Journal of Organometallic Chemistry, 88 (1975) 231–236

SOME ASPECTS OF THE CHEMISTRY OF $Fe_5(CO)_{15}C$

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(Received October 9th, 1974)

Summary

The series of complexes $Fe_5(CO)_{15-x}C(L)_x$ [$L = Ph_3P$, $x = 1$; $L = PhMe_2P$, $x = 1$-3; $L = (C_3H_7O)_3P$, $x = 1$-2; $L = (C_6H_5O)_3P$, $x = 2$] has been prepared by the reaction of $Fe_5(CO)_{15}C$ with the above Group V donor ligands under mild conditions. $Fe_5(CO)_{15}C$ is unaffected by strong acids but reaction with the acetylenes Ph_2C_2 or PhC_2Me results in cluster fragmentation. Reduction with strong bases (NaOH, $NaBH_4$, Na/Hg amalgam) leads to the formation of the anion $[Fe_5(CO)_{14}C]^{2-}$.

Introduction

The carbido-iron cluster $Fe_5(CO)_{15}C$ was first prepared in milligram quantities in 1962 [1]. More recently, improved methods of synthesis have been developed [2, 3], which mean that it is now possible to investigate the chemistry of this cluster more fully than hitherto. In this paper we present a brief study of the reaction of $Fe_5(CO)_{15}C$ and compare them with analogous reactions of the better known trinuclear complex $Fe_3(CO)_{12}$. The possibility that the carbide carbon atom of $Fe_5(CO)_{15}C$ might participate in chemical reactions, as does the methinyl carbon atom in tricobaltcarbon clusters [4-6], made a study of the chemistry of this cluster of particular interest.

Results and discussion

(a). Reaction with Group V donor ligands

The reaction of $Fe_5(CO)_{15}C$ with tertiary phosphines and phosphites occurred rapidly at room temperature in chloroform solution to yield a complex mixture of products. Stable complexes were isolated by thin layer chromatography (TLC) yielding mono-, di-, and tri-substituted compounds based on the Fe_5 cluster unit. The lability of some of the products of the reaction was very great,

TABLE 1

IR STRETCHING FREQUENCIES[a]

$Fe_5(CO)_{14}C(PPh_3)$	2080 m, 2037 vs, 2028 s, 2015 s, 2001 m, 1990 w, 1972 w, 1959 vw, 1941 vw
$Fe_5(CO)_{14}C(PMe_2Ph)$	2080 m, 2035 vs, 2026 s, 2010 s, 2003 (sh), 1982 (sh), 1974 m
$Fe_5(CO)_{13}C(PMe_2Ph)_2$	2061 m, 2031 s, 2020 (sh), 2000 vs, 1993 (sh), 1980 m, 1962 m, 1938 m
$Fe_5(CO)_{12}C(PMe_2Ph)_3$	2042 s, 2001 (sh), 1989 vs, 1969 m, 1955 m, 1941 m, 1925 (sh), 1904 w, 1825 w
$Fe_5(CO)_{13}C[P(OC_6H_5)_3]_2$	2067 w, 2033 vs, 2011 vs, 1998 (sh), 1975 (sh)
$Fe_5(CO)_{14}C[P(OC_3H_7)_3]$	2080 m, 2037 vs, 2028 s, 2014 s, 2003 m, 1990 (sh), 1977 (sh), 1940 vw
$Fe_5(CO)_{13}C[P(OC_3H_7)_3]_2$ (B)	2064 m, 2022 s, 2010 vs, 1999 vs, 1994 (sh), 1979 m, 1969 m, 1961 m, 1949 m, 1945 m, 1933 w, 1856 vw, 1822 vw
$Fe_5(CO)_{13}C[P(OC_3H_7)_3]_2$ (C)	2065 m, 2027 s, 2003 vs, 1966 (sh), 1940 (sh)

[a] Solution in hexane, 1mm NaCl cells.

and prevented characterization in these instances. This contrast with the stability of the reported [7, 8] Group V complexes of $Fe_3(CO)_{12}$ and finds a closer parallel in some Group V derivatives of $YCCo_3(CO)_9$ (Y = Me, Ph, halogen) reported by Robinson [9].

The IR spectra (Table 1) of the series of compounds $Fe_5(CO)_{15-x}C(L)_x$ (L = Group V ligand, x = 1-3) showed many bands in the carbonyl stretching region, consistent with multi-carbonyl species of low symmetry. In two cases, $Fe_5(CO)_{13}C[P(OC_6H_5)_3]_2$ and $Fe_5(CO)_{13}C[P(OC_3H_7)_3]_2$, the IR spectra were more simple, consisting of five bands each. This leads to the tentative suggestion that in these two compounds the position of substitution is such as to retain the plane of symmetry, which is the only element of symmetry in the parent cluster.

The ^1H NMR spectra of the complexes showed only one type of ligand environment in each case. This suggests in the case of those complexes with more than one Group V substituent that the clusters may exhibit fluxional behaviour in solution at room temperature.

(b). Reaction with acetylenes

The reaction of $Fe_5(CO)_{15}C$ with Ph_2C_2 and MeC_2Ph in n-hexane at 60-70° led to the isolation of the known complexes $Fe_2(CO)_6(AC)_2$, $Fe_3(CO)_9(AC)$, (AC = Ph_2C_2, MeC_2Ph), derived from break-up of the cluster. For comparison, the reaction of $Fe_3(CO)_{12}$ with Ph_2C_2 leads to the formation of $Fe_3(CO)_9C_2Ph_2$ in low yield [10]. The mechanism of this latter reaction is, however, unknown and may well proceed through the oligomerization of mononuclear species.

(c). Protonation

Unlike the carbide carbon atoms in clusters such as $[Fe_6(CO)_{16}C]^{2-}$ and $Ru_6(CO)_{17}C$, which are located at the centre of metal atom cages, the carbide atom in $Fe_5(CO)_{15}C$ lies below the basal plane of the pyramid of iron atoms to which it is bonded [1]. It seemed therefore, that it might be possible to protonate this carbon atom. However, the cluster was quite insoluble in concentrated

H_2SO_4 [$Fe_3(CO)_{12}$ decomposes in strong acid], although it did dissolve slowly in CF_3COOH to give a yellow-brown solution. The NMR of this solution did not show any resonances in the region τ 0-10 which would have indicated the formation of a C—H bond, nor were any high-field resonances detected which would have suggested the protonation of a metal site. Furthermore, no precipitate was obtained on addition of $NaPF_6$ to the CF_3COOH solution of the complex and the unprotonated complex was recovered unchanged on concentration of this solution. These data strongly suggest that $Fe_5(CO)_{15}C$ is not protonated by strong acids in contrast to a number of other polynuclear carbonyls on which protonation studies have been made [11]. In particular it seems that the carbide carbon atom is not a centre of negative charge in the complex.

(d). Reaction with nucleophiles

The reaction of $Fe_5(CO)_{15}C$ with strong bases (NaOH, $NaBH_4$, or Na/Hg amalgam) in THF proceeded smoothly to form $[Fe_5(CO)_{14}C]^{2-}$ in each case. The dark brown anion was isolated as its tetraethylammonium salt and characterized by elemental analysis. This may be contrasted with the reaction of $Fe_3(CO)_{12}$ with base where the product is highly dependent upon the base used. With $NaBH_4$ the red anion $[HFe_3(CO)_{11}]^-$ is formed, while cluster fragmentation is favoured by hydroxide and sodium amalgam. The addition of 2 electrons to the cluster to give $[Fe_5(CO)_{15}C]^{2-}$, predicted as a possibility by Wade [12], was not realized by any of these reagents.

Careful acidification (pH 1 to 2) of an aqueous solution of $Na_2[Fe_5(CO)_{14}C]$ with concentrated H_3PO_4 or HCl produced an intense red, petrol-soluble compound which was unstable at room temperature and decomposed within 15 min. Attempts at characterisation of the compound as a hydride by ^1H NMR and mass spectroscopy failed. This is consistent with the low stability of the protonation products of many of the iron carbonyl anions [13].

The IR spectrum of $[Fe_5(CO)_{14}C]^{2-}$ prepared herein is at variance with that reported for a compound of the same formulation prepared by the reduction of $Fe(CO)_5$ with $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ [14]. This latter compound was formulated as $[Fe_5(CO)_{14}C]^{2-}$ on the basis of analytical data and the fact that its IR spectrum was different from that of $[Fe_6(CO)_{16}C]^{2-}$ which is also prepared by the reduction of $Fe(CO)_5$ with metal carbonyl anions. The IR spectrum of $[Fe_6(CO)_{16}C]^{2-}$ itself, however, depends critically upon its method of preparation [2, 3], and it now seems possible that the compound originally reported as $[Fe_5(CO)_{14}C]^{2-}$ may have been a different isomer of $[Fe_6(CO)_{16}C]^{2-}$ or a mixture of $[Fe_6(CO)_{16}C]^{2-}$ and $[Fe_5(CO)_{14}C]^{2-}$. The calculated elemental analyses for these two anions are not very different and an X-ray structure determination is clearly needed to resolve this problem unequivocally*.

Experimental

Reactions were performed in $CHCl_3$ (A.R. grade) under N_2. The progress

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* *Note added proof:* A careful reexamination of the IR spectra of all these anions has shown that the compound originally reported as $[Fe_5(CO)_{14}C]^{2-}$ has a spectrum identical to that of $[Fe_6(CO)_{16}C]^{2-}$ as given in ref. 2. Furthermore the spectrum of this latter anion does not depend on its method of preparation and is erroneously reported in ref. 3.

of reactions was monitored by TLC on aliquots withdrawn from the reaction mixtures at different intervals. The developed chromatograms were complex but reproducible. Some bands represented stable complexes which were identified by their colour, R_F values and IR spectra. Other bands represent labile complexes which could not be characterized by these means. The extraction of one of these latter bands from the TLC plate was often followed by its conversion to a complex mixture of bands upon rechromatography.

Preparation of $Fe_5(CO)_{15-x}C[P(OC_3H_7)_3]_x$ *(x = 1 or 2)*

A solution of $(C_3H_7O)_3P$ (0.29 g, 1.6 mmol) in $CHCl_3$ (20 ml) was added to a solution of $Fe_5(CO)_{15}C$ (0.5 g, 0.7 mmol) in $CHCl_3$ (20 ml) at room temperature over 10 min. Immediate elution of the mixture on TLC plates using a solvent mixture of 3/1 hexane/CH_2Cl_2 afforded 2 main bands, (A, dark brown and B, yellow brown) in approximately equal ratios. A third, slow-moving band (C, purple) was of low intensity. Repeated chromatographic purification of bands A and B followed by crystallization from pentane afforded pure crystals which were formulated from elemental analysis as $Fe_5(CO)_{14}C[P(OC_3H_7)_3]$ (0.4 g) (A), and $Fe_5(CO)_{13}C[P(OC_3H_7)_3]_2$ (0.5 g) (B), each in approximately 30% yield.

By extending the reaction time to 2 h the yield of band C was increased. Dark purple crystals were isolated as described above to give $Fe_5(CO)_{13}C[P(OC_3H_7)_3]_2$ (0.4 g, 25% yield). The chromatogram of the reaction mixture after 2 h was very complex, containing many unstable products. After 8 h the chromatogram of the reaction mixture was far simpler containing only stable bands: band A of low intensity, band B of moderate intensity, band C (the major product), and band D (purple) of low intensity. Band D had the same IR spectrum as band C, and afforded an identical analysis. It is possible that compounds C and D interconverted during the extraction and purification stages or that the two compounds are isomers.

$Fe_5(CO)_{14}C[P(OC_3H_7)_3]$, (Found: C, 32.50; H, 2.51; P, 3.38. $C_{24}H_{21}Fe_5O_{17}P$ calcd.: C, 32.29; H, 2.35; P, 3.48%). NMR ($CDCl_3$): τ 5.3 (m, 1H, CH), 8.7 [d, 6H, CH_3, J(P—H) = 6Hz].

$Fe_5(CO)_{13}C[P(OC_3H_7)_3]_2$, [Found (Band B): C, 36.57; H, 4.11; P, 5.57. Found (Band C): C, 36.54; H, 4.03; P, 5.53. $C_{32}H_{42}Fe_5O_{19}P_2$ calcd.: C, 35.82; H, 3.92; P, 5.78%]. NMR ($CDCl_3$) (Bands B and C): τ 5.3 (m, 1H, CH), 8.7 (m, 6H, CH_3).

Preparation of $Fe_5(CO)_{15-x}C(PMe_2Ph)_x$ *(x = 1, 2, 3)*

A solution of Me_2PhP (0.19 g, 1.4 mmol) in $CHCl_3$ (20 ml) was added to $Fe_5(CO)_{15}C$ (0.5 g, 0.7 mmol) in $CHCl_3$ (20 ml) at room temperature over 10 min. Immediate elution of an aliquot of the reaction mixture on TLC plates using a solvent mixture of 3/1 hexane/CH_2Cl_2 gave a complex chromatogram of 2 stable bands and 4 unstable bands. After 4 h, the reaction mixture contained only stable products. Three bands were eluted: Band A (dark brown), band B (purple) and band C (dark brown). The compounds were extracted and rechromatographed to high purity and crystallized from pentane. Compounds A (0.25 g, 20%) and B (0.23 g, 20%) had identical IR spectra and both analyzed for $Fe_5(CO)_{14}C(PMe_2Ph)$ which suggests that they are isomers or that they have interconverted during the extraction and purification stages. Compound C

(0.13 g, 20%) was formulated on the basis of analytical data as $Fe_5(CO)_{13}C(PMe_2Ph)_2$.

Reaction of $Fe_5(CO)_{15}C$ with a three-fold excess of ligand during 24 h led to the isolation by TLC of a dark brown complex formulated from analytical data as $Fe_5(CO)_{12}C(PMe_2Ph)_3$ (0.6 g, 35%).

$Fe_5(CO)_{14}C(PMe_2Ph)$, (Found: C, 33.90; H, 1.48; P, 3.65. $C_{23}H_{11}Fe_5O_{14}P$ calcd.: C, 35.58; H, 1.34; P, 3.77%). NMR ($CDCl_3$): τ 2.6 (m, 5H, Ph), 8.3 [d, 6H, CH_3, $J(P-H)$ = 10Hz].

$Fe_5(CO)_{13}C(PMe_2Ph)_2$, (Found: C, 38.79; H, 2.70; P, 6.21. $C_{30}H_{22}Fe_5O_{13}P_2$ calcd.: C, 38.59; H, 2.36; P, 6.65%.) NMR ($CDCl_3$): τ 2.6 (m, 5H, Ph), 8.1 [d, 6H, CH_3, $J(P-H)$ = 9.3 Hz]. $Fe_5(CO)_{12}C(PMe_2Ph)_3$, (Found: C, 43.02; H, 3.28; P, 8.74. $C_{40}H_{33}Fe_5O_{12}P_3$ calcd.: C, 42.61; H, 3.17; P, 8.93%). NMR ($CDCl_3$): τ 2.7 (m, 5H, Ph), 8.4 (m, CH_3).

Preparation of $Fe_5(CO)_{14}C(PPh_3)$ and $Fe_5(CO)_{13}C[P(OC_6H_5)_3]_2$

The reaction of $Fe_5(CO)_{15}C$ with Ph_3P and $(C_6H_5O)_3P$ differ from the previous preparations only in the reaction times and the proportions of reactants.

A two-fold excess of Ph_3P reacted with $Fe_5(CO)_{15}C$ (0.5 g) during 15 min. Dark black crystals (0.2 g, 30%) of $Fe_5(CO)_{14}C(PPh_3)$ were obtained after work-up.

A three-fold excess of $(C_6H_5O)_3P$ reacted with $Fe_5(CO)_{15}C$ (0.5 g) during 4 h. Dark violet crystals of $Fe_5(CO)_{13}C[P(OC_6H_5)_3]_2$ (0.23 g, 30%) were obtained after work-up.

$Fe_5(CO)_{14}C(PPh_3)$, (Found: C, 42.08; H, 1.86; P, 3.08. $C_{33}H_{15}Fe_5O_{14}P$ calcd.: C, 41.86; H, 1.59; P, 3.28%). NMR ($CDCl_3$): τ 2.7 (m, Ph).

$Fe_5(CO)_{13}C[P(OC_6H_5)_3]_2$, (Found: C, 46.81; H, 2.53; P, 4.64. $C_{50}H_{30}Fe_5O_{19}P_2$ calcd.: C, 47.02; H, 2.35; P, 4.86%). NMR ($CDCl_3$): τ 2.85 (m, Ph).

Preparation of $[Fe_5(CO)_{14}C][Et_4N]_2$

A five-fold excess of base (NaOH, $NaBH_4$ or Na/Hg amalgam) was added to $Fe_5(CO)_{15}C$ (0.25 g, 0.0035 mmol) in 25 ml THF. The solution was stirred for 20 min after which the solvent was removed under vacuum and the residue extracted with water. Addition of excess Et_4NBr to the solution precipitated the product which was washed with water, dried and recrystallized from an acetone/diethyl ether mixture. Dark brown crystals of $[Fe_5(CO)_{14}C][Et_4N]_2$ (0.2 g, 80%) were obtained. (Found: C, 39.67; H, 4.33; Fe, 29.44; N, 2.94. $C_{31}H_{40}Fe_5O_{14}N_2$ calcd.: C, 39.40; H, 4.24; Fe, 29.66; N, 2.97%.) IR spectrum in THF, 0.1 mm NaCl cells: 2025 w, 2000 m, 1969 vs, 1940 (sh), 1890 (sh), 1760 (br).

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