

**133. Metal Carbonyls. Part VII.<sup>1</sup> Acid-induced Exchange of Carbon Monoxide with some Inert Metal Carbonyls.**

By F. BASOLO, A. T. BRAULT, and A. J. POË.

The effect of both trifluoroacetic acid and sulphuric acid on the exchange of carbon monoxide with some inert iron carbonyls has been examined. Iron pentacarbonyl, tetracarbonyltriphenylphosphineiron, and tricarbonylbis(triphenylphosphine)iron are usually inert to substitution but, in the presence of trifluoroacetic acid and in 1,2-dichloroethane, they become relatively labile. Even at  $-20$  to  $-30^\circ$ , iron pentacarbonyl and tetracarbonyltriphenylphosphineiron undergo quite rapid carbon monoxide exchange. Iron pentacarbonyl exchanges by a dissociative mechanism, two CO ligands exchanging more rapidly than the other three. Only three of the CO ligands in tetracarbonyltriphenylphosphineiron undergo exchange, but these do so extremely rapidly even at  $-30^\circ$  after an induction period, dependent on the acid concentration, of up to 2 hr. The exchange involving tricarbonylbis(triphenylphosphine)iron is the slowest, and reaction to form tetracarbonyltriphenylphosphineiron prevents a study of the rate of exchange.

Infrared absorption measurements show that, under the conditions of the exchange studies, clear evidence for the existence of protonated species involving a metal-proton bond is only obtained for the bis-phosphine-complex. Both tetracarbonyltriphenylphosphineiron and tricarbonylbis(triphenylphosphine)iron show complete protonation in concentrated sulphuric acid, but are inert to exchange or decomposition, whereas iron pentacarbonyl decomposes rapidly in this solvent. The implications of these results are discussed.

STUDIES on the interaction of strong acids with several organometallic compounds have shown that metal-proton bonds are often formed.<sup>2,3</sup> In the case of metal carbonyls, the effect of this is to increase the C-O stretching frequency of the co-ordinated carbon monoxide by as much as  $140\text{ cm.}^{-1}$ .<sup>3</sup> This is taken to indicate a decreased degree of back donation of  $d_\pi$  electrons from the metal to the ligands owing to their involvement in the metal-proton bond. The concomitant weakening of the metal-CO bond might be expected to result in acid catalysis of those exchange or replacement reactions in which bond-breaking plays a major part. This paper describes the effect of both trifluoroacetic acid and sulphuric acid on the exchange of carbon monoxide with the normally inert <sup>4</sup> complexes iron pentacarbonyl, tetracarbonyltriphenylphosphineiron, and tricarbonylbis(triphenylphosphine)iron.

<sup>1</sup> Part VI, Angelici, Basolo, and Poë, *J. Amer. Chem. Soc.*, 1963, **85**, 2215.

<sup>2</sup> Davison and Wilkinson, *Proc. Chem. Soc.*, 1960, 356.

<sup>3</sup> Davison, MacFarlane, Pratt, and Wilkinson, *J.*, 1962, 3653.

<sup>4</sup> Keeley and Johnson, *J. Inorg. Nuclear Chem.*, 1959, **11**, 33.

## EXPERIMENTAL

Techniques for measuring the rate of exchange of carbon monoxide with metal carbonyls have been described previously<sup>5</sup> and involve following the decrease in activity of the radioactive [<sup>14</sup>C]carbon monoxide gas which results from exchange with non-radioactive CO ligands in the complexes.

Iron pentacarbonyl was obtained from Antara Chemicals.

*Tetracarbonyltriphenylphosphineiron and Tricarbonylbis(triphenylphosphine)iron.*—These compounds were prepared<sup>6</sup> by the reaction of iron pentacarbonyl (5 ml.) and triphenylphosphine (9.8 g.) in an autoclave at 175–225° for 5 hr. The unchanged materials were dissolved in ethanol (200 ml.), and the crude product was collected on a filter. This yellow solid was dissolved in hot benzene (600 ml.), and the solution was then concentrated, by boiling, to ca. 200 ml. After the solution had been cooled in an ice bath, methanol (50 ml.) was added in 10-ml. portions, whereupon precipitation of tricarbonylbis(triphenylphosphine)iron occurred. After filtration, the filtrate was further concentrated to 50 ml. and methanol (300 ml.) was added. The resultant solution was heated to boiling, and then filtered. The filtrate was concentrated to 50 ml. by boiling; cooling in an ice bath then caused precipitation of tetracarbonyltriphenylphosphineiron. This compound was recrystallised from methanol, in which any traces of the tricarbonyl compound were insoluble. Both products were washed with ether, and dried in a vacuum desiccator for 10 hr. [Found: C, 62.0; H, 3.60. Calc. for Fe(CO)<sub>4</sub>PPh<sub>3</sub>: C, 61.5; H, 3.48%. Found: C, 70.4; H, 4.60. Calc. for Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>: C, 70.6; H, 4.52%. Yield: tetracarbonyltriphenylphosphineiron, 4 g.; tricarbonylbis(triphenylphosphine)iron, 6 g., *i.e.*, 50% yield with respect to iron pentacarbonyl.] The infrared (i.r.) spectra of these compounds agreed with values reported in the literature.<sup>7,8</sup> [Tetracarbonyltriphenylphosphineiron: 1942vs; 1978m; and 2055s cm.<sup>-1</sup>; tricarbonylbis(triphenylphosphine)iron: 1890vs cm.<sup>-1</sup>.]

Although protonation of these iron carbonyls had been observed<sup>3</sup> in concentrated sulphuric acid, and in mixtures of boron trifluoride monohydrate and trifluoroacetic acid, initial experimental difficulties with such solutions, and with solutions in pure trifluoroacetic acid, led to the adoption of 1,2-dichloroethane as solvent and the study of the effect of adding relatively small amounts of trifluoroacetic acid.

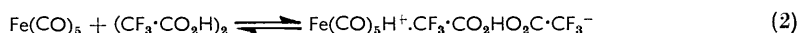
Infrared spectra of solutions of the compounds in 1,2-dichloroethane, and in trifluoroacetic acid alone, were measured with the Baird AB2 spectrophotometer. Spectra of solutions in concentrated sulphuric acid were obtained by using silver chloride plates.

## RESULTS

*Exchange Experiments.*—*Iron pentacarbonyl.* The rate of exchange of carbon monoxide with iron pentacarbonyl shows a dependence on acid concentration but no dependence on carbon monoxide concentration, as can be seen from the data in Tables 1 and 2, respectively. The rates of the reactions were obtained from equation (1):

$$R = k[\text{ES}]^a[\text{CO}]^b = \frac{[\text{CO}]_t[\text{Fe}(\text{CO})_5]X}{[\text{CO}]_t + [\text{Fe}(\text{CO})_5]X} \left( \frac{0.69}{t_{\frac{1}{2}}} \right) \quad (1)$$

where [ES] is the concentration of the exchanging species in solution, [CO] is the concentration of carbon monoxide in solution, [CO]<sub>t</sub> is the total concentration of carbon monoxide expressed as if all the carbon monoxide were in solution, *a* and *b* are the orders of the reaction with respect to the reactants ES and carbon monoxide, and *X* is the number of exchanging carbon monoxide ligands in the metal carbonyl. By assuming that ES is the protonated species, it is possible to relate [ES] to [Fe(CO)<sub>5</sub>] by use of equilibrium (2):



The acid is believed to be dimeric in 1,2-dichloroethane, so that

$$K_{\text{eq}} = \frac{[\text{Fe}(\text{CO})_5\text{H}^+ \cdot \text{CF}_3 \cdot \text{CO}_2 \cdot \text{HO}_2\text{C} \cdot \text{CF}_3^-]}{[\text{Fe}(\text{CO})_5][\text{CF}_3 \cdot \text{CO}_2 \cdot \text{H}]_2} \quad (3)$$

<sup>5</sup> Basolo and Wojcicki, *J. Amer. Chem. Soc.*, 1961, **83**, 520.

<sup>6</sup> Reppe and Schwkendiek, *Annalen*, 1948, **560**, 104.

<sup>7</sup> Cotton and Parrish, *J.*, 1960, 1440.

<sup>8</sup> Edgell, Wilson, and Summitt, *Spectrochim. Acta*, 1963, **19**, 863.

TABLE 1.

Acid-dependence of exchange of carbon monoxide with iron pentacarbonyl at  $-21^\circ$  in 1,2-dichloroethane.

$[\text{Fe}(\text{CO})_5] = 60 \text{ mm}$ ;  $[\text{CO}]_t = 310 \text{ mm}$ .

$[\text{CF}_3\text{CO}_2\text{H}]$ (mm)	$A_0$ (c.p.m.)	$A_\infty$ (theor.) (c.p.m.)	$A_\infty$ (exp.) (c.p.m.)	Number of exchanging carbon monoxide groups	$t_{\frac{1}{2}}$ (min.)	
					2CO	3CO
53	3810	2980 <sup>a</sup>	3090	2	29	long
106 <sup>b</sup>	5180	2600	2700	5	16	50
106	4900	2430	2680	5	15	66
106 <sup>c</sup>	5200	2480	2660	5	19	66
212	2990	1475	1510	5	9	28
424	4240	2100	2200	5	ca. 20	

<sup>a</sup> For exchange of 2CO groups. <sup>b</sup>  $[\text{CO}]_t = 320 \text{ mm}$ . <sup>c</sup>  $[\text{CO}]_t = 290 \text{ mm}$ .

TABLE 2.

Carbon monoxide-dependence of exchange of carbon monoxide with iron pentacarbonyl at  $-21^\circ$  in 1,2-dichloroethane.

$[\text{Fe}(\text{CO})_5] = 60 \text{ mm}$ ;  $[\text{CF}_3\text{CO}_2\text{H}] = 106 \text{ mm}$ .

$[\text{CO}]_t$ (mm)	$A_0$ (c.p.m.)	$A_\infty$ (theor.) (c.p.m.)	$A_\infty$ (exp.) (c.p.m.)	Number of exchanging carbon monoxide groups	$t_{\frac{1}{2}}$ (min.)		$kK_{\text{eq}} \times 10^2$ mole <sup>-1</sup> l. sec. <sup>-1</sup>	
					2CO	3CO	2CO	3CO
320	5180	2600	2700	5	16.0	50.0	3.49	0.81
310	4900	2430	2680	5	15.0	66.0	3.69	1.20
290	5200	2480	2660	5	19.0	66.0	2.82	1.12
53	7200	1100	1400	5	3.75	12.0	4.36	1.36
46	3200	540	600	5	5.0	14.0	2.90	1.03

\* See equations (3) and (4) below.

where the ion pair  $\text{Fe}(\text{CO})_5\text{H}^+\cdot\text{CF}_3\cdot\text{CO}_2\text{HO}_2\text{C}\cdot\text{CF}_3^-$  is ES. Thus, if the rate of exchange is of the zeroth order in carbon monoxide and of the first order in ES, then equation (1) reduces to:

$$kK_{\text{eq}} = \frac{[\text{CO}]_t X}{[(\text{CF}_3\text{CO}_2\text{H})_2][\text{CO}]_t + [\text{Fe}(\text{CO})_5]X} \left( \frac{0.69}{t_{\frac{1}{2}}} \right) \quad (4)$$

The semi-logarithmic plots of  $A_t - A_\infty$  against time ( $A$  = radioactivity) were not linear, and it was possible to resolve the curve into two straight lines corresponding to the faster exchange of two CO ligands and the relatively slower exchange of the other three. A typical plot is shown in the Figure and values of  $kK_{\text{eq}}$  are given in Table 2. In all of these exchanges there was a pressure increase of about 5% which was due to a release of co-ordinated carbon monoxide. The pressure increase was accompanied by a darkening of the solution to a reddish-brown colour and the precipitation of a small amount of a reddish-brown solid. This solid, and the colour of these mixtures, are believed to be due to ferric trifluoroacetate. This is supported by the observation that the ultraviolet and visible spectra of these mixtures are similar to those of a mixture of ferric nitrate and trifluoroacetic acid in 1,2-dichloroethane above  $320 \mu$ . The extent to which precipitation and colour change occur can be reduced by the careful exclusion of oxygen. No change in the i.r. spectra of solutions studied under the conditions of the reaction could be observed. Therefore, only a relatively small amount of the complex had decomposed. This decomposition was allowed for in plotting the data, by varying  $A_\infty$  linearly from its theoretical value at  $t = 0$ , to its experimental value at  $t_\infty$ .

*Tetracarbonyltriphenylphosphineiron*. The rate of exchange for this compound was found to increase with time and to be greater the longer it was left in contact with the acid before the exchange was initiated. After an induction period of 1–2 hr., at low concentrations of acid and at  $-30^\circ$ , the subsequent exchange was very rapid for three of the CO groups but exchange of the fourth did not occur. Half-times for the observed exchange were  $\leq 5$  min., being close to the lower limit attainable with the apparatus.<sup>5</sup> When oxygen was excluded from the system, only very slight colour changes were observed during the reaction; no precipitate was found and carbon monoxide was not evolved. Exchange was not observed in concentrated sulphuric acid solution, even at room temperature.

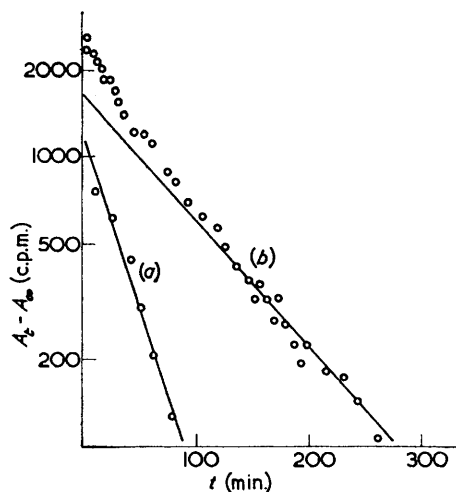
*Tricarbonylbis(triphenylphosphine)iron.* Exchange studies on this compound were complicated by reaction to form the tetracarbonyl compound, as was indicated by changes in the i.r. spectrum. Addition of trifluoroacetic acid to a solution of the tricarbonyl compound, kept at  $-20$  to  $-30^\circ$ , gave rise to an immediate loss of the pale yellow colour. The colourless solution then slowly became green and, finally, brownish-red. This reaction was considerably faster than the exchange, which is therefore much slower than the acid-induced exchange of either iron pentacarbonyl or tetracarbonyltriphenylphosphineiron. Reaction to form the tetracarbonyl compound was accompanied by a slight decrease in the pressure of carbon monoxide in the system. The pale yellow solutions of tricarbonylbis(triphenylphosphine)iron in concentrated sulphuric acid did not show exchange even at  $25^\circ$ .

*Infrared Studies.*—Neither under the conditions of the reactions, nor in pure trifluoroacetic acid, were high-field proton magnetic resonance signals observable, and the occurrence, or otherwise, of protonation was therefore investigated by i.r. spectroscopy at temperatures low enough to preclude rapid decomposition.

The spectra of iron pentacarbonyl and tetracarbonyltriphenylphosphineiron in 1,2-dichloroethane were unaffected by the addition of small amounts of trifluoroacetic acid. In the

Iron pentacarbonyl-carbon monoxide exchange at  $-21^\circ$ .

$[\text{FeCO}_5] = 60 \text{ mM}$ ;  $[\text{CF}_3\text{CO}_2\text{H}] = 106 \text{ mM}$ ;  
 $[\text{CO}]_t = 290 \text{ mM}$ ;  $A_\infty = 2480 \text{ c.p.m.}$  (a),  $t_{1/2} = 19 \text{ min.}$ ; (b),  $t_{1/2} = 65 \text{ min.}$



pure acid, the resolution was poor but increases of up to  $80 \text{ cm}^{-1}$  were observed for the C-O stretching frequencies, in agreement with those observed by Davison *et al.*<sup>3</sup> However, in the case of tricarbonylbis(triphenylphosphine)iron, the colourless species produced by addition of small amounts of trifluoroacetic acid to solutions of the complex in 1,2-dichloroethane at  $-20^\circ$ , had a spectrum quite different from that of the tricarbonyl compound itself. The single C-O absorption at  $1890 \text{ cm}^{-1}$  was replaced by strong bands at  $2030$ ,  $1790$ , and  $1770 \text{ cm}^{-1}$ . Addition of ether resulted in the disappearance of the  $2030$  and  $1790 \text{ cm}^{-1}$  bands and in the enhancement of that at  $1770 \text{ cm}^{-1}$ . The band at  $2030 \text{ cm}^{-1}$  is the same as that observed in concentrated sulphuric acid solutions,<sup>3</sup> and is assigned to the C-O stretch of protonated tricarbonylbis(triphenylphosphine)iron. The  $1790 \text{ cm}^{-1}$  band coincides with the C-O stretch in trifluoroacetic acid. We consider the  $1770 \text{ cm}^{-1}$  band to be the C-O stretch of  $\text{CF}_3\text{-CO}_2\text{HO}_2\text{C-CF}_3^-$ , ion-paired either with the protonated complex or with  $\text{Et}_2\text{OH}^+$ , the latter presumably being formed on addition of ether which is a stronger base than tricarbonylbis(triphenylphosphine)iron. The C-O stretching bands in the range  $2100\text{--}1700 \text{ cm}^{-1}$  probably mask the weak Fe-H absorption which also occurs in this region.<sup>3</sup> As the colourless solution turned green and then brown, the spectrum changed until it became identical with that of tetracarbonyltriphenylphosphineiron ( $1943\text{vs. } 1978\text{m, and } 2055\text{s cm}^{-1}$ ). In addition, a band at  $1650 \text{ cm}^{-1}$  also grew in intensity as the solution turned green. When the acid was added to the solution kept at room temperature, the solution immediately turned green and the spectrum showed bands characteristic of both the protonated and unprotonated tricarbonylbis(triphenylphosphine)iron, and also of tetracarbonyltriphenylphosphineiron. The  $1650 \text{ cm}^{-1}$  band was again present, being identical with a band observed when acid was added to

triphenylphosphine in 1,2-dichloroethane. Addition of ether always resulted in the disappearance of both the 2030 and the 1650  $\text{cm}^{-1}$  bands. Finally, when solutions of either tricarbonylbis(triphenylphosphine)iron or tetracarbonyltriphenylphosphineiron in trifluoroacetic acid were evaporated to dryness, the brown solid residues gave identical i.r. spectra in the C-O stretching region. Bands at 1996s and 2041vs  $\text{cm}^{-1}$  correspond to 1992s and 2036vs  $\text{cm}^{-1}$  for dicarbonylbis(triphenylphosphine)iron(II) bromide,<sup>9</sup> and this suggests that the brown product is largely dicarbonylbis(triphenylphosphine)iron(II) trifluoroacetate.

#### DISCUSSION

The main conclusion that can be drawn from these studies is that protonation, when it is observed to occur, does not have the expected effect on the rate of exchange and, in contrast, solutions for which there is no direct evidence of protonation do undergo rapid exchange. This does not mean, however, that protonated species are not involved. In the case of tricarbonylbis(triphenylphosphine)iron, the negligible effect of protonation is in accord with the observation that the protonated species has a C-O stretching frequency which is of the same order as those of unprotonated and inert iron pentacarbonyl and tetracarbonyltriphenylphosphineiron. This arises from the low C-O frequency in unprotonated tricarbonylbis(triphenylphosphine)iron in which the equatorial CO groups compete successfully for the  $d_{\pi}$  electrons with the more weakly  $\pi$ -bonded triphenylphosphine groups. The greater basicity of the tricarbonyl compound is also consistent with the greater availability of metal  $d_{\pi}$  electrons when two triphenylphosphine ligands are present.<sup>3</sup>

In the case of tetracarbonyltriphenylphosphineiron, protonation in concentrated sulphuric acid has no kinetic effect although bond weakening might well be expected here to be sufficient to cause reasonably fast exchange. This inertness of the protonated species in this medium is in striking contrast with the rapid exchange caused by relatively small amounts of trifluoroacetic acid in 1,2-dichloroethane. The inertness in concentrated sulphuric acid can perhaps be ascribed to some such unfavourable solvent property as viscosity or strong solvation. The fact that the trifluoroacetate anion would be expected to be ion-paired with the protonated species in 1,2-dichloroethane, whereas the hydrogen sulphate anion would not be expected to be so paired in concentrated sulphuric acid, offers another possible explanation.

The effect of trifluoroacetic acid on iron pentacarbonyl is explicable if a small amount of a protonated species is formed by a rapid pre-equilibration, followed by exchange involving the protonated species. This would be an  $S_N1CA$  mechanism (*i.e.*, an  $S_N1$  reaction of the conjugate acid). The difference between the rates for the equatorial and axial ligands is reasonable, since the axial CO ligands are almost certainly more weakly bound initially. This is indicated by the i.r. spectrum in which the less intense absorption (arising<sup>8</sup> from the asymmetric stretching of the two axial groups) has the higher frequency. By analogy with phosphoruspentachloride,<sup>10</sup> and on theoretical grounds,<sup>11</sup> the axial groups are expected to form weaker  $\sigma$  bonds. The axial groups can only compete for two of the four  $\pi$ -bonding pairs of electrons, whereas the equatorial CO groups can compete for all four  $\pi$ -bonding electron pairs and should, therefore, form stronger  $\pi$  bonds as well.

The inertness to exchange of one of the CO groups in tetracarbonyltriphenylphosphineiron (presumably the axial CO) is consistent with a decreased competition for  $d_{\pi}$  electrons by the group *trans* to it, as also occurs in  $\text{Mn}(\text{CO})_5\text{X}$ .<sup>5</sup> The slow induction period to form the rapidly exchanging species can be explained as follows. In order to protonate this very weak base, the trifluoroacetic acid dimer must be correctly oriented with a molecule of the tetracarbonyl compound before the dimer can cleave a hydrogen bond and transfer its proton. Once this protonation has taken place,  $\text{Fe}(\text{CO})_4\text{PPh}_3\text{H}^+$ , being a very strong acid,

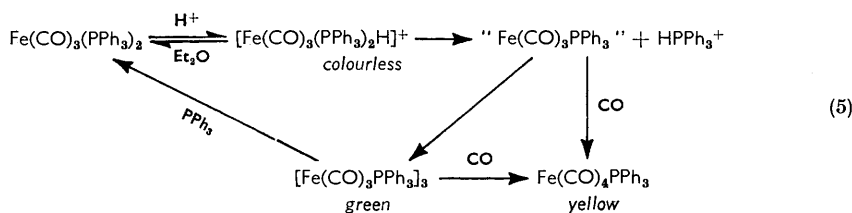
<sup>9</sup> Cohen, personal communication.

<sup>10</sup> Wilmshurst and Bernstein, *J. Chem. Phys.*, 1957, **27**, 661.

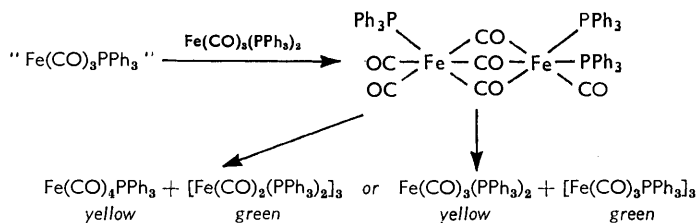
<sup>11</sup> Cotton, *J. Chem. Phys.*, 1961, **35**, 228.

transfers the proton rapidly to unprotonated tetracarbonyl compound and labilises the entire quantity of this compound. If the rates and degree of protonation of the three iron carbonyl species are compared, it can be seen that the replacement of CO by PPh<sub>3</sub> has two effects: (1) to make the molecule less accessible for acid attack, owing to the size of PPh<sub>3</sub>; and (2) to increase the basicity of the iron carbonyl, owing to the inductive effect of PPh<sub>3</sub>. In iron pentacarbonyl we have a molecule which is easily accessible for protonation, whereas in tricarbonylbis(triphenylphosphine)iron the equilibrium for protonation is far toward the protonated species. While both of these situations encourage a rapid protonation, tetracarbonyltriphenylphosphineiron can neither be readily attacked by the acid because of the bulky PPh<sub>3</sub> group, nor is its protonation equilibrium favourable.

Finally, the behaviour of tricarbonylbis(triphenylphosphine)iron with trifluoroacetic acid can be explained as follows. There is an equilibrium between protonated and unprotonated species which, at low temperature, lies far towards the protonated species but which at room temperature involves comparable amounts of each form. The colour changes, the formation of the tetracarbonyl compound and HPPH<sub>3</sub><sup>+</sup>, and the observed uptake of carbon monoxide, can be explained by the reaction scheme (5):



Because of the fact that some overall reaction occurs, even in the absence of an atmosphere of carbon monoxide, reactions such as those shown in (6) must be involved, either as an alternative to the reactions of "Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)" indicated in (5), or in addition to them.



The assumption that the trimers will be green, as is [Fe(CO)<sub>4</sub>]<sub>3</sub>, is reasonable in view of the small effect of replacing CO by PPh<sub>3</sub> on the colours of other carbonyls. These reactions are analogous to reactions known to occur for the unsubstituted iron carbonyls.<sup>12</sup>

*Note added in Proof.*—The rates of exchange of all the carbon monoxide ligands in HMn(CO)<sub>5</sub> are the same at -21° and are independent of [CO];<sup>13</sup>  $k_{\text{exchange}} \sim 2 \times 10^{-3}$  sec.<sup>-1</sup> and the exchange is therefore much slower than that of HFe(CO)<sub>5</sub><sup>+</sup> [ $kK_{\text{eq}} \sim (1-4) \times 10^{-2}$  mole<sup>-1</sup> l. sec.<sup>-1</sup>;  $K_{\text{eq}} \ll 1$ ]. This is consistent with the greater amount of back-donation expected from the lower nuclear charge in HMn(CO)<sub>5</sub>.

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INORGANIC CHEMISTRY LABORATORIES, NORTHWESTERN UNIVERSITY,  
EVANSTON, ILLINOIS, U.S.A.

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<sup>12</sup> Speyer and Wolf, *Ber.*, 1927, **60**, 1424.

<sup>13</sup> Basolo and Brault, unpublished work.