

SUBSTITUTION REACTIONS OF SOME POLYNUCLEAR CARBONYL ANIONS

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Summary

The reactions of $[\text{FeCo}_3(\text{CO})_{12}]^-$ and $[\text{MnFe}_2(\text{CO})_{12}]^-$ with a number of monodentate phosphorus donor ligands (L) are reported, and complexes of the type $[\text{FeCo}_3(\text{CO})_{11}\text{L}]^-$ and $[\text{MnFe}_2(\text{CO})_{11}\text{L}]^-$ have been isolated and characterised. Only with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (DPPE) was it possible to replace more than one CO group, the complex $[\text{FeCo}_3(\text{CO})_{10}(\text{DPPE})]^-$ being obtained. Protonation of the iron–cobalt anions leads to the neutral hydrido clusters and is accompanied by a large kinetic isotope effect, although not as large as for $[\text{FeCo}_3(\text{CO})_{12}]^-$ itself. The reaction of $[\text{FeCo}_3(\text{CO})_{12}]^-$ with Ph_2C_2 gives $[\text{FeCo}_3(\text{CO})_{10}(\text{Ph}_2\text{C}_2)]^-$.

Introduction

Although substitution reactions of neutral polynuclear carbonyl complexes have been studied in some detail, there is very little data on the substitution reactions of polynuclear carbonyl anions. The reaction of $[\text{Ni}_2\text{Co}_4(\text{CO})_{14}]^{2-}$ with Ph_3P has been reported [1] to give $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$, $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$, and $[\text{Co}(\text{CO})_3(\text{PPh}_3)]^-$ as the only isolable products, while from the reaction of $[\text{HIr}_4(\text{CO})_{11}]^-$ with Ph_3P only the neutral complex $\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2$ was formed [2]. Indeed, no substituted polynuclear carbonyl anions have ever been characterized.

This lack of data no doubt arises from the difficulty in characterizing the polynuclear carbonyl anions themselves [3] and from the strengthening of the metal–carbon bonds in the anions as compared to corresponding neutral complexes, which renders substitution more difficult. This latter effect has been well substantiated in the chemistry of mononuclear carbonyl complexes and, for example, the complexes $[\text{M}(\text{CO})_6]^-$ (M = V, Nb, or Ta) are much more difficult to substitute [4] than the corresponding neutral complexes $\text{M}(\text{CO})_6$ (M = Cr, Mo, or W) [5].

It might be expected that polynuclear carbonyl anions, in which the negative charge may be regarded as being 'spread' over a greater number of atoms, would not be as difficult to substitute as mononuclear anions. In order to test this hypothesis we have studied some substitution reactions of the polynuclear carbonyl anions $[\text{FeCo}_3(\text{CO})_{12}]^-$ and $[\text{MnFe}_2(\text{CO})_{12}]^-$. These complexes may be regarded respectively as the anionic analogues of $\text{Co}_4(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$, and substitution reactions of both of these neutral complexes have been studied in some detail [6–8]. For our comparison we have chosen the reaction of $[\text{FeCo}_3(\text{CO})_{12}]^-$ and $[\text{MnFe}_2(\text{CO})_{12}]^-$ with organophosphines and with diphenylacetylene.

Results and discussion

Reaction with organophosphines

An acetone solution of the anion $[\text{FeCo}_3(\text{CO})_{12}]^-$ does not react with the ligand Ph_2MeP at room temperature. On refluxing with a two-fold excess of the ligand for 12 h, however, the complex $[\text{FeCo}_3(\text{CO})_{11}(\text{PMePh}_2)]^-$ was formed, and was isolated as its tetraethylammonium salt in almost quantitative yield. No trace of any complex containing more than one coordinated Ph_2MeP ligand could be detected. In contrast, the reaction of $\text{Co}_4(\text{CO})_{12}$ with Ph_2MeP in CHCl_3 solution gives mono-, di-, and tri-substituted complexes, together with substituted complexes of lower nuclearity resulting from cleavage of metal–metal bonds in the cluster [6]. Reactions of $[\text{FeCo}_3(\text{CO})_{12}]^-$ with Ph_3P and with $(\text{C}_3\text{H}_7\text{O})_3\text{P}$ were also carried out. In each case the monosubstituted complex $[\text{FeCo}_3(\text{CO})_{11}\text{L}]^-$ was obtained. Only with the chelating ligand 1,2-bis-(diphenylphosphino)ethane (DPPE) could a disubstituted complex, $[\text{FeCo}_3(\text{CO})_{10}(\text{DPPE})]^-$, be prepared. Similarly, reaction of $[\text{MnFe}_2(\text{CO})_{12}]^-$ with L [L = Ph_3P , Ph_2MeP , or $(\text{C}_3\text{H}_7\text{O})_3\text{P}$] gave only the monosubstituted anions $[\text{MnFe}_2(\text{CO})_{11}\text{L}]^-$ whereas the reaction of $\text{Fe}_3(\text{CO})_{12}$ with Ph_2MeP gives the substituted complexes $\text{Fe}_3(\text{CO})_{12-x}\text{L}_x$ ($x = 1$ or 3) in addition to decomposition products [7]. The reaction of $[\text{MnFe}_2(\text{CO})_{12}]^-$ with DPPE led to rupture of the cluster and the formation of a complex mixture of products which were not separated successfully.

All of the above experimental data are consistent with the metal–carbon bonds in the anions being stronger than those in the related neutral clusters. Since the monosubstituted anions do not undergo further substitution it is also apparent that phosphine substitution at one metal strengthens all the metal–carbon bonds in the cluster.

It is clearly of interest in these mixed metal clusters to determine the site of substitution of the Group V ligand. Even for monosubstituted complexes, however, the number of possible isomers is such that infrared spectroscopy does not provide a reliable criterion for distinguishing between them. On the other hand, Mössbauer spectroscopy provides strong evidence that the neutral complexes $\text{HFeCo}_3(\text{CO})_{12-x}\text{L}_x$ ($x = 1-3$) are formed by stepwise substitution of one CO group on each cobalt atom [9]. Since the protonation of $[\text{FeCo}_3(\text{CO})_{11}\text{L}]^-$ is a convenient route to the neutral complexes $\text{HFeCo}_3(\text{CO})_{11}\text{L}$ it seems likely that the anions too are substituted at one of the cobalt atoms. The possibility of a rearrangement of ligands occurring on protonation is ruled out

TABLE 1
MÖSSBAUER DATA

Compound	C.S. (mm/sec)	Q.S. (mm/sec)
$[\text{MnFe}_2(\text{CO})_{12}][\text{Et}_4\text{N}]$	0.33	0.93
$[\text{MnFe}_2(\text{CO})_{11}\text{Ph}_3\text{P}][\text{Et}_4\text{N}]$	0.34 0.35	1.07 0.81

from the close similarity of the IR spectra of substituted anionic complexes and their protonated neutral analogues.

Mössbauer data were also recorded for the anions $[\text{MnFe}_2(\text{CO})_{11}(\text{PPh}_3)]^-$ and $[\text{MnFe}_2(\text{CO})_{12}]^-$ (Table 1). It can be seen that the two iron atoms, which are equivalent in the unsubstituted anion, are no longer equivalent in the substituted derivative. Although this suggests that substitution takes place at one of the iron atoms it does not rule out the possibility of substitution of an equatorial CO group on the manganese atom. Such substitution would also render the iron atoms inequivalent.

Protonation of the substituted iron-cobalt complexes leads, in each case, to the corresponding neutral polynuclear carbonyl hydride being formed. It has been shown previously [10] that protonation of the unsubstituted anion to give $\text{HFeCo}_3(\text{CO})_{12}$ is associated with an unusually large kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 17.8 \pm 1$). This was attributed to the proton having to "tunnel" through a face of the cluster in order to reach its site of attachment inside the metal atom cage [10, 11]. It was therefore of interest to determine whether substitution by an organophosphine ligand, which must affect the precise geometry of the cluster, would alter the magnitude of $k_{\text{H}}/k_{\text{D}}$ significantly. The H/D ratio in the neutral complexes can, however, only be measured with any degree of accuracy using mass spectroscopy. Only the triisopropylphosphite complex $\text{HFeCo}_3(\text{CO})_{11}[\text{P}(\text{OC}_3\text{H}_7)_3]$ was sufficiently volatile for its mass spectrum to be recorded, and the kinetic isotope effect for this complex was found to be 8.3 ± 1 . A possible explanation for this significantly lower value is that the phosphine ligand "opens up" one of the faces of the cluster thereby lowering the activation energy barrier for the proton.

Substitution of $[\text{FeCo}_3(\text{CO})_{12}]^-$ followed by protonation generally affords the complexes $\text{HFeCo}_3(\text{CO})_{11}\text{L}$ in better yield than does the direct substitution of $\text{HFeCo}_3(\text{CO})_{12}$ which, for the more basic phosphines, leads to more extensive metal-metal bond rupture [9]. This suggests that the negative charge in $[\text{FeCo}_3(\text{CO})_{12}]^-$ strengthens the metal-metal bonds as well as the metal-carbon bonds.

The complexes $[\text{MnFe}_2(\text{CO})_{11}\text{L}]^-$ reacted rapidly in CH_2Cl_2 solution with a few drops of CF_3COOH to yield dark green neutral products. These were unstable at room temperature and could not be characterised.

Reaction with diphenylacetylene

The complex $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$ reacts with Ph_2C_2 in refluxing acetone during five hours to give purple-black crystals of the complex $[\text{FeCo}_3(\text{CO})_{10}(\text{Ph}_2\text{C}_2)][\text{Et}_4\text{N}]$. The stoichiometry of the complex suggests that it is analogous

to the complex $\text{Co}_4(\text{CO})_{10}(\text{Ph}_2\text{C}_2)$, which is obtained from the reaction of $\text{Co}_4(\text{CO})_{12}$ with Ph_2C_2 and which has an unusual "butterfly" structure with the acetylene bridging two cobalt atoms, one of the metal-metal bonds having been broken [12]. $[\text{FeCo}_3(\text{CO})_{10}(\text{Ph}_2\text{C}_2)]^-$, however, has a infra-red spectrum which is very similar to that of $[\text{FeCo}_3(\text{CO})_{10}(\text{DPPE})]^-$ and $[\text{HFeCo}_3(\text{CO})_{10}(\text{DPPE})]$ and quite different from that of $\text{Co}_4(\text{CO})_{10}(\text{Ph}_2\text{C}_2)$. Since in $[\text{FeCo}_3(\text{CO})_{10}(\text{DPPE})]^-$ and $\text{HFeCo}_3(\text{CO})_{10}(\text{DPPE})$ the metal atom tetrahedron is almost certainly preserved intact [9], this would seem to indicate that $\text{Co}_4(\text{CO})_{10}(\text{Ph}_2\text{C}_2)$ and $[\text{FeCo}_3(\text{CO})_{10}(\text{Ph}_2\text{C}_2)]^-$ possess fundamentally different structures. This is explicable in terms of the negative charge on $[\text{FeCo}_3(\text{CO})_{12}]^-$ having a strengthening effect on the metal-metal bonds in the cluster. Clearly, however, an X-ray structure determination is required to prove that the metal-metal bonds do remain unbroken in the latter complex. Protonation of $[\text{FeCo}_3(\text{CO})_{10}(\text{Ph}_2\text{C}_2)]^-$ does not give the acetylene-substituted hydrido complex and neither can this complex be prepared by direct substitution of $\text{HFeCo}_3(\text{CO})_{12}$ with Ph_2C_2 . Instead, both of these reactions lead to the trinuclear complex $\text{FeCo}_2(\text{CO})_8(\text{Ph}_2\text{C}_2)$ being formed. A crystalline sample of this complex for analysis could not be obtained and it was identified by its mass spectrum. The series of positive ions $\text{FeCo}_2(\text{CO})_{8-x}\text{Ph}_2\text{C}_2^+$ ($x = 0$ to 8) were clearly observed with no peaks at higher mass numbers, and the calculated isotopic pattern for the parent peak was in agreement with the observed multiplet. This complex is isoelectronic with the known $\text{Fe}_3(\text{CO})_9\text{Ph}_2\text{C}_2$ [13] and is probably analogous to it. In addition to $\text{FeCo}_2(\text{CO})_8\text{Ph}_2\text{C}_2$, the complex $\text{Co}_2(\text{CO})_6\text{Ph}_2\text{C}_2$ was formed in the reaction of $\text{HFeCo}_3(\text{CO})_{12}$ with Ph_2C_2 .

The reaction of $[\text{MnFe}_2(\text{CO})_{12}]^-$ with Ph_2C_2 under the same conditions gave an intractable mixture of products.

Conclusions

The above experiments confirm our original hypothesis that polynuclear metal carbonyl anions, whilst more difficult to substitute than related neutral complexes, are not as difficult to substitute as mononuclear carbonyl anions. In addition, the data obtained suggest that the presence of a negative charge strengthens not only the metal-carbon bonds but also the metal-metal bonds as compared to those in neutral clusters.

Experimental

Analyses were carried out by the Microanalytical Department of the University Chemical Laboratory. Proton NMR spectra were recorded on a Varian HA 100 spectrometer. Infra-red spectra were recorded on a Perkin-Elmer 257 spectrometer with carbon monoxide as calibrant and are quoted to an accuracy of $\pm 1 \text{ cm}^{-1}$. Mössbauer spectra were recorded at the P.C.M. unit at Harwell on crystalline samples at 77 K. All the data are quoted relative to sodium nitroprusside standard.

Reactions were carried out in an atmosphere of dry nitrogen and solvents were degassed before use. $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$ [14] and $[\text{MnFe}_2(\text{CO})_{12}][\text{Et}_4\text{N}]$ [15] were prepared by literature methods. Organophosphines and organophosphites were used as purchased.

$[FeCo_3(CO)_{11}(PMePh_2)] [Et_4N]$

A two-fold excess of Ph_2MeP (0.3 g, 1.5 mmole) reacted with $[FeCo_3(CO)_{12}][Et_4N]$ (0.5 g, 0.72 mmole) in 50 ml refluxing acetone during 12 h. Excess Ph_2MeP was removed from the dark purple product by repeated precipitation from acetone solution with diethyl ether. Recrystallization from an acetone/diethyl ether mixture at 0° afforded 0.6 g of black crystals (yield 97%). (Found: C, 43.91; H, 3.82; P, 3.50; N, 1.73. $C_{32}H_{33}Co_3FeNO_{11}P$ calcd.: C, 44.09; H, 3.79; P, 3.56; N, 1.61%.) 1H NMR (deuteroacetone): τ 2.6(m); 6.58(q), $J(H-H)$ 7.3 Hz; 8.16 (d), $J(P-H)$ 7.6 Hz; 8.65(t), $J(H-H)$ 7.3 Hz. (for 10, 8, 3, 12, protons respectively). IR (THF): 2007s, 1961vs, 1941s, 1934s, 1905m (sh), 1815vw, 1773m (br).

$[FeCo_3(CO)_{11}(PPh_3)] [Et_4N]$

A two-fold excess of Ph_3P (0.4 g, 1.5 mmole) reacted with $[FeCo_3(CO)_{12}][Et_4N]$ (0.5 g, 0.72 mmole) in 50 ml refluxing acetone during 24 h. The dark purple product was isolated by the procedure previously described for $[FeCo_3(CO)_{11}(PMePh_2)] [Et_4N]$ and crystallized from an acetone/diethyl ether mixture at 0° affording 0.6 g of black crystals (yield 95%). (Found: C, 47.32; H, 3.81; P, 3.29; N, 1.25. $C_{37}H_{35}Co_3FeNO_{11}P$ calcd.: C, 47.59; H, 3.75; P, 3.32; N, 1.50%.) 1H NMR (deuteroacetone): τ 2.65(m); 6.53(q), $J(H-H)$ 7.3 Hz; 8.6 (t of t), $J(H-H)$ 7.3 Hz, $J(^{14}N-H)$ 1.7 Hz (for 15, 8, 12, protons respectively). IR (THF): 2033m, 1980vs, 1956m, 1941m (sh), 1914w, 1836vw, 1806n, 1790m.

$[FeCo_3(CO)_{10}(DPPE)] [Et_4N]$

A two-fold excess of DPPE (0.57 g, 1.4 mmole) reacted with $[FeCo_3(CO)_{12}][Et_4N]$ (0.5 g, 0.72 mmole) in 50 ml refluxing acetone during 10 min. The dark purple product was isolated by the procedure described above for $[FeCo_3(CO)_{11}(PMePh_2)] [Et_4N]$ and crystallized from an acetone/diethyl ether mixture at 0° affording 0.74 g of black crystals (yield 95%). (Found: C, 50.57; H, 4.32; N, 1.45; P, 5.73. $C_{44}H_{44}Co_3FeNO_{10}P_2$ calcd.: C, 50.72; H, 4.23; N, 1.34; P, 5.96%.) 1H NMR (deuteroacetone): τ 2.6(m); 6.55(q), $J(H-H)$ 7.2 Hz; 8.2(m); 8.61 (t of t), $J(H-H)$ 7.2 Hz, $J(^{14}N-H)$ 1.6 Hz. (for 20, 8, 4, 12, protons respectively). IR (THF): 2011s, 1963vs, 1944vs, 1895m (sh), 1807w, 1774m, 1749m.

$[FeCo_3(CO)_{11}\{P(OC_3H_7)_3\}] [Et_4N]$

A four-fold excess of $(C_3H_7O)_3P$ (0.6 g, 2.9 mmole) reacted with $[FeCo_3(CO)_{12}][Et_4N]$ (0.5 g, 0.72 mmole) in 50 ml refluxing acetone during 4 h. Acetone was removed under vacuum, and the product dissolved in diethyl ether from which it was precipitated with light petrol ether several times to remove the excess $(C_3H_7O)_3P$. The product was crystallized from a diethyl ether solution cooled to -20°. 0.4 g of fine needles were obtained (60% yield). (Found: C, 38.38; H, 4.74; P, 3.56; N, 1.59. $C_{28}H_{41}Co_3FeNO_{11}P$ calcd.: C, 38.27; H, 4.66; P, 3.53; N, 1.57%.) 1H NMR (deuteroacetone): τ 5.4(m); 6.5(q), $J(H-H)$ 7.3 Hz; 8.6(t), $J(H-H)$ 7.3 Hz; 8.74(d), $J(H-H)$ 6.0 Hz (for 3, 8, 20, protons respectively, τ 8.6 and 8.74 overlapping). IR (THF): 2037m, 1985vs, 1958s, 1912m, 1884m, 1833vw, 1801m, 1788m.

[MnFe₂(CO)₁₁(PPh₃)] [Et₄N]

A three-fold excess of Ph₃P (1.4 g, 5.5 mmole) was reacted with [MnFe₂(CO)₁₂][Et₄N] (1.0 g, 1.5 mmole) in 50 ml refluxing acetone. The deep blue solution turned dark green over 2½ h, after which the product was precipitated several times from acetone solution with diethyl ether to remove the excess Ph₃P. Final traces of Ph₃P were removed by recrystallization from acetone/diethyl ether mixture at 0°. Dark green crystals (1.2 g) were obtained (yield 90%). (Found: C, 50.57; H, 4.05; N, 1.51; P, 3.67. C₃₇H₃₅MnNO₁₁P calcd.: C, 51.21; H, 4.04; N, 1.61; P, 3.58%.) ¹H NMR (deuteroacetone): τ 2.65(m); 6.6(q), *J*(H—H) 6.6 Hz; 8.65 (t of t), *J*(H—H) 6.6 Hz, *J*(¹⁴N—H) 1.8 Hz (for 15, 8, 12, protons respectively). IR (THF): 2040m, 1997w (sh), 1974s, 1953s, 1927m, 1887w, 1785w, 1750w.

[MnFe₂(CO)₁₁(PMePh₂)] [Et₄N]

A two-fold excess of Ph₂MeP (0.34 g, 1.7 mmole) reacted with [MnFe₂(CO)₁₂][Et₄N] (0.5 g, 0.78 mmole) in 50 ml refluxing acetone during 15 min. Isolation of the dark green product was by the procedure previously described for [MnFe₂(CO)₁₁(PPh₃)] [Et₄N]. Crystallization from an acetone/diethyl ether mixture at 0° afforded 0.6 g of dark green crystals (90% yield). (Found: C, 47.64; H, 4.29; N, 1.73; P, 3.80. C₃₂H₃₃Fe₂MnNO₁₁P calcd.: C, 47.70; H, 4.10; N, 1.74; P, 3.85%.) ¹H NMR (deuteroacetone): τ 2.65(m); 6.6(q), *J*(H—H) 6.6 Hz; 8.15(d), *J*(P—H) 8.4 Hz; 8.65 (t of t), *J*(H—H) 6.6 Hz, *J*(¹⁴N—H) 1.5 Hz (for 10, 8, 3, 12, protons respectively). IR (THF): 2039m, 1974s, 1952s, 1924m, 1882w, 1780w, 1744w.

[MnFe₂(CO)₁₁{P(OC₃H₇)₃}] [Et₄N]

A four-fold excess of (C₃H₇O)₃P (0.82 g, 3.9 mmole) reacted with [MnFe₂(CO)₁₂][Et₄N] (0.5 g, 0.78 mmole) in 50 ml refluxing acetone during 30 min. The product was isolated by the procedure previously described for [MnFe₂(CO)₁₁(PPh₃)] [Et₄N]. Crystallization from an acetone/diethyl ether mixture at 0° afforded 0.58 g of dark green crystals (90% yield). (Found: C, 41.08; H, 5.08; N, 1.52; P, 3.93. C₂₈H₄₁Fe₂MnNO₁₁P calcd.: C, 41.33; H, 5.04; N, 1.72; P, 3.81%.) ¹H NMR (deuteroacetone): τ 5.35(m); 6.5(q), *J*(H—H) 6.6 Hz; 8.65(t), *J*(H—H) 6.6 Hz; 8.74(d), *J*(H—H) 6.6 Hz (for 3, 8, 30 protons respectively, τ 8.65 and 8.74 overlapping). IR (THF): 2041m, 1976s, 1952s, 1924m, 1882w, 1795w, 1762w.

[FeCo₃(CO)₁₀(Ph₂C₂)] [Et₄N]

A five-fold excess of Ph₂C₂ (0.65 g, 3.7 mmole) reacted with [FeCo₃(CO)₁₂][Et₄N] (0.5 g, 0.72 mmole) in 50 ml refluxing acetone during five hours. The intense violet-black product was recrystallized several times from acetone/diethyl ether solution at -20°. Black crystals (0.47 g) were obtained in 80% yield. (Found: C, 46.30; H, 3.42; N, 1.72; Co, 21.66; Fe, 6.62. C₃₂H₃₀Co₃FeNO₁₀ calcd.: C, 46.77; H, 3.65; N, 1.71; Co, 21.56; Fe, 6.28%.) ¹H NMR (deuteroacetone): τ 3.1(m); 6.6(q), *J*(H—H) 7.3 Hz; 8.65 (t of t), *J*(H—H) 7.3 Hz, *J*(¹⁴N—H) 2 Hz (for 10, 8, 12 protons respectively). IR (THF): 2043m, 1994s, 1980s (sh), 1973s (sh), 1969s (sh), 1935m, 1850w, 1815m.

Measurement of the kinetic isotope effect

A 1/1 mixture of DCl and HCl (totalling 1 ml) was made up using a micropipette. A sample of $[\text{FeCo}_3(\text{CO})_{11} \{\text{P}(\text{OC}_3\text{H}_7)_3\}] [\text{Et}_4\text{N}]$ (ca. 30 mg) was dissolved in 50 ml CH_2Cl_2 and the acid mixture was added to this solution, which was then shaken for 3 min. About 30 ml of water was added to the mixture and the dichloromethane layer separated in a funnel. The solvent was reduced in volume under vacuum and the product purified by TLC., eluting with a 9/1 mixture of $n\text{-C}_6\text{H}_{14}$ and CH_2Cl_2 . The procedure was repeated on another sample of $[\text{FeCo}_3(\text{CO})_{11} \{\text{P}(\text{OC}_3\text{H}_7)_3\}] [\text{Et}_4\text{N}]$ using an acid mixture (1 ml) with an H/D ratio of 1/10. The mass spectra of the two products were recorded at 50° . Calculation of the relative proportions of H and D in the parent peaks was accomplished using a computer programme written by Dr. G.M. Sheldrick of this department. The ^1H NMR spectrum of pure $\text{DFeCo}_3(\text{CO})_{11} [\text{P}(\text{OC}_3\text{H}_7)_3]$ showed that no deuterium was incorporated in the $(\text{C}_3\text{H}_7\text{O})_3\text{P}$ ligand. The mass spectrum of $\text{DFeCo}_3(\text{CO})_{11} [\text{P}(\text{OC}_3\text{H}_7)_3]$ was unchanged after allowing the complex to stand with conc. HCl for 5 min. This proves that exchange of co-ordinated deuterium in the product with protons of the protonating source had not occurred.

The ratio of H/D in the products was divided by the ratio of HCl/DCl for the particular acid mixture used, giving the kinetic isotope effect. For the 1/1 acid mixture, a value of 8.5 ± 1 was obtained and for the 1/10 mixture a value of 9.2 ± 1 .

These results are thus within experimental error of each other.

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