are two IR inactive vibrations ( $B_1$  and  $B_2$ ), and in the case of the mixed manganese–cobalt derivative (III) one vibration is inactive ( $B_1$ ). A sixth, very weak band at  $1962\text{ cm}^{-1}$  in the spectrum of  $\text{Mn}_2(\text{CO})_9\text{PPh}_3$  is, according to calculations<sup>14</sup>, an isotopic band.

We suggest an axial substitution for  $\text{MnCo}(\text{CO})_8\text{P}(\text{C}_6\text{H}_5)_3$  for two reasons: (i) It has an spectrum analogous to that of the other two monosubstituted compounds, and (ii) In the case of disubstituted  $\text{RCo}(\text{CO})_3\text{L}$  derivatives with trigonal bipyramidal configuration (where R represents a one-electron donor, such as an organic group or H, and L a two-electron donor ligand such as a phosphine) only the *trans* form is known. In the case of (III),  $\text{R}=\text{Mn}(\text{CO})_5$ .

A report of a detailed group theoretical treatment of the “free-rotational model” will be published elsewhere.

#### EXPERIMENTAL

$\text{Re}_2(\text{CO})_{10}$  and  $\text{Mn}_2(\text{CO})_{10}$  were commercial products (Fluka A.G.) and were used without further purification. Normal hexane and benzene were distilled from calcium hydride under nitrogen, and tetrahydrofuran was purified just before use by distillation under nitrogen from lithium aluminium hydride.

The salt  $\text{Na}[\text{Co}(\text{CO})_4]$  was kindly donated by Prof. P. Chini. The solution of the anion  $[\text{Co}(\text{CO})_4]^-$  was obtained by the reaction between dicobalt octacarbonyl and a Na/K alloy in THF. Chromatographic separations were performed under nitrogen on a silica gel column.

Infrared spectra were recorded on a Perkin–Elmer 621 spectrophotometer, using linear wave number scale in the  $2200\text{--}1800\text{ cm}^{-1}$  region, with expanded scale ( $1\text{ cm} = 10\text{ cm}^{-1}$ ). Mass spectra were obtained on a Hitachi–Perkin–Elmer RMU-6E mass spectrometer.

#### *Preparation of $\text{MnCo}(\text{CO})_9$*

$\text{Na}[\text{Co}(\text{CO})_4]$  (370 mg; 1.91 mmol) was added under nitrogen at room temperature to a stirred THF solution of  $\text{Mn}(\text{CO})_5\text{Br}$ , prepared as previously described<sup>15</sup> (430 mg; 1.565 mmol) in 50 ml of solvent (molar ratio Mn/Co = 1/1.22). The pale-yellow solution changed first to orange and then to red-orange. The reaction was monitored through the IR spectrum, by following the disappearance of the characteristic band of the anion  $[\text{Co}(\text{CO})_4]^-$  at about  $1890\text{ cm}^{-1}$ <sup>16</sup>; the time required for the reaction to go to completion was about 1 h. The solvent was removed by evaporation under vacuum, and the solid residue was treated with normal hexane. The soluble part was chromatographed on silica gel with n-hexane as eluant, and gave a single orange-red fraction which, when kept at dry-ice temperature overnight, gave red-orange needles of pure  $\text{MnCo}(\text{CO})_9$ .

When crystals of the compound are stored under nitrogen at room temperature, the first signs of decomposition and contamination with  $\text{Mn}_2(\text{CO})_{10}$  appear during only one day. Thus for spectroscopic studies the sample must be re-purified immediately before use.

The compound was identified by its mass spectrum, which showed: (i) the

parent ion at 366  $m/e$  (calcd.: 366); (ii) the complete series  $MnCo(CO)_{9-n}^+$  ( $n=1-9$ ), with intense peaks for  $n=1, 6, 7, 8$ , and 9; (iii) the series  $Co(CO)_3^+$ ,  $Co(CO)_2^+$ ,  $Co(CO)^+$ ; (iv) intense peaks corresponding to  $Mn^+$  and  $Co^+$ ; and (v) the complete series for  $Mn(CO)_n^+$  with  $n=1-5$ .

#### Preparation of $ReCo(CO)_9$

$Na[Co(CO)_4]$  (213 mg; 1.1 mmol) was added under nitrogen to a stirred THF solution of  $Re(CO)_5Br$ , prepared according to ref. 17 (343 mg; 0.845 mmol) in 40 ml of solvent (ratio  $Re/Co=1/1.3$ ). After two days' stirring at 40°, the reaction was considered complete, and the solvent was evaporated *in vacuo*. The residue was treated with n-hexane and the solution was chromatographed on silica gel with n-hexane as eluant. This gave a single yellow fraction of  $ReCo(CO)_9$ , which on being kept at dry-ice temperature overnight gave golden-yellow crystals. In some cases the colourless fraction coming off the chromatography column before the main product contained trace quantities of  $Re_2(CO)_{10}$ , and we also observed a light brownish third zone due to a little  $Co_4(CO)_{12}$ .

Rhenium cobalt nonacarbonyl seems to be somewhat more stable than its manganese analogue, but after some days a little  $Re_2(CO)_{10}$  is present, having been formed in a disproportionation process. (Dicobalt octacarbonyl could not be detected at such dilution.)

The mass spectrum contained (i) parent ions at  $m/e$  496 and 498 corresponding to the isotopic abundance  $^{185}Re=37\%$  and  $^{187}Re=63\%$  (molecular ion peaks calcd.: 496 and 498); (ii) complete series of the isotopic doublets for  $ReCo(CO)_{9-n}^+$  ( $n=1-9$ ) with intense peaks for  $n=4-9$ ; (iii) the series  $Co(CO)_n^+$  with  $n=1, 2$ , and 3; and (iv) intense peaks for  $Co^+$  and  $^{185/187}Re^+$ . (The intensity ratio of the doublets belonging to fragments containing rhenium correspond to the natural abundances of the two isotopes of this element.)

#### Preparation of $(CO)_5MnCo(CO)_3P(C_6H_5)_3$

$MnCo(CO)_9$  (24.1 mg; 0.066 mmol), freshly recrystallized, and  $P(C_6H_5)_3$  (17.3 mg; 0.066 mmol) were dissolved in 15 ml of normal hexane, and the solution was stirred at room temperature under nitrogen. After 2 days the reaction was considered complete, since the bands of  $MnCo(CO)_9$  had almost disappeared, and the spectrum showed the presence of a new carbonyl compound. The solution was poured onto a silica gel column and eluted with n-hexane. The first chromatographic fraction consisted of unreacted  $MnCo(CO)_9$ , and subsequent elution with n-hexane containing 5% benzene gave the desired product as an orange fraction. Evaporation of the solvent, left an oil which crystallized with difficulty from n-hexane.

The compound was identified by its mass spectrum which showed (i) the parent ion at 600  $m/e$  (mol. wt. calcd.: 600); (ii) members of the series  $MnCoP(C_6H_5)_3(CO)_{8-n}^+$  with  $n=3, 4, 5$ , and 7; (iii) intense peaks for the fragments  $CoP(C_6H_5)_3(CO)_{3-n}^+$  ( $n=0-3$ ); and (iv) intense peaks for  $Mn^+$  and  $P(C_6H_5)_m^+$  ( $m=1, 2$ , and 3).

#### ACKNOWLEDGEMENTS

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