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HALOALKYL COMPLEXES OF THE TRANSITION METALS

I. THE SYNTHESIS AND SOME REACTIONS OF THE HALOALKYL COMPLEXES FORMED BY THE REACTION OF SODIUM (*pentahapto*-CYCLOPENTADIENYL)DICARBONYLIRON WITH α,ω-DIHALOALKANES *

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Summary

The reactions of $\mathrm{Na[CpFe(CO)_2]}$ ($\mathrm{Cp} = \eta^5\text{-}\mathrm{C_5H_5}$) with α,ω-dihaloalkanes at —20°C yield ω-haloalkyl complexes of the type $\mathrm{CpFe(CO)_2(CH_2)}_n\mathrm{X}$ ($n = 3$, 4 or 5, X = Br; $n = 3$, X = Cl). $\mathrm{CpFe(CO)_2(CH_2)}_n\mathrm{Br}$ reacts with $\mathrm{Na[CpFe(CO)_2]}$ to give the known binuclear complexes $\mathrm{[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]}$ ($n = 3$, 4 or 5) and with $\mathrm{Na[CpMo(CO)_3]}$ to give the mixed metal complex $\mathrm{CpFe(CO)_2[\mu\text{-}(CH_2)_3]CpMo(CO)_3}$. Triphenylphosphine reacts with $\mathrm{CpFe(CO)_2(CH_2)_3Br}$ in refluxing acetonitrile to give the carbene cation $[\mathrm{CpFe(CO)(PPh_3)}\overline{\mathrm{COCH_2CH_2C}}\mathrm{H_2}]^+$, isolated as the $\mathrm{PF_6}^-$ and $\mathrm{BPh_4}^-$ salts, and the cationic acyl complex $\mathrm{[CpFe(CO)(PPh_3)CO(CH_2)_3PPh_3]^+Br^-}$.

Introduction

Fischer and Tropsch originally suggested the polymerisation of methylene groups on a metal surface to account for the formation of products in the Fischer-Tropsch reaction [1]. Recent evidence [2] has been found to be consistent with this proposal and this has resulted in considerable current interest in dinuclear complexes containing bridging methylene [3] or polymethylene groups. A possible route to such complexes is via haloalkyl complexes.

The reactions of $\mathrm{Na[CpFe(CO)_2]}$ with α,ω-dihaloalkanes in refluxing tetrahydrofuran (THF) have been reported to yield the dinuclear complexes

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$[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ [4] and the structures of the complexes where $n = 3$ or 4 have been determined by X-ray crystallography [5]. Although it has been proposed that these binuclear complexes are formed from the haloalkyl complexes $CpFe(CO)_2(CH_2)_nX$, these mononuclear complexes have not previously been characterized [6].

As part of a general study on transition metal haloalkyl complexes, we now report on the synthesis of the complexes $CpFe(CO)_2(CH_2)_nX$ ($n = 3$, 4 or 5, X = Br; $n = 3$, X = Cl) and demonstrate their ability to act as precursors for dinuclear complexes containing polymethylene bridges and for cyclic carbene complexes.

Results and discussion

We find that if $Na[CpFe(CO)_2]$ is added to an excess of $Br(CH_2)_3Br$ in THF at −20°C, then the 3-bromo-n-propyl complex $CpFe(CO)_2(CH_2)_3Br$ (I) can be isolated in high yield from the reaction mixture. Other α,ω-dihaloalkanes react under similar conditions to give high yields of the corresponding ω-haloalkyl complexes

$$Na[CpFe(CO)_2] + X(CH_2)_nX \xrightarrow[\text{THF}]{-20^\circ\text{C}} CpFe(CO)_2(CH_2)_nX$$

$$\begin{array}{l}(\text{I})\ n = 3,\ X = Br\\(\text{II})\ n = 4,\ X = Br\\(\text{III})\ n = 5,\ X = Br\\(\text{IV})\ n = 3,\ X = Cl\end{array}$$

The reaction of the iron anion with α,ω-dihaloalkanes is thus temperature dependent. Similarly, the products from the reaction of *cis*-3,4-dichlorocyclobutene have also been reported to be dependent on reaction temperature [7]. In contrast, we find that the reaction of $Na[CpFe(CO)_2]$ with 1,2-dibromoethane at −20°C gave an almost quantitative yield of $[CpFe(CO)_2]_2$, as had previously been found for this reaction at higher temperatures [4]. The different types of products obtained in the reactions of $Na[CpFe(CO)_2]$ [4], $Na[CpMo(CO)_3]$ [8] and $Na[Mn(CO)_5]$ [9] with 1,3-dibromopropane can be rationalized on the basis of the nucleophilicity of the anion concerned and the ease with which the initially formed 3-bromo-n-propyl complex undergoes carbonyl insertion or nucleophilic attack at $-CH_2Br$.

Compound IV was also obtained by the decarbonylation of hexane solutions of $CpFe(CO)_2CO(CH_2)_3Cl$ on UV irradiation.

The products I—IV were obtained as reasonably air-stable yellow oils or low-melting solids and characterized by elemental analysis, IR and ^1H NMR spectra. Also, the mass spectra of these compounds showed parent molecular ions with the expected isotope patterns.

The ω-bromoalkyl complexes react at room temperature with $Na[CpFe(CO)_2]$ to yield the previously reported dinuclear complexes [4,5]

$$CpFe(CO)_2(CH_2)_nBr \xrightarrow[\text{THF}]{Na[CpFe(CO)_2]} CpFe(CO)_2[\mu\text{-}(CH_2)_n]Fe(CO)_2Cp$$

$$(n = 3,\ 4 \text{ or } 5)$$

An attempt to prepare a mixed metal dinuclear complex containing a polymethylene bridge has been reported by the reaction of $Na[CpFe(CO)_2]$ with $CpMo(CO)_3(CH_2)_3Br$ [8]; however, this reaction gave only $[CpFe(CO)_2]_2$-$[\mu$-$(CH_2)_3]$, presumably a result of the strong nucleophilicity of the iron anion. We find that the reaction of $CpFe(CO)_2(CH_2)_3Br$ with $Na[CpMo(CO)_3]$ in refluxing THF results in the mixed metal dinuclear complex $CpFe(CO)_2[\mu$-$(CH_2)_3]$-$Mo(CO)_3Cp$ (V) (albeit in low yield). V was isolated as yellow needles and shows

$$CpFe(CO)_2(CH_2)_3Br + Na[CpMo(CO)_3] \rightarrow \underset{\text{(V)}}{CpFe(CO)_2[\mu\text{-}(CH_2)_3]Mo(CO)_3Cp}$$

two Cp resonances in its ^1H NMR spectrum and five strong $\nu(CO)$ bands in its IR spectrum, in agreement with the proposed structure.

It has been demonstrated that 3-bromo-n-propyl-metal complexes are useful precursors for cyclic carbene complexes, thus $CpMo(CO)_3(CH_2)_3Br$ reacts readily with PPh_3 to yield the cyclic carbene complex $[CpMo(CO)_2(PPh_3)\overline{COCH_2CH_2CH_2}]^+$-$Br^-$ in high yield [10]. We find that although $CpFe(CO)_2(CH_2)_3Br$ does not react with PPh_3 in acetonitrile at room temperature over several days, reaction does occur on refluxing the solution for about 6 hours and two products are obtained. These were shown to be the cyclic carbene complex $[CpFe(CO)(PPh_3)$ $(\overline{COCH_2CH_2CH_2}]^+Br^-$ (VI) and the acyl complex $[CpFe(CO)(PPh_3)CO(CH_2)_3$-$PPh_3]^+Br^-$ (VII). The facile reaction of $CpMo(CO)_3(CH_2)_3Br$ with PPh_3, relative to $CpFe(CO)_2(CH_2)_3Br$, is presumably a result of the carbonyl insertion reaction occurring more readily with the molybdenum complex.

$$\begin{tikzcd}
CpFe(CO)_2(CH_2)_3Br + PPh_3 \arrow[r, "\text{reflux}", "\text{acetonitrile}"'] & {[CpFe(CO)(PPh_3)\overline{COCH_2CH_2CH_2}]^+Br^-} \arrow[d, "\text{(VI)}"', "\begin{array}{l}PPh_3\\ \text{reflux acetonitrile}\end{array}"] \\
 & {[CpFe(CO)(PPh_3)CO(CH_2)_3PPh_3]^+Br^-} \\
 & \text{(VII)}
\end{tikzcd}$$

VI could not be recrystallized and was not obtained analytically pure; however, it was characterized as the corresponding PF_6^- (VIII) or BPh_4^- (IX) salts. That VI is a precursor of VII was demonstrated by refluxing VI with PPh_3 in acetonitrile, when VII could be isolated. This type of ring-opening reaction has been observed previously on reaction of $[CpFe(CO)_2\overline{COCH_2CH_2CH_2}]^+$ with halide anions [11].

Experimental

^1H NMR spectra were recorded on a Perkin-Elmer R12 spectrometer using tetramethylsilane as internal standard. IR spectra were recorded on a Perkin-Elmer 180 spectrophotometer. Mass spectra were recorded on an AEI MS30 spectrometer operating at 70 eV with source temperatures in the range 30—70°C; samples were introduced by direct insertion. Melting points were determined on a Kofler hot-stage microscope and are uncorrected. All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran and hexane were distilled from lithium aluminium hydride under nitrogen. $[CpFe(CO)_2]_2$ was prepared from $Fe(CO)_5$ and reduced to the sodium salt of the anion by published procedures [12]. $CpFe(CO)_2CO(CH_2)_3Cl$ was prepared by the method of Game et al. [11] but was further purified by column chromatography using Merck alumina (activity II—III) with a 10 cm column. Microanalyses were performed by F. and E. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany. Conductivity measurements were made on ca. 10^{-3} *M* solutions in nitrobenzene.

Preparation of $CpFe(CO)_2(CH_2)_3Br$ (I)

A solution of $Na[CpFe(CO)_2]$ (19.92 mmol) in THF (50 ml) was added dropwise over 20 min to 1,3-dibromopropane (5.94 g, 29.42 mmol) with stirring at —20°C. The reaction mixture was stirred for a further 15 min at —20°C, then allowed to warm up to room temperature over 45 min. The solvent was removed under reduced pressure and the resulting brown oil was extracted with hexane (4 × 20 ml), filtered and the solvent reduced to a small volume, then chromatographed. Elution with hexane gave a yellow band which was concentrated and cooled to —78°C to yield yellow needles of I (4.17 g, 70%) m.p. 22—24°C (Found: C, 39.96; H, 3.57; Br, 26.74. $C_{10}H_{11}BrFeO_2$ calcd.: C, 40.18; H, 3.71; Br, 26.73%); ν(CO) (cyclohexane) 2011s, 1960s, 1957(sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.76 (s, 5 H, C_5H_5), 3.34 (t, 2 H, CH_2Br, $J(HH) = 7.2$ Hz), 1.95 (m, 2 H, —CH_2—), 1.33 ppm (m, 2 H, Fe—CH_2). A red band was eluted with hexane-diethyl ether and shown to be $[CpFe(CO)_2]_2$.

Preparation of $CpFe(CO)_2(CH_2)_4Br$ (II)

This was prepared similarly from $Na[CpFe(CO)_2]$ (12.16 mmol) and 1,4-dibromobutane (15.24 mmol) and gave II as a yellow oil (74%) which was further purified by molecular distillation (60°C/10^{-2} mmHg). (Found: C, 42.58; H, 4.23; Br, 26.78. $C_{11}H_{13}BrFeO_2$ calcd.: C, 42.21; H, 4.19; Br, 25.53%); ν(CO) (cyclohexane) 2009s, 1956s cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.77 (s, 5 H, C_5H_5), 3.45 (t, 2 H, CH_2Br, $J(HH) = 6.6$ Hz), 1.84, 1.49 ppm (m, 6 H, $(CH_2)_3$). Other minor products obtained in this reaction were $[CpFe(CO)_2]_2$ and $[CpFe(CO)_2]_2$-$[\mu$-$(CH_2)_4]$.

Preparation of $CpFe(CO)_2(CH_2)_5Br$ (III)

This was prepared similarly from $Na[CpFe(CO)_2]$ (10.60 mmol) and 1,5-dibromopentane (11.09 mmol) and gave III as a yellow oil (88%). (Found: C, 44.28; H, 4.60; Br, 25.28. $C_{12}H_{15}BrFeO_2$ calcd.: C, 44.08; H, 4.62; Br, 24.44%), ν(CO) (cyclohexane) 2009s, 1955s cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.76 (s, 5 H, C_5H_5) 3.42 (t, 2 H, CH_2Br, $J(HH) = 6.6$ Hz), 1.84, 1.48 ppm (m, 8 H, $(CH_2)_4$).

Preparation of $CpFe(CO)_2(CH_2)_3Cl$ (IV)

This was prepared similarly from $Na[CpFe(CO)_2]$ (11.34 mmol) and 1,3-dichloropropane (13.98 mmol) and gave IV as a yellow oil (82%). (Found: C, 47.32; H, 4.34; Cl, 13.72. $C_{10}H_{11}ClFeO_2$ calcd.: C, 47.20; H, 4.36; Cl, 13.93%), ν(CO) (cyclohexane) 2012s, 1960s, 1958(sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.77 (s, 5 H, C_5H_5), 3.45 (t, 2 H, CH_2Cl, $J(HH) = 6.8$ Hz), 1.88 (m, 2 H, —CH_2—), 1.35 ppm (m, 2 H, CH_2Fe). IV was also obtained (in 41% yield) on UV irradiation of a hexane solution of $CpFe(CO)_2CO(CH_2)_3Cl$ and after chromatography to remove any acyl starting material.

Reaction of $CpFe(CO)_2(CH_2)_3Br$ (I) with $Na[CpFe(CO)_2]$

A solution of $Na[CpFe(CO)_2]$ (1.95 mmol) in THF (7 ml) was added to a solution of I (1.61 mmol) in THF (2 ml) and the reaction mixture allowed to stand at room temperature for 18 h. The solvent was removed and the residue extracted with dichloromethane (4 × 10 ml). Removal of the solvent and recrystallization of the residue from hexane gave $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_3]$ as yellow plates (63%) m.p. 104—106°C (Lit. [4] 103—105°C); an IR spectrum of this product was identical to that of an authentic sample.

Reaction of $CpFe(CO)_2(CH_2)_4Br$ (II) with $Na[CpFe(CO)_2]$

Similarly, II and $Na[CpFe(CO)_2]$ gave $[CpFe(CO)_4]_2[\mu\text{-}(CH_2)_4]$ (67%) m.p. 125—129°C (Lit. [4] 123—124°C).

Reaction of $CpFe(CO)_2(CH_2)_5Br$ (III) with $Na[CpFe(CO)_2]$

Similarly III and $Na[CpFe(CO)_2]$ gave $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_5]$ (44%) m.p. 82—86°C (Lit. [4] 82—83°C).

Reaction of I with $Na[CpMo(CO)_3]$

A solution of I (0.37 g, 1.23 mmol) and $Na[CpMo(CO)_3]$ (5.58 mmol) in THF (24 ml) was allowed to stand at room temperature for 3 h and then refluxed for 21 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (4 × 10 ml), filtered and solvent removed. The oily residue was taken up in hexane (15 ml) and chromatographed. Elution with hexane and subsequent work-up gave a yellow oil of I (0.10 g) and a yellow solid (0.102 g, 18%) which was recrystallized from hexane to give $[CpFe(CO)_2][\mu\text{-}(CH_2)_3][CpMo(CO)_3]$ (V) as yellow needles m.p. 97—99°C. (Found: C, 46.58; H, 3.47; O, 17.24. $C_{18}H_{16}FeMoO_5$ calcd.: C, 47.14; H, 3.75; O, 18.30%). ν(CO) (cyclohexane) 2015s, 2004s, 1953(sh), 1950s, 1935s, 1930(sh), 1927s cm^{-1}; ^1H NMR (C_6H_6) δ 4.62 (s, 5 H, Fe—C_5H_5) 4.17 (s, 5 H, Mo—C_5H_5) 1.79 ppm (m, 6 H, $(CH_2)_3$).

Reaction of I with triphenylphosphine

A solution of I (0.52 g, 1.75 mmol) and PPh_3 (0.52 g, 1.96 mmol) in acetonitrile (15 ml) was refluxed for 5 h. The solvent was removed under reduced pressure and the resulting yellow oil solidified on addition of ether to give a yellow powder. Recrystallization of this powder from methanol-water gave $[CpFe(CO)(PPh_3)CO(CH_2)_3PPh_3]^+Br^-$ (VII) as yellow platelets (0.27 g, 19%). This product was further purified by recrystallization from dichloromethane-ether to give yellow microcrystals, m.p. 188—190°C. (Found: C, 65.86; H, 5.40; Br, 9.53; P, 7.43. $C_{46}H_{41}BrFeO_2P_2$ calcd.: C, 67.09; H, 5.02; Br, 9.70; P, 7.52%). ν(CO) (CH_2Cl_2) 1918s, 1603m(br), 1589(sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82—7.36 (m, 30 H, Ph), 4.46 (d, 5 H, C_5H_5, J(PH) = 1 Hz), 3.09, 2.38, 1.32 ppm (m, $(CH_2)_3$); the equivalent conductance was 25.6 ohm^{-1} cm^2 mol^{-1}. The methanol-water filtrate obtained above was extracted with dichloromethane (3 × 20 ml) and the yellow organic layer dried (Na_2SO_4) filtered and the solvent removed. The resulting yellow oil solidified on addition of ether to give $[CpFe(CO)(PPh_3)\overline{COCH_2CH_2C}H_2]^+Br^-$ (VI) as a yellow powder (0.28 g, 29%) ν(CO) (CH_2Cl_2) 1978 cm^{-1}; equivalent conductance was 23.9 ohm^{-1} cm^2 mol^{-1}. VI was characterized as the PF_6^- and BPh_4^- salts (see below).

Preparation of $[CpFe(CO)(PPh_3)\overline{COCH_2CH_2C}H_2]^+PF_6^-$ *(VIII)*

A solution of VI (0.21 g, 0.38 mmol) in a minimum volume of methanol was treated with a saturated solution of NH_4PF_6 (0.11 g, 0.64 mmol) in methanol. The yellow precipitate which formed was filtered off and recrystallized from dichloromethane-ether to give VIII as yellow platelets (0.17 g, 71%), m.p. 223—227°C (decomp.). (Found: C, 53.65; H, 4.04; P, 10.55. $C_{28}H_{26}F_6FeO_2P_2$ calcd.: C, 53.70; H, 4.18; P, 9.89%), ν(CO) (CH_2Cl_2) 1980s cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.64 (m, 15 H, Ph), 5.18 (d, 5 H, C_5H_5, J(PH) = 1.8 Hz), 4.69 (t, 2 H, OCH_2, J(HH) = 8 Hz), 3.54 (t, 2 H, CCH_2, J(HH) = 8 Hz), 1.69 ppm (q, 2 H, —CH_2—, J(HH) = 8 Hz); the equivalent conductance was 26.3 ohm^{-1} cm^2 mol^{-1}.

Preparation of $[CpFe(CO)(PPh_3)\overline{COCH_2CH_2C}H_2]^+BPh_4^-$ *(IX)*

Similarly, a solution of VI (0.24 mmol) in methanol was treated with $NaBPh_4$ (0.24 mmol) in methanol to give an immediate precipitate. Recrystallization of this product from dichloromethane-ether gave IX as yellow needles (44%), m.p. 182—185°C. (Found: C, 77.41; H, 5.93; P, 3.88. $C_{52}H_{46}BFeO_2P$ calcd.: C, 78.01; H, 5.79; P, 3.87%); ν(CO) (CH_2Cl_2) 1982s cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.64—6.87 (m, 35 H, Ph), 5.14 (d, 5 H, C_5H_5, J(PH) = 1.5 Hz), 4.63 (br, 2 H), 3.47 (t, 2 H, CCH_2, J(HH) = 8 Hz), 1.47 ppm (q, 2 H, —CH_2—, J(HH) = 8 Hz); the equivalent conductance was 21.0 ohm^{-1} cm^2 mol^{-1}.

Reaction of VI with triphenylphosphine

A solution of VI (0.15 g, 0.26 mmol) in acetonitrile (10 ml) was treated with PPh_3 (0.09 g, 0.34 mmol) and the solution refluxed for 6 h. Subsequent work up gave a light-brown solid which showed ν(CO) bands of VI and VII. Recrystallization of this solid from methanol-water and then from dichloromethane-ether gave yellow microprisms (0.033 g) whose IR spectrum was identical to that of an authentic sample of VII.

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References

1 F. Fischer and H. Tropsch, Brennst. Chem., 7 (1926) 97.
2 R.C. Brady and R. Pettit, J. Amer. Chem. Soc., 102 (1980) 6181; R.C. Brady and R. Pettit, J. Amer. Chem. Soc., 103 (1981) 1287.
3 W.A. Hermann, J. Plank, D. Riedel, M.L. Ziegler, K. Weidenhammer, E. Guggolz and B. Balbach, J. Amer. Chem. Soc., 103 (1981) 63; W.A. Hermann, Ch. Bauer, J. Plank, W. Kalcher, D. Speth and M.L.

Ziegler, Angew. Chem. Int. Ed. Engl., 20 (1981) 193; D.L. Davies, A.F. Dyke, S.A.R. Knox and M.J. Morris, J. Organometal. Chem., 215 (1981) C30.

4 R.B. King, Inorg. Chem., 2 (1963) 531.

5 L. Pope, P. Sommerville, M. Laing, K.J. Hindson and J.R. Moss, J. Organometal. Chem., 112 (1976) 309.

6 C.P. Casey, C.R. Cyr, R.L. Anderson and D.F. Marten, J. Amer. Chem. Soc., 97 (1975) 3053.

7 A. Sanders and W.P. Giering, J. Organometal. Chem., 104 (1976) 67.

8 R.B. King and M.B. Bisnette, J. Organometal. Chem., 7 (1967) 311.

9 C.P. Casey and R.L. Anderson, J. Amer. Chem. Soc., 93 (1971) 3554.

10 F.A. Cotton and C.M. Lukehart, J. Amer. Chem. Soc., 93 (1971) 2672.

11 C.H. Game, M. Green, J.R. Moss and F.G.A. Stone, J. Chem. Soc. Dalton, (1974) 351.

12 R.B. King and F.G.A. Stone, Inorg. Syntheses, 7 (1963) 110.