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STEREOCHEMICALLY NONRIGID SIX-COORDINATE METAL CARBONYL COMPLEXES

IV *. A ^{13}C NMR INVESTIGATION OF *cis*-$M(CO)_4X_2$ AND $M'(CO)_5X$ DERIVATIVES ($M = Fe, Ru, Os$; $M' = Mn, Re$; $X = H, I$)

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Summary

The ^{13}C NMR spectra of *cis*-$M(CO)_4X_2$ and $M'(CO)_5X$ ($M = Fe, Ru, Os$; $M' = Mn, Re$; $X = H, I$) and *cis*-$Os(CO)_4Me_2$ are reported. Variable temperature spectra demonstrated the stereochemical nonrigidity of *cis*-$Fe(CO)_4H_2$ and the stereochemical rigidity of the rest. The carbonyl averaging process in *cis*-$Fe(CO)_4H_2$ occurs without ligand dissociation. Improved syntheses of some of these derivatives are also given.

Introduction

Over the past seven years there has been an increasing number of reports on the polytopal rearrangement of six-coordinate complexes in solution. Among the most studied were compounds of the type ML_4H_2, where $M = Fe, Ru$; L = phosphine, phosphite [1—5]. The presence of six ligand nuclei with spin 1/2 enabled a detailed analysis of NMR line shapes and led to the suggestion of the "tetrahedral jump" mechanism for the rearrangement of such complexes.

Recent ^{13}C NMR studies from this laboratory demonstrated the polytopal rearrangement in another series of compounds of the type $M(CO)_4(ER_3)_2$ ($M = Fe, Ru, Os$; $E = Si, Ge, Sn, Pb$; R = organic group, Cl) [6—8]. This rearrangement, which involves a *cis*—*trans* isomerization [7], has been shown to be more facile or iron derivatives than either the ruthenium and osmium derivatives.

In order to establish the degree to which the *cis*-$M(CO)_4(ER_3)_2$ complexes are unique, we have extended our ^{13}C NMR investigations to $M(CO)_4X_2$ and $M'(CO)_5X$ derivatives ($M = Fe, Ru, Os$; $M' = Mn, Re$; $X = H, I$) and to $Os(CO)_4Me_2$. The results of this study are presented here. A brief reference to the ^{13}C NMR spectrum of *cis*-$Os(CO)_4H_2$ has previously been made [9].

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* For part III see ref. 8.

Results and discussion

The *cis* or *trans* geometry of $M(CO)_4X_2$ derivatives in solution may be rigorously established by ^{13}C NMR provided the compounds are stereochemically rigid on the NMR time scale. For a *cis*-$M(CO)_4X_2$ derivative two ^{13}CO resonances of equal intensity are expected; only one ^{13}CO resonance is expected for a *trans*-$M(CO)_4X_2$ derivative. Two resonances were observed for *cis*-$M(CO)_4X_2$ (M =Fe, Ru, Os; X = H, I) and *cis*-$Os(CO)_4Me_2$, with the single exception of $Fe(CO)_4H_2$ noted below. The ^{13}C chemical shift values are given in Table 1, and will be discussed below.

Assignment of ^{13}CO resonances

The two ^{13}CO resonances of *cis*-$M(CO)_4H_2$ (M = Ru, Os) may be unambiguously assigned from the ^1H-coupled ^{13}C NMR spectra. These showed an A_2X pattern at lower field for the axial carbonyls and an $AA'X$ pattern for the equatorial carbonyls at higher field *. Thus, Fig. 1 shows the ^1H-decoupled and ^1H-coupled ^{13}C NMR spectra of *cis*-$Os(CO)_4H_2$. The positions of the carbonyl resonances are in agreement with previous findings in the *cis*-$M(CO)_4(ER_3)_2$ series [6—8], where, for the great majority of cases, the ^{13}C resonance of the carbonyl *trans* to the one-electron donor ligand was at higher field.

Assignment of the ^{13}CO resonances of *cis*-$M(CO)_4I_2$ (M = Fe, Ru, Os) and *cis*-$Os(CO)_4Me_2$ was assumed to be the same as for the hydrido species. The coupling constant method of assigning ^{13}CO resonances failed for *cis*-$Os(CO)_4Me_2$ because the $^3J(^1H—^{13}CO)$ coupling was too small to be resolved (the half-widths of the carbonyl resonances at 177.7 and 170.6 ppm were 7.3 and 5.7 Hz, respectively, in the ^1H-coupled spectrum; the corresponding hald-widths in the ^1H-decoupled spectrum were 2.6 and 2.5 Hz).

On the other hand, for $M'(CO)_5X$ derivatives, the assignment is straightforward as two ^{13}CO resonances of relative intensity 4/1, due to the radial and axial carbonyls, are expected. This was observed for $Re(CO)_5H$ (Table 1). However, the ^{13}C NMR spectra of $Mn(CO)_5H$, $Mn(CO)_5I$, and $Re(CO)_5I$ showed only one broad peak at room temperature. This is due to the quadrupole moment of the ^{55}Mn, ^{185}Re, and ^{187}Re isotopes, which can potentially broaden the signals of carbon atoms bound directly to them [10]. The radial and axial ^{13}CO resonances can nevertheless be resolved by "thermal decoupling", a method long known in ^{11}B NMR [11], but only recently applied to ^{13}C NMR [10]. Thus, Fig. 2 shows the variable temperature ^{13}C NMR spectra of ^{13}CO-enriched $Re(CO)_5I$. At room temperature the half-width of the ^{13}CO resonance is 7 Hz. Lowering the temperature causes a dramatic narrowing of this resonance, to 3.6 Hz at —50° C, such that the ^{13}CO signal due to the axial carbonyl may be clearly resolved.

It is, of course, the greater viscosity of the solution at lower temperatures that is the basis of "thermal decoupling", so that the choice of solvent is important **. For example, we determined the ^{13}C NMR spectrum of $Mn(CO)_5H$ in CD_2Cl_2 at —70° C, which was no better (as far as the half-width of the car-

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[*] As is usual with such systems, axial and equatorial CO groups are defined so that the central metal atom and the non-carbonyl ligands lie in the equatorial plane.

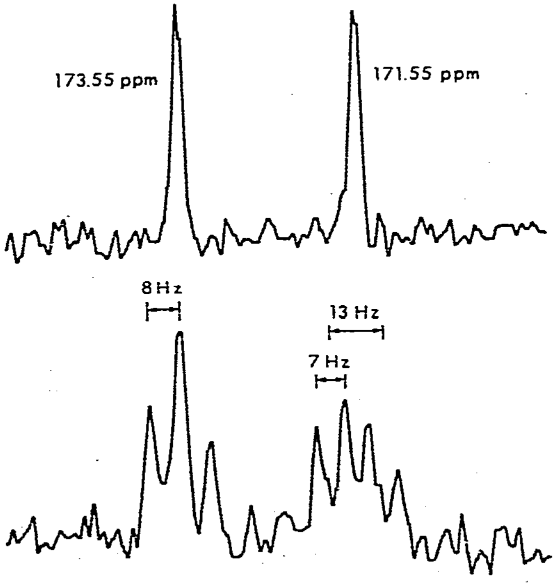
[**] Helpful discussions with Dr. J. Takats on this point are gratefully acknowledged.

ABLE 1

^{3}C CHEMICAL SHIFTS AND ^{13}C—^{1}H COUPLING CONSTANTS IN *cis*-M(CO)$_4$X$_2$ AND M′(CO)$_5$X
ERIVATIVES [a]

ompound	CO$_{ax}$	CO$_{eq}$	Coupling constants [b]		Temperature (K)
e(CO)$_4$H$_2$	205.3			9 [c]	193 [d]
u(CO)$_4$H$_2$	192.5	190.1			223
	192.6	190.4		7	223 [e]
s(CO)$_4$H$_2$	173.5	171.6		8	300 [f]
e(CO)$_4$I$_2$	204.6	198.5			298
	204.8	198.5			303 [g]
u(CO)$_4$I$_2$	178.2	177.8		4 [l]	303 [g]
s(CO)$_4$I$_2$	159.2	156.4			303 [g]
s(CO)$_4$Me$_2$ [h]	177.7	170.6			303
n(CO)$_5$H	210.8	211.4	7	14	193 [i]
n(CO)$_5$I	[j]	205.4			183
e(CO)$_5$H	182.7	183.2	8	7	293
e(CO)$_5$I	176.1	176.5			223 [k]

Chemical shifts in ppm downfield from TMS; coupling constants in Hz. Solvent is toluene-d_8 except as oted. For *cis*-M(CO)$_4$X$_2$ derivatives, axial and equatorial groups defined so that the central metal atom ad the two X ligands lie in the equatorial plane. For M′(CO)$_5$X derivatives, the axial CO is the one *trans* X. Assignment of ^{13}CO resonances of *cis*-M(CO)$_4$I$_2$ and *cis*-Os(CO)$_4$Me$_2$ is tentative only (see text). The coupling constant given for *cis*-M(CO)$_4$H$_2$ derivatives represents $^2J(^1H—^{13}CO_{ax})$, see text. The vo coupling constants given for M′(CO)$_5$H represent $^2J(^1H—^{13}CO_{ax})$ and $^2J(^1H—^{13}CO_{eq})$, respectively. Average value of the three coupling constants $^2J(^1H—^{13}CO_{ax})$, $^2J(^1H_{cis}—^{13}CO_{eq})$, and $^2J(^1H_{trans}—$ $^3CO_{eq})$, see text. Solvent methylcyclohexane-d_{14}, temperature 223 K. [d] CD$_2$Cl$_2$/CF$_2$HCl (3/1) solvent. Methylcyclohexane-d_{14} solvent. [f] Benzene-d_6/heptane (1/3) or toluene-d_8 solvent. ^{1}H NMR spectrum toluene-d_8 afforded $^1J(^{189}Os—^1H)$ 40.5 Hz. [g] CD$_2$Cl$_2$ solvent. [h] Chemical shift of ^{13}CH$_3$ — 7.6 ppm; $J(^1H—^{13}CH_3)$ 131 Hz. [i] Toluene-d_8/CD$_2$Cl$_2$ (3/1) solvent. [j] Resonance not observed, see text. [k] Toluene-$_8$/CD$_2$Cl$_2$ (1/1) solvent. [l] $^2J(^{13}CO_{ax}—^{13}CO_{eq})$; ref. 19.



g. 1. ^{1}H-decoupled (top) and ^{1}H-coupled ^{13}C NMR spectra of *cis*-Os(CO)$_4$H$_2$ in benzene-d_6/heptane /3). Numbers referring to the 171.55 ppm resonance indicate spacings between the apparent doublet of oublets. They would represent coupling constants only if $J(H—H') = 0$, or nearly so [17], and this has not en shown.

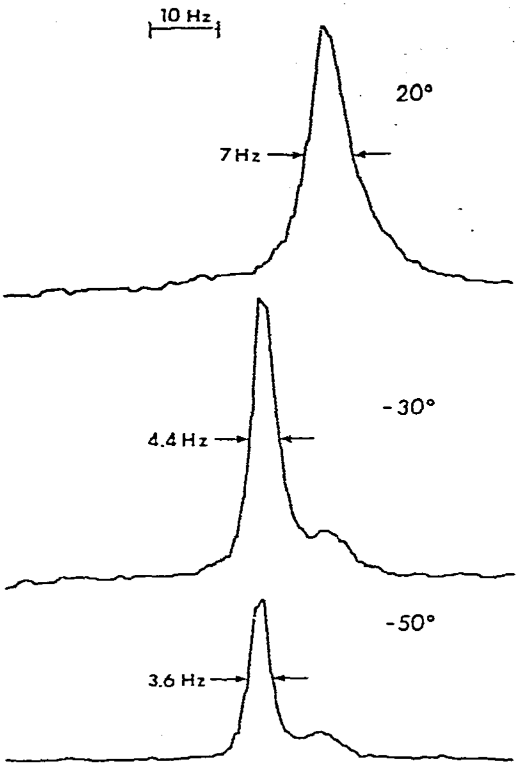


Fig. 2. Variable temperature ^{13}C NMR spectra (carbonyl portion) of $Re(CO)_5I$ in toluene-d_8 (top spectrum) and toluene-d_8/CD_2Cl_2 (1/1).

bonyl resonance was concerned) than the spectrum of the same compound at −30°C in toluene-d_8 (half-width 20 Hz). The resonances due to the radial and axial carbonyls of ^{13}CO—enriched $Mn(CO)_5H$ were resolved at −80°C in toluene-d_8/CD_2Cl_2 (3/1). The half-width of the radial carbonyl resonance was 6.2 Hz.

In all $M'(CO)_5X$ derivatives studied here, the ^{13}C resonance of the axial carbonyl (*trans* to the one-electron donor) is at higher field than the ^{13}C resonance of the radial carbonyls. This was also found for other pentacarbonylmanganese and pentacarbonylrhenium derivatives which have been investigated [10,12,13].

The axial ^{13}CO resonance of $Mn(CO)_5I$ was not observed despite a careful search. Only one ^{13}CO peak was observed in toluene-d_8 at −90°C (half-width 6.7 Hz) or in CF_2HCl at −110°C (half-width 1.5 Hz). It seems likely that the axial and radial carbonyl resonances are accidently degenerate in this compound. The chemical shift difference between radial and axial ^{13}CO resonances decreases on going from $Re(CO)_5H$ to $Re(CO)_5I$ (Table 1), and the same may also apply to $Mn(CO)_5H$ and $Mn(CO)_5I$. We do not consider it likely that the single resonance is the result of rapid axial-radial carbonyl averaging, in view of the rigidity of the homologs.

Carbon-13 chemical shifts

The ^{13}C chemical shift values are given in Table 1. The ^{13}C NMR of $Fe(CO)_4$-

H_2 at −80°C shows only one resonance rather than the expected two resonances. This aspect will be fully discussed below.

The ^{13}CO resonances are shifted upfield on descending a group of the periodic table or on going to the right in a given period [12]. Thus, the order of shielding is Fe < Ru < Os, Mn < Re, Mn < Fe, and Re < Os.

^{13}CO chemical shifts are greatly influenced by the substituent X. For example, in *cis*-$Os(CO)_4Me_2$, the ^{13}CO resonances are shifted upfield by 5 and 12 ppm as compared to $Os(CO)_5$ *. The corresponding upfield shifts in *cis*-$Os(CO)_4H_2$ are 9 and 11 ppm, while in *cis*-$Os(CO)_4I_2$, the upfield shifts are even more pronounced, 23 and 26 ppm.

The upfield shifts observed on replacing a hydrogen by iodine in ruthenium and osmium derivatives were between 12—15 ppm. This effect was less marked for manganese and rhenium derivatives, where the upfield shift was 5—7 ppm.

It is interesting to note that the chemical shift difference between axial and equatorial ^{13}CO resonances in the iron, ruthenium, and osmium derivatives varied from 0.4 to 7 ppm. However, the corresponding difference between radial and axial ^{13}CO resonances in manganese and rhenium derivatives was considerably smaller (0.4—0.6 ppm).

The ^{13}C NMR of $Mn(CO)_5H$ has been determined before [14], and two very broad resonances (width of approximately 75 Hz) at 0.1 (intensity 1) and −17.7 ppm (intensity 4) with respect to carbon disulfide were reported. On the TMS scale [16], these values would correspond to 192.7 and 210.5 ppm, respectively. Although the chemical shift of the radial carbonyl resonance is fairly close to the value given in Table 1, we believe that the chemical shift of the axial carbonyl reported by these authors [14] is in error. The half width of our radial ^{13}CO resonance at −80°C was 6.2 Hz, just sufficient to resolve the axial ^{13}CO resonance.

Carbon-13 coupling constants

The ^1H—^{13}C coupling constants observed in *cis*-$M(CO)_4H_2$ and $M'(CO)_5H$ derivatives (M = Fe, Ru, Os; M' = Mn, Re) are given in Table 1. As described previously, the ^1H-coupled ^{13}C NMR spectrum of a *cis*-$M(CO)_4H_2$ derivative is expected to show an A_2X system for the axial carbonyls and an $AA'X$ system for the equatorial carbonyls. This was observed for *cis*-$Ru(CO)_4H_2$ and *cis*-$Os(CO)_4H_2$ (Fig. 1). Analysis of an $AA'X$ system is complex [17,18] and has not been attempted here. For this reason, Table 1 lists only $^2J(^1H—^{13}CO_{ax})$ values for these derivatives.

Analysis of the ^{13}C NMR spectrum of ^{13}CO-enriched *cis*-$Ru(CO)_4I_2$ (AB system at an early stage of enrichment) afforded $^2J(^{13}CO_{ax}—^{13}CO_{eq})$ 4 Hz [19].

For $M'(CO)_5H$ derivatives, the *cis* and *trans* $^2J(^1H—^{13}CO)$ coupling constants were readily observed in the ^1H-coupled ^{13}C NMR spectrum of $Re(CO)_5H$, although very low temperature and ^{13}C enrichment were required to resolve these couplings in $Mn(CO)_5H$. The ^1H—^{13}CO coupling constants for $Mn(CO)_5H$ were reported previously from the ^1H NMR spectrum [15], and we confirm these values. As noted earlier [15] the *cis* coupling in $Mn(CO)_5H$ was larger than the *trans* coupling. However, the situation reverses for $Re(CO)_5H$, and the *trans* coupling is slightly larger than the *cis* coupling.

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* The ^{13}C NMR of $Os(CO)_5$ in toluene-d_8 shows one resonance at 182.7 ppm down to −70°C. Presumably, the molecule is stereochemically nonrigid.

Stereochemical nonrigidity

Although the infrared [20,21] and Raman [22] spectra of $Fe(CO)_4H_2$ indicate *cis* geometry in solution, the ^1H-decoupled ^{13}C NMR spectrum of this compound in CD_2Cl_2/CF_2HCl (3/1) showed a single ^{13}CO resonance at −80° C, with a half-width of 3 Hz. At −100° C, the spectrum showed a very broad, flat peak, with a half-width of 16 Hz (Fig. 3), which could be due to the two resonances of *cis*-$Fe(CO)_4H_2$. This suggests a carbonyl averaging process which is rapid on the NMR time scale at −80° C. Spectra at lower temperatures could not be obtained because of the reduced solubility of the compound. The ^1H-coupled ^{13}C NMR spectrum of $Fe(CO)_4H_2$ in methylcyclohexane-d_{14} showed a binomial triplet at −50° C, thus proving the intramolecular nature of the carbonyl averaging process. The single coupling constant of 9 Hz would correspond to the average of those expected for a *cis* molecule; if any *trans* form is present, it would contribute to the average value as well.

The ^{13}C NMR of *cis*-$Ru(CO)_4H_2$ showed stereochemical rigidity on the NMR time scale at −50 and −20° C. Higher temperatures were not attempted because of the low thermal stability of this compound. Similarly *cis*-$Os(CO)_4H_2$ and *cis*-$Os(CO)_4Me_2$ were rigid at room temperature and at 90° C.

The room temperature ^{13}C NMR spectra of *cis*-$Fe(CO)_4I_2$ in toluene-d_8 or CD_2Cl_2 showed two resonances due to the axial and equatorial carbonyl groups. However, when the ^{13}C NMR spectrum of *cis*-$Fe(CO)_4I_2$ was determined in a mixture of toluene-d_8 and $CHCl_3$ and no precaution was taken against exposing the sample to the light, a peak at 199.9 ppm was observed in addition to the two resonances mentioned above. It is very likely that this resonance is due to the *trans* isomer of this species. The conversion of *cis*-$Fe(CO)_4I_2$ to the *trans* isomer by light has been investigated earlier [23]. An attempt has been made to determine the ^{13}C NMR spectrum of *cis*-$Fe(CO)_4I_2$ (^{13}CO enriched sample in

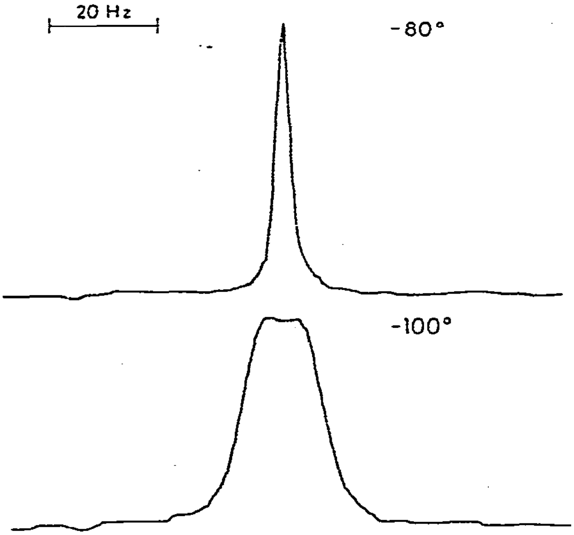

Fig. 3. Variable temperature ^{13}C NMR spectra of *cis*-$Fe(CO)_4H_2$ in CD_2Cl_2/CF_2HCl (3/1).

toluene-d_8 solution, degassed and sealed under vacuum) above room temperature. However, the compound decomposed rapidly as the probe was heated to 80° C.

It is interesting to note that a recent electron diffraction study of *cis*-Fe$(CO)_4H_2$ [24] showed significant distortion from regular octahedral towards bicapped tetrahedral. This may well be related to the low barrier for carbonyl rearrangement [8].

Experimental section

NMR instrumentation and techniques have been described [6,7]. The ^1H-coupled ^{13}C NMR spectrum of *cis*-$Os(CO)_4H_2$ was determined using gated decoupling.

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen or argon. Hydrocarbon solvents were distilled from $LiAlH_4$ and saturated with nitrogen or argon. NMR solvents were dried over type 4A Molecular Sieves.

Carbonyls of ruthenium [25] and osmium [26] were obtained by literature methods. All other starting materials were commercially available and were used as received.

Preparations of *cis*-$Ru(CO)_4H_2$ [27], *cis*-$Os(CO)_4H_2$ [28], $Mn(CO)_5H$ [29], $Re(CO)_5H$ [30], *cis*-$Fe(CO)_4I_2$ [31], and *cis*-$Os(CO)_4Me_2$ [32] were carried out according to published procedures.

"Polar night synthesis": preparation of cis-$Fe(CO)_4H_2$

Although the preparation of this compound from H_3PO_4 and $Na_2Fe(CO)_4$ has been described recently [33], we give here a modification of an earlier procedure [20], which reduces significantly the reaction time from about five days to 16 h, and affords a very pure sample.

To potassium hydroxide (10 g) and barium hydroxide (13 g) were added water (60 ml) and iron pentacarbonyl (10 ml), under nitrogen. The mixture was degassed by several freeze-thaw cycles at —196° C, and was shaken at room temperature in the dark for 12 h. The resulting slurry was filtered to yield an orange solution. The solution was concentrated to half its original volume under vacuum. From this point on, all operations were performed outside, in the middle of a mild Alberta winter night, when temperatures were around —10 to —20° C. A standard high-vacuum line equipped with a water-cooled mercury diffusion pump operated satisfactorily under these conditions. Apiezon L grease was used on all stopcocks; turning the stopcocks at these temperatures was facilitated by warming them with a heat gun.

The flask with the orange solution containing $Fe(CO)_4H^- K^+$ was attached to the high-vacuum line, and concentrated H_2SO_4 (15 ml) was added dropwise, over 2 h. The volatile materials were fractionated under vacuum using two —63° C traps and a —196° C trap. The *cis*-$Fe(CO)_4H_2$ was collected in the —196° C trap. The hydride and the solvent were distilled into the NMR tube, and the tube was sealed under vacuum.

The hydride *cis*-$Fe(CO)_4H_2$ has been stored in the dark at —196° C, in a tube sealed under vacuum, for up to six months. However, the compound decomposes rapidly above —20° C. Also, exposure of a tube containing *cis*-$Fe(CO)_4H_2$

at —196° C to laboratory fluorescent light brought about decomposition as evidenced by the appearance of a red color in 15—30 sec.

Reactions under CO pressure *

Preparation of cis-Os(CO)$_4$I$_2$

Triosmium dodecacarbonyl (0.5 g, 0.55 mmol), iodine (0.42 g, 1.65 mmol) and benzene (15 ml) were placed in a 200-ml Parr autoclave which was pressurized with CO to 600 psi. The autoclave was heated, with stirring, at 160° C for 13 h, cooled to room temperature, and then the gases were vented. Yellow crystals of *cis*-$Os(CO)_4I_2$ separated out, which were removed by filtration and were washed with pentane (15 ml) to yield 0.8 g (87%) of product.

The infrared spectrum of *cis*-$Os(CO)_4I_2$ was similar to that reported by others [34], and it showed bands at 2163(1.8), 2100(10.0), 2085(7.3), and 2050(8.5) cm^{-1} in heptane.

The ruthenium analog, *cis*-$Ru(CO)_4I_2$, has been prepared similarly by Dr. R.K. Pomeroy in over 90% yield. The reaction temperature was 100° C. The preparation of this derivative has been described previously [35], but attempts to repeat the synthesis in this laboratory were unsuccessful.

Preparation of Mn(CO)$_5$I

Dimanganese decacarbonyl (1.5 g, 3.85 mmol), iodine (0.976 g, 3.85 mmol) and benzene (15 ml) were placed in a 200-ml Parr autoclave which was pressurized with CO to 550 psi. The autoclave was heated, with stirring, at 130° C for 6 h, cooled to room temperature, and then the gases were vented.

Filtration yielded 0.76 g of ruby-red $Mn(CO)_5I$, which was washed with pentane (15 ml). The librate was evaporated at reduced pressure (10 mmHg) and sublimation (room temperature and 0.005 mmHg) afforded an additional 1.11 g of product (total yield 76%). The infrared spectrum of $Mn(CO)_5I$ [36] showed no impurities.

Earlier this compound was prepared by direct reaction of $Mn_2(CO)_{10}$ with iodine in a sealed Carius tube at 130—140° C [37] or 90° C [38]. The reported yields were lower (50%) [38] and the product was contaminated with $Mn_2(CO)_{10}$.

Preparation of Re(CO)$_5$I

Dirhenium decacarbonyl (1.304 g, 2 mmol), iodine (0.508 g, 2 mmol) and benzene (15 ml) were placed in a 200-ml Parr autoclave which was pressurized with CO to 1000 psi. The autoclave was heated, with stirring, at 150° C for 21 h, cooled to room temperature, and then the gases were vented. Filtration afforded 1.38 g of pale-yellow $Re(CO)_5I$, which was washed with pentane (15 ml). The infrared spectrum [36] of the product showed no impurities. The filtrate was evaporated at reduced pressure (10 mmHg) and sublimation (room temperature and 0.005 mmHg) yielded 0.17 g of product, which contained a small amount of $Re_2(CO)_{10}$ (total yield 86%).

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* The use of moderate CO pressure to improve yields of carbonyl halides is an outgrowth of earlier studies by R.K. Pomeroy (Ph.D. Thesis, University of Alberta, 1972).

Enrichment with ^{13}CO

The following compounds were enriched with ^{13}CO: *cis*-$Fe(CO)_4I_2$ [39], *cis*-$Ru(CO)_4I_2$ [40], $Mn(CO)_5H$ [15], $Mn(CO)_5I$, and $Re(CO)_5I$. The enrichment of the last two compounds was carried out as described [7], under ultraviolet irradiation in cyclohexane. The irradiation times (140 watt Engelhard—Hanovia Inc. lamp, at 10 cm from the flask) were 30 min and 17 h, respectively.

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