Reactions of Metal Carbonyl Derivatives. Part XVIII.[1] Synthesis and Redox Properties of Some Binuclear Derivatives of Iron Bridged by both Carbonyl and Alkylthio-groups

By **Robin B. English** and **Raymond J. Haines,*** Department of Inorganic Chemistry, University of Cape Town, Private Bag, Rondebosch, Cape Town, Republic of South Africa
Christian R. Nolte, Department of Inorganic and Analytical Chemistry, University of Pretoria, Pretoria, Republic of South Africa

The metal-containing sulphide RSMR′ [R = Et or Bu^t, MR′ = $Fe(CO)_2(cp)$] reacts with $[Fe(cp)(CO)_2(OCMe_2)]^+$ to afford $[\{Fe(cp)(CO)_2\}_2(SR)]^+$, in which the two iron atoms are linked through the alkylthio-group (cp = η-cyclopentadienyl). U.v. irradiation of $[\{Fe(cp)(CO)_2\}_2(SR)][SbF_6]$in tetrahydrofuran effects the loss of a carbonyl group and rearrangement of the resulting species to $[Fe_2(cp)_2(CO)_3SR][SbF_6]$ containing both a bridging carbonyl and a bridging alkylthio-ligand. Similar treatment of $[\{Fe(cp)(CO)_2\}_2(SEt)][BPh_4]$ results in extraction of a phenyl group from the tetraphenylborate anion and formation of $[Fe(cp)(CO)_2Ph]$. The cation $[Fe_2(cp)_2(CO)_3SEt]^+$ is readily reduced by sodium amalgam to $[Fe_2(cp)_2(CO)_3SEt]$ and $[Fe_2(cp)_2(CO)_3SEt]^-$.

THE redox properties of binuclear derivatives containing two bridging ligands have received considerable attention of late. Examples of systems studied include $[\{Fe(CO)_3PMe_2\}_2]$,[2-4] $[\{Cr(CO)_4PMe_2\}_2]$,[2-4] $[\{Fe(cp)(CO)SMe\}_2]$,[5] and $[\{Mn(cp)(NO)SBu^t\}_2]$ [6] (cp = η-cyclopentadienyl). Structural studies have revealed that oxidation of $[\{Fe(cp)(CO)PPh_2\}_2]$ to $[\{Fe(cp)(CO)PPh_2\}_2]^+$ and $[\{Fe(cp)(CO)PPh_2\}_2]^{2+}$ and of $[\{Fe(cp)(CO)SR\}_2]$ to $[\{Fe(cp)(CO)SR\}_2]^+$ (R = alkyl or aryl group) is accompanied by a *decrease* in the metal–metal distance from 349·8 to 314 and 276·4 pm and from *ca.* 340 to *ca.* 290 pm respectively.[7-9] On this basis it has been proposed that removal of electrons from derivatives of the type $[\{Fe(cp)(CO)SR\}_2]$ or $[\{Fe(cp)(CO)PR_2\}_2]$ or addition of electrons to compounds of the type $[\{Fe(CO)_3PR_2\}_2]$ or $[\{Cr(CO)_4PR_2\}_2]$ (R = alkyl or aryl group) involves an orbital which is antibonding with respect to the two metal atoms. Two bonding descriptions have been suggested.[9,10] One considers this antibonding orbital as being of σ-symmetry while the other is based on it being of π-symmetry.

Few reports have been made of oxidation of doubly

---

[1] Part XVII, R. J. Haines, J. A. de Beer, and R. Greatrex, *J. Organometallic Chem.*, 1975, **85**, 89.

[2] R. E. Dessy, R. Kornmann, C. Smith, and R. Hayter, *J. Amer. Chem. Soc.*, 1968, **90**, 2001.

[3] R. E. Dessy and L. Wieczorek, *J. Amer. Chem. Soc.*, 1969, **91**, 4963.

[4] R. E. Dessy, A. L. Rheingold, and G. D. Howard, *J. Amer. Chem. Soc.*, 1972, **94**, 746.

[5] J. A. de Beer, R. J. Haines, R. Greatrex, and J. A. van Wyk, *J.C.S. Dalton*, 1973, 2341.

[6] P. Hydes, J. A. McCleverty, and D. G. Orchard, *J. Chem. Soc.* (*A*), 1971, 3660.

[7] G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Comm.*, 1968, 1165.

[8] N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7472.

[9] B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organometallic Chem.*, 1974, **70**, 413.

[10] R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.

bridged compounds where the two metal atoms are also effectively linked by a metal–metal bond. This particularly applies to crystallographic studies. One-electron oxidation of [{Fe(cp)(CO)}$_2$(Ph$_2$PCH$_2$PPh$_2$)] to [{Fe(cp)-(CO)}$_2$(Ph$_2$PCH$_2$PPh$_2$)]$^+$ has been shown to result in a slight *increase* in the metal–metal distance from 251 to 256 pm.[11,12] A similar small increase from 260·3 to 261·7 pm has been observed for the oxidation of [{Mo(cp)(SMe)$_2$}$_2$] to [{Mo(cp)(SMe)$_2$}$_2$]$^+$.[13] The essential invariance of the metal–metal distance may result from steric constraints being placed on the molecule by the presence of other bridging ligands, however.

The inability to oxidise [{Fe(cp)(CO)SR}$_2$] beyond [{Fe(cp)(CO)SR}$_2$]$^{2+}$ (R = alkyl or aryl group) has been attributed to the high positive charge on the dicationic product.[5] Attempts have thus been made to isolate [Fe$_2$(cp)$_2$(CO)$_3$SR]$^+$, structurally related to [{Fe(cp)-(CO)SR}$_2$]$^{2+}$, and to establish whether this could be oxidised to [Fe$_2$(cp)$_2$(CO)$_3$SR]$^{2+}$, as well as reduced to [Fe$_2$(cp)$_2$(CO)$_3$SR] and [Fe$_2$(cp)$_2$(CO)$_3$SR]$^-$; the oxidised and reduced products would be employed further for structural studies.

TABLE 1

Colours and conductivity and analytical data

Compound	Colour	Λ*/S cm² mol⁻¹	Analyses/% Found C	Found H	Found S	Calc. C	Calc. H	Calc. S
[{Fe(cp)(CO)$_2$}$_2$(SEt)][SbF$_6$]	Red-brown	140	29·5	2·4	4·8	29·5	2·3	4·9
[{Fe(cp)(CO)$_2$}$_2$(SEt)][BPh$_4$]	Red-purple	98	65·3	4·8	5·0	65·4	4·8	4·4
[Fe$_2$(cp)$_2$(CO)$_3$SEt][SbF$_6$]	Olive green	131	28·6	2·7	5·1	28·9	2·4	5·2
[Fe$_2$(cp)$_2$(CO)$_3$SEt][BPh$_4$]	Green	103	65·7	5·1		65·7	5·1	
[Fe$_2$(cp)$_2$(CO)$_3$SBu^t][BPh$_4$]	Green	100	66·4	5·4		67·1	5·4	

* 1 × 10⁻⁴—10 × 10⁻⁴M Solutions in acetone.

TABLE 2

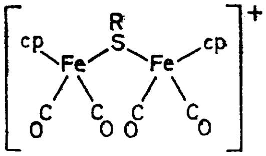
I.r. and n.m.r. spectroscopic data

Compound	$\bar{\nu}$(CO) [a]/cm⁻¹	τ at 38 °C [b] C$_5$H$_5$ proton resonances	Other resonances
[{Fe(cp)(CO)$_2$}$_2$(SEt)][SbF$_6$]	2 057vs, 2 043s, 2 007vs, 2 002sh [c]	4·45 [d]	7·50(q) [J(HH) 7·3] (CH$_2$) 8·50(t) [J(HH) 7·3] (CH$_3$)
[{Fe(cp)(CO)$_2$}$_2$(SEt)][BPh$_4$]	2 058vs, 2 041s, 2 008vs, 2 003sh [c]	4·60 [d]	3·0(mt) (C$_6$H$_5$) 7·60(q) [J(HH) 7·3] (CH$_2$) 8·80(t) [J(HH) 7·3] (CH$_3$)
[{Fe(cp)(CO)$_2$}$_2$(SEt)][BF$_4$]	2 053s, 2 007s [e]		
[{Fe(cp)(CO)$_2$}$_2$(SEt)][ClO$_4$]	2 051s, 2 008s [c]		
[{Fe(cp)(CO)$_2$}$_2$(SBu^t)][SbF$_6$]	2 052s, 2 008s [c]		
[Fe$_2$(cp)$_2$(CO)$_3$SEt][SbF$_6$]	2 044s, 2 005s, 1 829s [e]	4·27 [d]	7·26(q) [J(HH) 7·4] (CH$_2$) 8·30(t) [J(HH) 7·4] (CH$_3$)
[Fe$_2$(cp)$_2$(CO)$_3$SEt][BPh$_4$]	2 034s, 2 009m (sh), 1 845m [e]	5·08 [f]	2·78(mt) (C$_6$H$_5$) 8·83(t) [J(HH) 8·0] (CH$_3$)
[Fe$_2$(cp)$_2$(CO)$_3$SBu^t][BPh$_4$]	2 030s, 2 003m (sh), 1 842m [e]		
[Fe$_2$(cp)$_2$(CO)$_3$SEt]	1 970ms, 1 773s [c]		
[(Ph$_3$P)$_2$N][Fe$_2$(cp)$_2$(CO)$_3$SEt]	1 927ms, 1 690s [e]		
[Fe(cp)(CO)$_2$Ph]	2 022s, 1 971s [g]	4·70 [h]	2·5(mt) (C$_6$H$_5$)

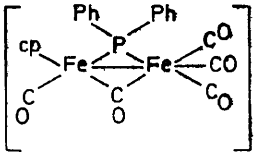
[a] vs = Very strong, s = strong, m = medium, ms = medium strong, and sh = shoulder. [b] t = Triplet, q = quartet, and mt = multiplet; J values in Hz. [c] Measured in CH$_2$Cl$_2$. [d] Measured in (CD$_3$)$_2$CO. [e] Measured as Nujol mull. [f] Measured in CD$_2$Cl$_2$. [g] Measured in cyclohexane. [h] Measured in CDCl$_3$.

RESULTS AND DISCUSSION

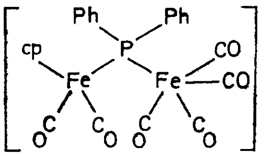
The tertiary phosphine PPh$_2$MR′ [MR′ = Fe(CO)$_2$(cp)] readily displaced the chloro-group in [Fe(cp)(CO)$_2$Cl] in methanol to yield [{Fe(cp)(CO)$_2$}$_2$(PPh$_2$)]$^+$.[14] The corresponding sulphido-species [{Fe(cp)(CO)$_2$}$_2$(SR)]$^+$, (I), were not formed analogously from [Fe(cp)(CO)$_2$Cl] and the metal-containing sulphides RSMR′ [R = Et or Bu^t, MR′ = Fe(CO)$_2$(cp)], however, but were obtained by treatment of [Fe(cp)(CO)$_2$(OCMe$_2$)]$^+$ with the latter.



(I)



(II)



(III)

---

[11] R. J. Haines and A. L. du Preez, *Inorg. Chem.*, 1972, **11**, 330.

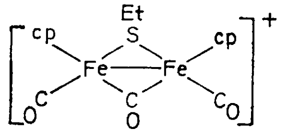
[12] R. Mason, personal communication.

[13] N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7470.

[14] R. J. Haines, A. L. du Preez, and C. R. Nolte, *J. Organometallic Chem.*, 1973, **55**, 199.

While the i.r. spectra of $[\{Fe(cp)(CO)_2\}_2(SEt)]A$ ($A = BF_4$ or ClO_4) and $[\{Fe(cp)(CO)_2\}_2(SBu^t)][SbF_6]$, measured in dichloromethane, contained two peaks in the terminal carbonyl-stretching region, those of $[\{Fe(cp)(CO)_2\}_2(SEt)]A$ ($A = SbF_6$ or BPh_4) revealed four bands in this region. This is attributed to the latter compounds occurring as more than one conformer in solution as has previously been found for $[\{Fe(cp)(CO)_2\}_2(SnCl_2)]$.[15] Not inconsistent with this suggestion is the observation that irradiation of $[\{Fe(cp)(CO)_2\}_2(SEt)][SbF_6]$ with u.v. light led to an increase in intensity of the C–O stretching peaks at 2 043 and 2 002 cm^{-1} and a decrease in intensity of those at 2 057 and 2 007 cm^{-1}.

The formation of the bridging-carbonyl derivative $[Fe_2(cp)(CO)_5PPh_2]$, (II), from $[Fe_2(cp)(CO)_6PPh_2]$, (III), is readily effected photochemically.[16] Consequently, with a view to synthesising compounds of the type $[Fe_2(cp)_2(CO)_3SR]A$, $[\{Fe(cp)(CO)_2\}_2(SEt)]A$ ($A = BF_4$ or SbF_6) in tetrahydrofuran (thf) was irradiated with u.v. light for a short period. Characterisation of the product which separated from solution established it to be $[Fe_2(cp)_2(CO)_3SEt]A$ ($A = BF_4$ or SbF_6). Its i.r. spectrum contained both bridging and terminal carbonyl-stretching peaks indicating that loss of a carbonyl group from $[\{Fe(cp)(CO)_2\}_2(SEt)]^+$ has been accompanied by a structural rearrangement giving a compound with structure (IV).



(IV)

Photolysis of $[\{Fe(cp)(CO)_2\}_2(SEt)][BPh_4]$ gave $[Fe_2(cp)_2(CO)_3SEt][BPh_4]$ as minor product only. The major product was found to be the σ-phenyl derivative $[Fe(cp)(CO)_2Ph]$ [17] formed as a result of the extraction of a phenyl group from the tetraphenylborate anion. Refluxing of a dichloromethane solution of $[\{Fe(cp)(CO)_2\}_2(SEt)][BPh_4]$ also led to formation of $[Fe(cp)(CO)_2Ph]$ but in lower yield. Phenyl-transfer reactions of this type have previously been reported for *cis*-$[Pt(PEt_3)_2Cl_2]$,[18] $[Pt(PMe_2Ph)_2(HOMe)Me]^+$, [19] $[Ni(cp)(PPh_3)_2]^+$,[20] and $[\{Ru(cp)(CO)_2\}_2X]^+$ (X = Cl or Br),[21] the products being *trans*-$[Pt(PEt_3)_2Ph_2]$, *trans*-$[Pt(PMe_2Ph)_2Ph_2]$, $[Ni(cp)(PPh_3)Ph]$, and $[Ru(cp)(CO)_2Ph]$, respectively.

On the basis of the corresponding reaction involving $[Fe(cp)(CO)_2PPh_2]$, it had been expected that treatment of $[\{Rh(C_8H_{12})Cl\}_2]$ with $[Fe(cp)(CO)_2SR]$ (R = Et or Bu^t) in ethanol in the presence of $Na[BPh_4]$ would yield $[Rh\{Fe(cp)(CO)_2SR\}_2][BPh_4]$.[22] However, the product isolated from solution was established by means of *X*-ray fluorescence analysis not to contain rhodium and was characterised as $[Fe_2(cp)_2(CO)_3SR][BPh_4]$, (IV). This reaction thus provides an alternative method of obtaining $[Fe_2(cp)_2(CO)_3SR]^+$, the rhodium compound functioning as an extractor of carbon monoxide from $[\{Fe(cp)(CO)_2\}_2(SR)]^+$.

Controlled reduction of $[Fe_2(cp)_2(CO)_3SEt]^+$ by sodium amalgam gave a green, neutral, benzene-soluble compound which is very sensitive to oxidation and rapidly reverts to $[Fe_2(cp)_2(CO)_3SEt]^+$ in air. The product decomposes in solution to $[\{Fe(cp)(CO)SEt\}_2]^+$ and thus could not be obtained analytically pure. However, the band pattern of the peaks in the C–O stretching region of its i.r. spectrum is very similar to that of $[Fe_2(cp)_2(CO)_3SEt]^+$ but shifted to lower frequency, while its magnetic susceptibility corresponds to a magnetic moment of *ca.* 1·5 B.M.* This evidence is indicative of the product being $[Fe_2(cp)_2(CO)_3SEt]$, having a structure similar to that of the parent compound, and of one-electron reduction of $[Fe_2(cp)_2(CO)_3SEt]^+$ having been effected.

Reaction of $[Fe_2(cp)_2(CO)_3SEt]^+$ with excess of sodium amalgam led to formation of a red product which was immediately oxidised to $[Fe_2(cp)_2(CO)_3SEt]$ and then $[Fe_2(cp)_2(CO)_3SEt]^+$ on introduction of small amounts of air. The i.r. spectrum of this species in dichloromethane in the presence of $[(Ph_3P)_2N]Cl$ contained strong peaks at 1 928 and 1 690 cm^{-1} as well as peaks at 1 970 and 1 775 cm^{-1} ascribed to $[Fe_2(cp)_2(CO)_3SEt]$. This i.r. evidence, coupled with the susceptibility of the compound to oxidation, suggests it to be $[Fe_2(cp)_2(CO)_3SEt]^-$. The instability of this compound in solution prevented its isolation as the $[(Ph_3P)_2N]^+$ salt however.

Attempts to obtain $[Fe_2(cp)_2(CO)_3SEt]^{2+}$ from $[Fe_2(cp)_2(CO)_3SEt]^+$ proved unsuccessful. Oxidants such as iodine, bromine, and silver(I) hexafluoroantimonate were employed but each time decomposition of the parent compound was effected.

EXPERIMENTAL

The compounds $[Fe(cp)(CO)_2SR]$ (R = Et and Bu^t) were synthesised according to literature methods.[23] All experiments were made under a nitrogen atmosphere. I.r. spectra were measured on either a Perkin-Elmer model 21 or a Beckmann IR 12 spectrophotometer. N.m.r. spectra were recorded using Varian HA 100 and XL 100 instruments. Conductivities were obtained by conventional methods. The magnetic susceptibility was measured on a Newport Instruments Gouy balance. Elemental analyses were obtained by the Alfred Bernhardt Microanalytical Laboratory, Elbach-uber Engelskirchen, West Germany, and by Mr. W. T. Hemstead of the University of Cape Town.

---

* 1 B.M. ≈ 9·27 × 10^{-24} A m^2.

[15] R. H. Herber and Y. Goscinny, *Inorg. Chem.*, 1968, **7**, 1293.

[16] R. J. Haines and C. R. Nolte, *J. Organometallic Chem.*, 1972, **36**, 163.

[17] R. B. King and M. B. Bisnette, *J. Organometallic Chem.*, 1964, **2**, 15.

[18] H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 1969, **91**, 596.

[19] H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 1970, **9**, 1226.

[20] P. M. Treichel and R. L. Shubkin, *Inorg. Chim. Acta*, 1968, **2**, 485.

[21] R. J. Haines and A. L. du Preez, *J.C.S. Dalton*, 1972, 944.

[22] R. J. Haines, J. A. Zubieta, R. Mason, and C. R. Nolte, *J.C.S. Chem. Comm.*, 1972, 990.

[23] M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 1.

μ-Alkylthio-bis[dicarbonyl(η-cyclopentadienyl)iron] Salts.—[{Fe(cp)$(CO)_2$}$_2$(SR)][SbF_6] (I; R = Et *or* Bu^t). The compound [Fe(cp)$(CO)_2$SEt] (0·7 g, 3 mmol) or [Fe(cp)$(CO)_2$SBu^t] (0·8 g, 3 mmol) in acetone (50 cm^3) was added dropwise to a stirred acetone solution (60 cm^3) of [Fe(cp)$(CO)_2$($OCMe_2$)][SbF_6] (3 mmol), prepared *in situ* from [{Fe(cp)$(CO)_2$}$_2$] and two equivalents of Ag[SbF_6], and the resulting solution stirred for 30 min. The solvent was removed under reduced pressure to afford a red *residue* which was washed with benzene and light petroleum. The compound [{Fe(cp)$(CO)_2$}$_2$(SEt)][SbF_6] was crystallised from dichloromethane–light petroleum (yield 90%) while [{Fe(cp)$(CO)_2$}$_2$(SBu^t)][SbF_6] was identified by means of i.r. only. The tetrafluoroborate salts were obtained analogously employing Ag[BF_4] as oxidant.

[{Fe(cp)$(CO)_2$}$_2$(SEt)][BPh_4]. A solution of [{Fe(cp)$(CO)_2$}$_2$(SEt)][ClO_4] (3 mmol) in acetone (50 cm^3) was obtained as above using $AgClO_4$ as oxidant. The solvent was removed under reduced pressure and the residue redissolved in methanol (30 cm^3). Excess of Na[BPh_4] in methanol (20 cm^3) was added and the *product* which separated from solution isolated. Further recrystallisation was not necessary, yield 90%.

μ-Carbonyl-μ-alkylthio-bis[carbonyl(η-cyclopentadienyl)iron] (Fe–Fe) *Salts,* (IV).—[$Fe_2$$(cp)_2$$(CO)_3$SEt][$SbF_6$]. A solution of [{Fe(cp)$(CO)_2$}$_2$(SEt)][SbF_6] (0·47 g, 2 mmol) in thf (150 cm^3) was irradiated with u.v. light for 120 min. The *product* which separated from solution was isolated, washed with dichloromethane, and crystallised from acetone–dichloromethane, yield 50%.

[$Fe_2$$(cp)_2$$(CO)_3$SR][$BPh_4$] (R = Et *or* Bu^t). The compound [Fe(cp)$(CO)_2$SEt] (0·5 g, 2·1 mmol) or [Fe(cp)$(CO)_2$SBu^t] (0·65 g, 2·4 mmol) in methanol (20 cm^3) was added dropwise to a stirred suspension of [{Rh(C_8H_{12})Cl}$_2$] (0·2 g, 0·4 mmol) in methanol (20 cm^3) and stirring continued until all [{Rh(C_8H_{12})Cl}$_2$] had dissolved. Sodium tetraphenylborate (0·4 g, 1·2 mmol) in methanol (10 cm^3) was then added and the mixture stirred for a further hour. The solvent was removed under reduced pressure and the *residue* washed in turn with methanol (at −78 °C), light petroleum, benzene, and finally light petroleum. The compound [$Fe_2$$(cp)_2$$(CO)_3$SEt][$BPh_4$] was crystallised from dichloromethane–light petroleum (yield 40%) while [$Fe_2$$(cp)_2$$(CO)_3$SBu^t][$BPh_4$] was crystallised from acetone–ethanol–light petroleum (yield 10%).

Formation of [Fe(cp)$(CO)_2$Ph] *from* [{Fe(cp)$(CO)_2$}$_2$(SEt)][BPh_4].—(a) *Photochemically.* The compound [{Fe(cp)$(CO)_2$}$_2$(SEt)][BPh_4] (0·5 g, 0·8 mmol) in thf (150 cm^3) was irradiated with u.v. light for 120 min. The solvent was removed under reduced pressure and the residue extracted with benzene. Evaporation of the extract afforded a brown residue which was re-extracted with cyclohexane. Removal of the solvent gave [Fe(cp)$(CO)_2$Ph] as a brown crystalline material. The compound was identified by means of i.r. and n.m.r. spectroscopy only, yield 20%.

(b) *Thermally.* A dichloromethane solution (50 cm^3) of [{Fe(cp)$(CO)_2$}$_2$(SEt)][BPh_4] (0·5 g, 0·8 mmol) was heated under reflux for 60 min. The solvent was removed under reduced pressure and the residue extracted with benzene; [Fe(cp)$(CO)_2$Ph] was isolated from this solution and purified as described above, yield 10%.

[$Fe_2$$(cp)_2$$(CO)_3$SEt].—A suspension of [$Fe_2$$(cp)_2$$(CO)_3$SEt][$SbF_6$] (0·24 g, 1 mmol) in thf (50 cm^3) was stirred over a stoicheiometric amount of 1% sodium amalgam for 10 min. The solution was filtered and the solvent removed under reduced pressure to afford the *product* as a green crystalline material.

We thank the South African Council for Scientific and Industrial Research and the Universities of Cape Town and Pretoria for support.

[4/2232 *Received, 29th October,* 1974]