# Bis(trifluoromethyl)dithiolene Tricarbonyl Iron and its Lewis Base Derivatives

By **C. J. Jones, J. A. McCleverty,*** and **D. G. Orchard,** Chemistry Department, The University, Sheffield S3 7HF

Reaction of $Fe_2(CO)_9$ with $S_2C_2(CF_3)_2$ under mild conditions gives $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$. On the basis of i.r. and electronic spectral, and solution molecular-weight studies, $n$ is thought to be 2 in solution; $n = 2$ in the solid state. The complex reacts with Lewis bases, L, giving $[Fe(CO)_{3-n}(PPh_3)_n\{S_2C_2(CF_3)_2\}]$ ($n = 1$ or 2), $[Fe(CO)_{3-n}L_n\{S_2C_2(CF_3)_2\}]$ [L = $CN(Bu^t)$, $CN(p\text{-}ClC_6H_4)$, or $P(OEt)_3$], $[Fe(CO)(LL')\{S_2C_2(CF_3)_2\}]$ [LL' = *cis*-$Ph_2PCH{:}CHPPh_2$, $Ph_2PCH_2CH_2PPh_2$, or *o*-$C_6H_4(AsMe_2)_2$], $[Fe\{P(OEt)_3\}(LL')\text{-}\{S_2C_2(CF_3)\}]$ (LL' = $Ph_2PCH_2CH_2PPh_2$), and $[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]^z$ (LL' = *cis*-$Ph_2PCH{:}CHPPh_2$ or $Ph_2PCH_2CH_2PPh_2$; $z = 0$ or $+1$). All species except the parent complex were thought to have square-pyramidal geometries. Only the complexes $[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]^0$ and $[Fe(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}]^0$ exhibited reversible one-electron voltammetric oxidation waves.

THE binuclear iron dithiolene, $[Fe\{S_2C_2(CF_3)_2\}_2]_2^0$, is most conveniently synthesised[1] by reacting $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with $S_2C_2(CF_3)_2$ in n-pentane. The final product is blue-black and sparingly soluble in pentane, but if the reaction mixture is carefully watched after initiation, it may be observed to undergo several interesting colour changes. Beginning with orange $\{Fe(CO)_5\}$ or dark green $\{Fe_3(CO)_{12}\}$, the colour becomes orange-red then magenta, and finally nearly black. In attempting to stop the reaction at the magenta stage, we found that there were three species present in solution: (*a*) small amounts of $[Fe\{S_2C_2(CF_3)_2\}_2]_2^0$; (*b*) unchanged $Fe(CO)_5$ or $Fe(CO)_{12}$; (*c*) a new carbonyl dithiolene complex of iron. The similarities in volatility and solubility between the new complex and $Fe(CO)_5$ were such that it was impossible to separate them satisfactorily. However, we found that by reacting $S_2C_2(CF_3)_2$ with $Fe_2(CO)_9$ in suitable solvent mixtures, moderate yields of the magenta complex could be obtained.

The new compound, which we have formulated empirically[2] as $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$, is extremely reactive towards Lewis bases, readily losing CO. The characterisation of the tricarbonyl complex, and a full report of its reactions are given in this paper; some related results have also been presented by Miller and Balch.[3] The only other fully characterised carbonyl dithiolene complex of iron is $[Fe_2(CO)_6\{S_2C_2(CF_3)_2\}]$.[4]

## EXPERIMENTAL

Conductivity measurements were made in acetone solution at room temperature (20 ± 2°) with a Phillips conductivity meter. Visible and u.v. spectra were obtained with a Unicam SP 700 spectrophotometer and i.r. spectra were obtained using Perkin Elmer 457 and Unicam SP 100 spectrophotometers. Mass spectra were obtained with AEI MS9 and MS12 instruments, at probe temperatures of 65 and 250 °C.

Voltammetric measurements were made using a Beckman Electroscan 30 Polarograph with a platinum electrode rotating at 620 rev. $min^{-1}$. All measurements were made at at room temperature and were standardised against a saturated calomel electrode 1M in aqueous LiCl. The solvent was dichloromethane and the supporting electrolyte $[Et_4N][ClO_4]$. The solutions were $10^{-3}$M in complex and 0·05M in base electrolyte; all data were corrected for *iR* drop where necessary, and the estimated error is ±10 mV. Cyclic voltammograms were obtained using a stationary platinum wire electrode at scan speeds of 0·05 V $s^{-1}$.

Analytical data were obtained by the Microanalytical Laboratory of this Department, and molecular weights were determined mass spectrometrically and by osmometry in benzene, chloroform and/or acetone.

*General Synthetic Procedure.*—Many of the complexes were prepared by similar methods, that is, by mixing the reactants in either dichloromethane or benzene, and warming these gently until gas evolution had ceased. The amounts of reactants are summarised in Table 1, and the details of recrystallisation and other special conditions are described below, the annotation following that in Table 1.

(1) Addition of n-hexane to the reaction mixture, followed by partial evaporation of the solvent *in vacuo*, led to the precipitation of a dark red solid. This was filtered off and recrystallised from dichloromethane–n-hexane–n-octane, giving $[Fe(CO)(PPh_3)\{S_2C_2(CF_3)_2\}]$ as dark red crystals.

(2) The compound was precipitated as described above, and was recrystallised from dichloromethane–n-hexane, giving $[Fe(CO)_2(p\text{-}ClC_6H_4NC)\{S_2C_2(CF_3)_2\}]$ as red-brown microcrystals. It was soluble in acetone or dichloromethane giving purple solutions.

(3) The compound was precipitated as described above, and was twice recrystallised from dichloromethane–n-hexane, giving $[Fe(CO)_2(Bu^tNC)\{S_2C_2(CF_3)_2\}]$ as dark brown crystals.

(4) The benzene was removed *in vacuo* leaving a dark green residue which was redissolved in dichloromethane and filtered. To the filtrate was added n-hexane, and on partial evaporation of the mixture *in vacuo*, dark green crystals of $[Fe(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}]$ formed.

(5) The dichloromethane was evaporated *in vacuo* leaving a tarry red solid which was dissolved in acetone. Addition of several drops of water, followed by slow removal of the acetone *in vacuo*, afforded $[Fe(CO)\{P(OEt)_3\}_2\{S_2C_2(CF_3)_2\}]$ as dark red crystals.

(6) The dichloromethane was evaporated *in vacuo* leaving an orange solid which was redissolved in acetone and chromatographed on alumina (Spence type neutral).

---

[1] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1964, **3**, 814; A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, 1968, **90**, 1139.

[2] C. J. Jones, J. A. McCleverty, and D. G. Orchard, *J. Organometallic Chem.*, 1971, **26**, C19.

[3] J. Miller and A. L. Balch, *Inorg. Chem.*, 1971, **10**, 1410.

[4] R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1584.

Elution, using acetone, of the purple band followed by addition of propan-2-ol and slow evaporation of the solvent using a water pump afforded $[Fe(CO)(Bu^tNC)_2\{S_2C_2(CF_3)_2\}]$ as orange-brown microcrystals. The compound dissolves in acetone and dichloromethane giving purple solutions.

(7) Addition of n-hexane, followed by slow evaporation of the solid *in vacuo*, afforded a purple precipitate. This was filtered off, washed with n-hexane and crystallised from dichloromethane–n-hexane giving $[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ as purple crystals.

(8) The complex, $[Fe(CO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}]$ was obtained in the same way as $[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ (7).

(9) To the dichloromethane was added light petroleum (b.p. 40—60°), and the solvent was removed *in vacuo*. The purple residue was dissolved in the minimum amount of acetone and chromatographed on alumina (Spence type neutral). The purple band was eluted using acetone, and propan-2-ol was added to the eluate. Removal of the solvent *in vacuo* afforded a tarry purple solid which was stored under n-hexane for several hours. Filtration of the mixture afforded $[Fe(CO)\{C_6H_4(AsMe_2)_2\}\{S_2C_2(CF_3)_2\}]$ as purple crystals.

TABLE 1

Synthetic procedures for some carbonyl and Lewis base sulphur complexes of iron

| Product | Reactants (g) $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$ | Reactants (g) L [a] | Solvent (ml) | Yield g (%) | M.p. (°C) |
|---|---|---|---|---|---|
| $[Fe(CO)_2L\{S_2C_2(CF_3)_2\}]$ | | | | | |
| (1) L = $PPh_3$ | 0·40 | 0·30 | $CH_2Cl_2$(50) | 0·5(76) | 92—95 |
| (2) L = $p$-$ClC_6H_4NC$ | 0·50 | 0·18 | $C_6H_6$(60) | 0·4(62) | 170 |
| (3) L = $Bu^tNC$ | 0·50 | 0·11 | $CH_2Cl_2$(50) | 0·9(70) | |
| $[Fe(CO)L_2\{S_2C_2(CF_3)_2\}]$ | | | | | |
| (4) L = $PPh_3$ | 0·50 | 1·50 | $CH_2Cl_2$(100) [b] | 0·8(70) | 125 |
| (5) L = $P(OEt)_3$ | 0·60 | 0·54 | $CH_2Cl_2$(60) | 0·5(42) | 43—45 |
| (6) L = $Bu^tNC$ | 0·30 | 0·14 | $CH_2Cl_2$(40) | 0·3(77) | 140 |
| (7) $L_2$ = $Ph_2PCH_2CH_2PPh_2$ | 0·50 | 0·50 | $CH_2Cl_2$(50) | 0·8(85) | 190 |
| (8) $L_2$ = $Ph_2PCH{:}CHPPh_2$ | 0·30 | 0·33 | $CH_2Cl_2$(50) | 0·95(78) | 197—200 |
| (9) $L_2$ = $o$-$C_6H_4(AsMe_2)_2$ | 0·30 | Excess | $CH_2Cl_2$(50) | 0·2(35) | 220 |
| $[FeL_3\{S_2C_2(CF_3)_2\}]$ | | | | | |
| (10) L = $p$-$ClC_6H_4NC$ | 0·40 | 0·45 | $CH_2Cl_2$(60) | 0·6(81) | 230 |
| (11) L = $P(OEt)_3$ | 0·50 | 0·90 | $C_6H_6$(100) [c] | 0·7(66) | 120 |
| (12) L = $Bu^tNC$ | 0·50 | 0·40 | $CH_2Cl_2$(100) | 0·5(59) | 180 |

[a] L as in Column 1. [b] Reflux for 3 h. [c] Reflux for 2·5 h.

(10) n-Hexane was added to the solution and, on partial removal of the solvent, an orange solid was formed. This was dissolved in the minimum volume of acetone and chromatographed on alumina (Spence type neutral). The dark green eluate was treated with propan-2-ol, and on partial removal of the solvent *in vacuo* $[Fe(p\text{-}ClC_6H_4NC)_3\{S_2C_2(CF_3)_2\}]$ was formed as an orange-brown powder. The complex dissolved in dichloromethane or acetone solutions giving green solutions.

(11) Removal, *in vacuo*, of the solvent from the purple reaction mixture gave a purple oil. This was dissolved in acetone to which n-octane was added, and on slow removal of the solvent using a water pump, $[Fe\{P(OEt)_3\}_3\{S_2C_2(CF_3)_2\}]$ was formed as dark purple-blue crystals.

(12) The compound $[Fe(Bu^tNC)_3\{S_2C_2(CF_3)_2\}]$, was obtained in the same way as its $p$-$ClC_6H_4NC$ analogue. The complex dissolved in acetone and dichloromethane giving green solutions.

$[Fe\{P(OEt_3)\}(Ph_2PCH_2CH_2PPh_2)\{S_3C_2(CF_3)_2\}]$.— $[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ (0·5 g), dissolved in benzene (50 ml) was treated with triethyl phosphite (0·11 g), and the resulting mixture was refluxed overnight on a steam-bath. The resulting bright green reaction mixture was then cooled and the solvent removed *in vacuo*. The green residue was dissolved in n-hexane, the solution filtered, and the solvent partially removed *in vacuo* affording a green precipitate. This was recrystallised from dichloromethane–n-hexane giving the complex (0·4 g, 67%) as green crystals (m.p. 179—182°).

$[Fe(CO)(PPh_3)(p\text{-}ClC_6H_4NC)\{S_2C_2(CF_3)_2\}]$.— $[Fe(CO)_2(p\text{-}ClC_6H_4NC)\{S_2C_2(CF_3)_2\}]$ (0·1 g), dissolved in dichloromethane (20 ml) was treated with $PPh_3$ (0·05 g); the reaction mixture became green immediately. After gentle warming for a few minutes, the mixture was treated with n-hexane and the solvent was partially removed *in vacuo*. The dark green solid which precipitated was dissolved in the minimum amount of acetone and chromatographed on alumina (Spence type neutral). The green band was eluted with acetone, treated with propan-2-ol, and, on partial evaporation *in vacuo*, afforded the complex (0·1 g, 51%) as dark green crystals (m.p. 68°).

$[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$.— $[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ (0·5 g), dissolved in benzene (100 ml), was treated with an excess of solid $NOPF_6$; the resulting reaction mixture was refluxed on a steam-bath until it had become red-brown in colour (*ca.* 1 h). Removal of the solvent under reduced pressure, followed by addition of n-hexane to the residue, afforded a red-brown solid. This was dissolved in the minimum volume of acetone and was chromatographed on alumina (Spence type neutral). On development of the chromatogram the initially red-brown band became black and, on elution of the black band, followed by addition of propan-2-ol and partial removal of the solvent *in vacuo*, afforded a black solid. This was recrystallised from acetone–propan-2-ol affording the complex (0·35 g, 69%) as black crystals (m.p. 212°).

$[Fe(NO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_6)_2\}]$.—This complex was prepared in the same way as that described above, and was obtained as black crystals (0·5 g, 68%; m.p. 200°).

$[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}][PF_6]$.— $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ (0·1 g) dissolved in in dichloromethane (20 ml), was treated with an excess of solid $AgPF_6$; the reaction mixture immediately became red-brown. Removal of the solvent *in vacuo* afforded a red-brown solid which was twice recrystallised from dichloromethane–n-hexane giving the complex (0·08 g, 67%) as red-brown microcrystals.

$[Fe(NO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}][PF_6]$.— This complex was prepared in the same way as that described above, and was obtained as red-brown crystals (0·1 g, 70%).

$[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$.—A mixture of $Fe_2(CO)_9$ (0·6 g) and $S_2C_2(CF_3)_2$ (0·75 g) in n-pentane–n-hexane (40 ml, 1 : 1 v/v) was refluxed for 45 min. The reaction mixture was cooled and filtered; the purple filtrate was evaporated to low bulk using a water pump. The solution was allowed to stand at −5° and the purple crystals which formed were filtered off and recrystallised from dichloromethane–n-pentane–n-octane, thus affording the complex (0·7 g, 49%).

*Mass Spectral Studies.*—Unless otherwise stated these were obtained at a source temperature of 250° and an ionising voltage of 70 eV.

$[Fe(CO)_2(PPh_3)\{S_2C_2(CF_3)_2\}]$.—Parent ion, $P^+$ ($m/e$ = 600), $[P - CO]^+$ (572), $[P - 2CO]^+$ (544), $[P - 2CO - F]^+$ (425).

$[Fe(CO)_2(p\text{-}ClC_6H_4NC)\{S_2C_2(CF_3)_2\}]$.—Parent ion, ($P^+$), not observed; other ions included $[P - CO]^+$ ($m/e$ = 419), $[P - 2CO - F]^+$ (400).

$[Fe(CO)\{P(OEt)_3\}_2\{S_2C_2(CF_3)_2\}]$.—Parent ion, $P^+$ ($m/e$ = 642), $[P - CO]^+$ (614), $[P - CO - F]^+$ (595).

$[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$.—Parent ion, $P^+$ ($m/e$ = 708), $[P - CO]^+$ (680), $[P - CO - F]^+$ (661).

$[Fe(CO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}]$.—Parent ion, $P^+$ ($m/e$ = 706), $[P - CO]^+$ (678), $[P - CO - F]^+$ (659).

$[Fe(CO)\{C_6H_4(AsMe_2)_2\}\{S_2C_2(CF_3)_2\}]$.—Parent ion, $P^+$ ($m/e$ = 596), $[P - CO]^+$ (549).

$[Fe\{P(OEt)_3\}_3\{S_2C_2(CF_3)_2\}]$.—Parent ion, $P^+$ ($m/e$ = 780).

$[Fe(Bu^tNC)_3\{S_2C_2(CF_3)_2\}]$.—Parent ion, $P^+$ ($m/e$ = 531).

$[Fe\{P(OEt)_3\}(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)\}]$.— Parent ion, $P^+$, not observed; other ions included $[P - P(OEt)_3]^+$ ($m/e$ = 680).

$[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$.—Parent ion, $P^+$ ($m/e$ = 710), $[P - NO]^+$ (680), $[P - NO - F]^+$ (661).

$[Fe(NO)(Ph_2PCH{=}CHPPh_2)\{S_2C_2(CF_3)_2\}]$.—Parent ion $P^+$ ($m/e$ = 708), $[P - NO]^+$ (678), $[P - NO - F]^+$ (659).

## RESULTS AND DISCUSSION

$[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$.—Nonacarbonyldi-iron reacted in refluxing n-pentane–n-hexane with $S_2C_2(CF_3)_2$ giving the magenta complex $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$. This compound dissolved in acetonitrile, ethanol, or wet acetone giving brown solutions whose i.r. spectra exhibited no CO stretching frequencies. It dissolved, however, in benzene, pentane, and dichloromethane without decomposition.

An $X$-ray crystallographic examination of the molecule [5] has revealed that, in the solid state at least, the complex is binuclear (Figure 1), and contains two octahedrally co-ordinated Fe atoms. Molecular-weight measurements of the complex in chloroform or benzene gave results (Table 2) indicating that the molecule dissociated to some extent in solution. The mass spectrum of the compound could be obtained only if a sample was introduced into the mass spectrometer at low temperatures (100°), but exhibited an intense ion at $m/e$ = ($[P/2]^+$), along with other strong ions at $m/e$ = 338, 310, and 282. These ions correspond to the formulation $[Fe(CO)_n\{S_2C_2(CF_3)_2\}]^+$ ($n$ = 3, 2, 1, or 0), in agreement with our elemental analytical data (Table 2). However, we were unable to detect any ion higher than $m/e$ = 366. The i.r. spectrum of the complex in n-pentane solution (Table 3) exhibited three CO stretching frequencies, the low-frequency bands being components of a doublet. Such a spectrum is consistent with the dimer (Figure 1), or with a monomer derived from it by fission of the ' apical ' Fe–S bonds. Satisfactory electronic spectra (Table 4) of the compound in the solid state could not be obtained, and so a comparison of these obtained in chloroform or benzene solution was not possible.

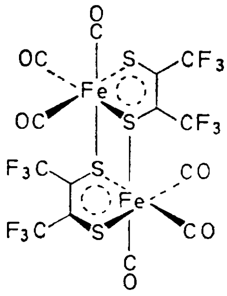

FIGURE 1

*Lewis Base Derivatives of* $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$.—The magenta compound reacts very rapidly with a variety of Lewis bases forming crystalline complexes as shown in Table 2. The compounds were satisfactorily characterised by elemental analyses, conductivity measurements, molecular-weight determinations (Table 2), and spectral studies. The complexes $[Fe(CO)_2(PPh_3)\{S_2C_2(CF_3)_2\}]$ and $[Fe(CO)(PPh_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ have already been reported.[3]

On treatment of $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$ in dichloromethane with an excess of $PPh_3$ only $[Fe(CO)_2(PPh_3)\{S_2C_2(CF_3)_2\}]$, was formed. Replacement of a second CO group by $PPh_3$ could only be achieved in refluxing benzene, and under no conditions could we effect removal of the third CO group by this phosphine. Reaction of $[Fe(CO)_2(PPh_3)\{S_2C_2(CF_3)_2\}]$ with LL′ (LL′ = *cis*-$Ph_2PCH{:}CHPPh_2$ or $Ph_2PCH_2CH_2PPh_2$) led only to the formation of $[Fe(CO)(LL')\{S_2C_2(CF_3)_2\}]$, (also obtained directly from $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$ with LL′) and not, as we had hoped, to the formation of the totally decarbonylated product, $[Fe(PPh_3)(LL')\{S_2C_2(CF_3)_2\}]$.

Reaction of $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$ with one, two, or three moles of CNR (R = $Bu^t$ or $p$-$ClC_6H_4$) or $P(OEt)_3$

gave $[Fe(CO)_{3-n}L_n\{S_2C_2(CF_3)_2\}]$ (L = phosphite or isonitrile), although $[Fe(CO)_2\{P(OEt)_3\}\{S_2C_2(CF_3)_2\}]$ could not be isolated and was identified solely by its i.r. spectrum in solution (Table 3).

TABLE 2

Analytical and molecular-weight data obtained from new iron–sulphur complexes

| Complex | Analytical data | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Calculated | | | | Found | | | | |
| | C | H | N | S | C | H | N | S | *M* [a] |
| $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$ | 22·9 | | | 17·5 | 22·6 | | | 17·4 | 366 [b] |
| $[Fe(CO)_2(PPh_3)\{S_2C_2(CF_3)_2\}]$ | 48·0 | 2·5 | | 10·7 | 48·6 | 3·1 | | 10·8 | 600 |
| $[Fe(CO)_2(p\text{-}ClC_6H_4NC)\{S_2C_2(CF_3)_2\}]$ | 32·8 | 0·8 | 3·0 | 13·5 | 32·4 | 1·7 | 3·0 | 13·0 | |
| $[Fe(CO)_2(Bu^tNC)\{S_2C_2(CF_3)_2\}]$ | 31·4 | 2·1 | 3·3 | 15·2 | 30·9 | 2·3 | 3·5 | 16·0 | |
| $[Fe(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}]$ | 59·0 | 3·5 | | 7·7 | 58·6 | 3·9 | | 8·1 | |
| $[Fe(CO)(Bu^tNC)_2\{S_2C_2(CF_3)_2\}]$ | 37·8 | 3·8 | 6·3 | 13·4 | 37·9 | 4·4 | 6·2 | 13·5 | |
| $[Fe(CO)\{P(OEt)_3\}_2\{S_2C_2(CF_3)_2\}]$ | 31·8 | 4·7 | | 10·0 | 31·8 | 4·8 | | 10·1 | 642 [c] |
| $[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ | 52·5 | 3·4 | | 9·0 | 52·3 | 3·7 | | 9·7 | 708 [d] |
| $[Fe(CO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}]$ | 52·7 | 3·1 | | 9·1 | 52·3 | 3·5 | | 9·6 | 706 |
| $[Fe(CO)\{C_6H_4(AsMe_2)_2\}\{S_2C_2(CF_3)_2\}]$ | 30·2 | 2·7 | | 10·7 | 31·0 | 3·2 | | 11·1 | 596 |
| $[Fe(CO)(p\text{-}ClC_6H_4NC)(PPh_3)\{S_2C_2(CF_3)_2\}]$ | 50·5 | 2·7 | 2·0 | 9·0 | 50·1 | 2·4 | 2·0 | 9·7 | |
| $[Fe(Bu^tNC)_3\{S_2C_2(CF_3)_2\}]$ | 42·9 | 5·1 | 7·9 | 12·1 | 43·0 | 4·9 | 7·9 | 11·6 | 531 |
| $[Fe\{P(OEt)_3\}_3\{S_2C_2(CF_3)_2\}]$ | 33·9 | 5·8 | | 8·2 | 34·6 | 5·6 | | 9·4 | 780 |
| $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ | 50·7 | 3·4 | 2·0 | 9·0 | 50·6 | 3·8 | 1·8 | 10·4 | 710 |
| $[Fe(NO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}]$ | 50·9 | 3·1 | 2·0 | 9·1 | 51·7 | 3·1 | 2·2 | 10·5 | 708 |
| $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}][PF_6]$ | 42·1 | 2·8 | 1·6 | 7·5 | 42·0 | 3·0 | 1·7 | 7·5 | *e* |
| $[Fe(NO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}][PF_6]$ | 42·2 | 2·6 | 1·6 | 7·5 | 41·5 | 3·1 | 1·5 | 7·7 | *f* |
| $[Fe\{P(OEt)_3\}(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ | 51·0 | 4·6 | | 7·6 | 50·5 | 4·8 | | 7·8 | |

[a] Molecular weight determined mass spectrally unless otherwise stated at 250°. [b] Obtained at 65° ($n = 1$); 640 in chloroform and 598 in benzene solution (calc. 732). [c] 626 Obtained at 65 and 250° in chloroform; 638 in acetone (osmometrically) (calc. 642). [d] 642 In acetone (osmometrically) (calc. 708). [e] Conductivity 131 cm$^2$ mol $\Omega^{-1}$ in $10^{-4}$M-acetone solution. [f] Conductivity 142 cm$^2$ mol $\Omega^{-1}$ in $10^{-4}$M-acetone solution.

TABLE 3

Carbonyl, isonitrile-CN, and nitrosyl stretching frequences obtained from new iron–sulphur complexes

| Complex | I.r. data (cm$^{-1}$) | | | |
|---|---|---|---|---|
| | Solution | | KBr | |
| | $\nu_{CO/NO}$ | $\nu_{ON}$ [a] | $\nu_{CO/NO}$ | $\nu_{CN}$ |
| $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$ | 2089, 2037, 2030 [b] | | | |
| $[Fe(CO)_2(PPh_3)\{S_2C_2(CF_3)_2\}]$ | 2015, 1975 | | 2015, 1975 | |
| $[Fe(CO)_2\{P(OEt)_3\}\{S_2C_2(CF_3)_2\}]$ | | | 2050, 1993 | |
| $[Fe(CO)_2(p\text{-}ClC_6H_4NC)\{S_2C_2(CF_3)_2\}]$ | 2060, 2020 | 2170 | 2070, 2030 | 2180 |
| $[Fe(CO)_2(Bu^tNC)\{S_2C_2(CF_3)_2\}]$ | 2060, 2020 | 2190 | 2070, 2025 | 2190 |
| $[Fe(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}]$ | 1950 | | 1953 | |
| $[Fe(CO)\{P(OEt)_3\}\{S_2C_2(CF_3)_2\}]$ | 1980 | | 1980 | |
| $[Fe(CO)(Bu^tNC)_2\{S_2C_2(CF_3)_2\}]$ | 2060 | 2180, 2160 | 2060 | 2180, 2160 |
| $[Fe(CO)(p\text{-}ClC_6H_4NC)(PPh_3)\{S_2C_2(CF_3)_2\}]$ | 2075 | 2118 | 2075 | 2118 |
| $[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ | 1940 | | 1943 | |
| $[Fe(CO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}]$ | 1953 | | 1955 | |
| $[Fe(CO)\{C_6H_4(AsMe_2)_2\}\{S_2C_2(CF_3)_2\}]$ | 1940 | | 1930 | |
| $[Fe(p\text{-}ClC_6H_4NC)_3\{S_2C_2(CF_3)_2\}]$ | | 2150, 2115, 2090 | | 2150, 2110, 2090 |
| $[Fe(Bu^tNC)_3\{S_2C_2(CF_3)_2\}]$ | | 2160, 2130, 2010 | | 2160, 2130, 2010 |
| $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]$ | 1712 [c] | | 1710 [c] | |
| $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\{S_2C_2(CF_3)_2\}]^+$ | 1832 [c] | | 1832 [c] | |
| $[Fe(NO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}]$ | 1725 [c] | | 1725 [c] | |
| $[Fe(NO)(Ph_2PCH{:}CHPPh_2)\{S_2C_2(CF_3)_2\}]^+$ | 1840 [c] | | 1850 [c] | |

[a] In dichloromethane unless otherwise stated. [b] In n-pentane. [c] $\nu_{NO}$.

As was mentioned above, $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$ reacted with LL′ giving $[Fe(CO)(LL')\{S_2C_2(CF_3)_2\}]$, but displacement of the unique CO group by $PPh_3$ or isonitriles could not be achieved. However, that CO group could be displaced by $P(OEt)_3$ giving $[Fe\{P(OEt)_3\}(LL')\{S_2C_2(CF_3)_2\}]$. Further, when treated with $[NO][PF_6]$ in warm benzene, $[Fe(CO)(LL')\{S_2C_2(CF_3)_2\}]$ (LL′ = *cis*-$Ph_2PCH{:}CHPPh$ or $Ph_2PCH_2CH_2PPh_2$) afforded a red-brown solid which exhibited two NO stretching frequencies in its i.r. spectrum (at *ca.* 1840 and *ca.* 1720 cm.$^{-1}$). Chromatography of this compound in acetone on alumina afforded a black eluate from which $[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]$ was isolated, and oxidation of this with $AgPF_6$ afforded $[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}][PF_6]$. It appears that displacement of the CO group by the isoelectronic $NO^+$ is accompanied by partial reduction of the monocation (*vide* spectral data) which, on chromatography in acetone, is completely reduced to the neutral mononitrosyl; reoxidation of the neutral species with silver(I) ion afforded the expected monocation. Analogous reactions using $[NO][PF_6]$ were attempted with [Fe(CO)-

LL′$\{S_2C_2(CF_3)_2\}$] (L = L′ = $PPh_3$ or CN($p$-$ClC_6H_4$); LL′ = $o$-$C_6H_4$ ($AsMe_2$; L = CO, L′ = $PPh_3$), but in no case could a nitrosyl-containing species be isolated.

Osmometric molecular-weight determinations (Table 2) of some of these new Lewis base complexes indicated that they were monomeric, and their mass spectra exhibited ions due only to mononuclear species. It would appear therefore, that the tricarbonyl compound may be unique in being binuclear, and that the iron atom in the phosphine, isonitrile, and nitrosyl species prefers to be five-co-ordinate.

TABLE 4

Electronic spectral data obtained from new iron–sulphur complexes

| Complex | Frequencies (intensities) [a] |
|---|---|
| $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$ | 12,200w;[b] 18,200m; 24,000s; 34,800vs<br>18,200m;[c] 24,000s; 28,100sh; 34,800vs |
| $[Fe(CO)_2(PPh_3)\{S_2C_2(CF_3)_2\}]$ | 17,800 (1·9); 23,400 (2·7); 32,800 (6·94); 38,400 (17·3) |
| $[Fe(CO)_2(p\text{-}ClC_6H_4NC)\text{-}\{S_2C_2(CF_3)_2\}]$ | 17,400 (2·64); 24,000 (2·98); 32,800 (13·3); 38,400 (21·1) |
| $[Fe(CO)_2(Bu^tNC)\{S_2C_2(CF_3)_2\}]$ | 16,600 (1·92); 23,800 (2·1); 33,000 (5·12); 38,600 (10·3) |
| $[Fe(CO)(PPh_3)_2\{S_2C_2(CF_3)_2]$ | 16,200 (1·29); 21,400 (1·77); 30,600 (7·34); 38,400 (19·4) |
| $[Fe(CO)\{P(OEt)_3\}_2\{S_2C_2(CF_3)_2\}]$ | 19,300 (1·88); 24,600 (2·23); 32,800 (6·48); 38,600 (8·43) |
| $[Fe(CO)(Bu^tNC)_2\{S_2C_2(CF_3)_2\}]$ | 17,400 (1·43); 24,200 (2·13); 32,800 (5·74); 38,600 (11·8) |
| $[Fe(CO)(PPh_3)(p\text{-}ClC_6H_4NC)\text{-}\{S_2C_2(CF_3)_2\}]$ | 15,800 (1·3); 23,400 (0·9); 23,300 (8·2); 31,200 (6·5sh); 38,400 (21·5) |
| $[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\text{-}\{S_2C_2(CF_3)_2\}]$ | 17,600 (2·1); 24,200 (2·2); 32,000 (8·9); 38,400 (24·0) |
| $[Fe(CO)(Ph_2PCH{:}CHPPh_2)\text{-}\{S_2C_2(CF_3)_2\}]$ | 17,400 (1·4); 23,600 (1·9); 32,000 (7·95); 38,000 (20·1) |
| $[Fe(CO)\{o\text{-}C_6H_4(AsMe_2)_2\}\text{-}\{S_2C_2(CF_3)_2\}]$ | 12,600 (0·33); 17,000 (0·46); 24,600 (1·37); 31,600 (3·97); 38,800 (17·6) |
| $[Fe\{P(OEt)_3\}_3\{S_2C_2(CF_3)_2\}]$ | 17,000 (1·27); 24,200 (1·25); 30,200 (7·07); 38,000 (9·41) |
| $[Fe\{P(OEt)_3\}(Ph_2PCH_2CH_2\text{-}PPh_2)\{S_2C_2(CF_3)_2\}]$ | 15,800 (1·3); 23,400 (0·9); 28,300 (8·2); 31,200 (6·5sh); 38,400 (21·5) |
| $[Fe(p\text{-}ClC_6H_4NC)_3\{S_2C_2(CF_3)_2\}]$ | 16,400 (1·45); 23,200 (5·27); 31,200 (33·2) |
| $[Fe(Bu^tNC)_3\{S_2C_2(CF_3)_2\}]$ | 16,400 (1·46); 23,800 (2·15); 30,000 (6·1); 38,800 (17·1) |
| $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\text{-}\{S_2C_2(CF_3)_2\}]$ | 12,000 (0·33); 16,600 (0·75); 20,600 (0·96); 27,600 (3·01); 32,800 (10·8); 38,600 (24·4) |
| $[Fe(NO)(Ph_2PCH{:}CHPPh_2)\text{-}\{S_2C_2(CF_3)_2\}]$ | 12,000 (0·38); 16,600 (0·86); 20,800 (1·25); 27,600 (3·8) 32,800 (12·8); 38,600 (30·1) |
| $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\text{-}\{S_2C_2(CF_3)_2\}]^+$ | 21,300 (4·4); 34,400 (18·4) |
| $[Fe(NO)(Ph_2PCH{:}CHPPh_2)\text{-}\{S_2C_2(CF_3)_2\}]^+$ | 21,300 (3·3); 34,400 (15·2) |

[a] In dichloromethane; frequencies in $cm^{-1}$, intensities ($\times 10^{-3}$) in l $mol^{-1}$ $cm^{-1}$. [b] In chloroform. [c] In hexane.

*Spectral Studies.*—The electronic spectra of the new complexes were measured in dichloromethane solution and the data are given in Table 4. All species, except those containing NO, exhibited similar spectra suggesting that they had similar molecular structures. The spectra of these compounds are markedly different to that of their precursor, $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$, which, we believe, contains six-co-ordinate Fe atoms.

Although the spectra of the phosphine and isonitrile complexes are generally very similar, the positions of the absorption maxima of several of the bands show a dependence on the nature of the ligands in a given isostructural complex, and a correlation between the band shifts and the $\pi$-acceptor ability of the ligands can be made. Thus, the absorption maxima decrease in frequency in the order L = CO > $P(OEt)_3$ > CNR > $PPh_3$.

The nitrosyl complexes, $[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]^+$, although formally isoelectronic with their neutral carbonyl analogues, are spectrally dissimilar to these, and to $[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]^0$.

The spectra of the new complexes differ markedly from those of the bis-dithiolene phosphine and nitrosyl adducts,[6] $[Fe(L)\{S_2C_2(CF_3)_2\}_2]^z$ ($z = 0, -1$; L = NO or $Ph_3$), in that the intense transitions in the visible and near-i.r. regions present in those of the latter are absent in those of the former.

The neutral nitrosyl complexes, $[Fe(NO)(LL')\}\text{-}\{S_2C_2(CF_3)_2\}]$, were paramagnetic, having one unpaired spin ($\mu$ = 1·78 B.M.), and their e.s.r. spectra consisted of a single line. The $g$ factors (2·033 for both) and lack of $^{14}N$ ($I = 1$) or $^{31}P$ ($I = \frac{1}{2}$) hyperfine splittings contrast with the data obtained from the formally isoelectronic $[Fe(NO)\{S_2C_2(CF_3)_2\}_2]^{2-}$ and its analogues ($g_{av}$ = 2·026 and $\langle A \rangle_N$ = 14·9 gauss).

The i.r. spectra of the complexes were measured in the solid state and in dichloromethane solution, and the CO, CN, and NO frequencies are given in Table 3.

Within a given series of complexes, some correlations can be made between stretching frequencies and the nature of the Lewis base. Thus, in $[Fe(CO)(LL')\text{-}\{S_2C_2(CF_3)_2\}]$, $\nu_{CO}$ was found to decrease in the order LL′ = $cis$-$Ph_2PCH{:}CHPPh_2$ > $PH_2PCH_2CH_2PPh_2$ > $o$-$C_6H_4(AsMe_2)_2$, and this order is also reflected in the position of $\nu_{NO}$ in the corresponding neutral and mono-cationic nitrosyl species. Apparently the unsaturated diphosphine is a better $\pi$-acceptor that its saturated analogue which, in turn, is a better acceptor than the diarsine. This may appear surprising until it is realised that in the diarsine, the donor atoms each carry two electron-releasing methyl groups, whereas the other two ligands contain donor atoms carrying two electron-withdrawing phenyl groups.

For the series $[Fe(CO)_2L\{S_2C_2(CF_3)_2\}]$ and $[Fe(CO)\text{-}L_2\{S_2C_2(CF_3)_2\}]$ the CO stretching frequencies were found to decrease in the order L = CNR > $P(OEt)_3$ > $PPh_3$, which does not follow exactly the order expressed in terms of $\pi$-acceptor abilities. However, coupling between the CN and CO stretching modes could give rise to anomalous shifts of $\nu_{CO}$.

---

[5] N. A. Bailey, private communication.

[6] J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *J. Amer. Chem. Soc.*, 1967, **89**, 6082; J. A. McCleverty, N. M. Atherton, N. G. Connelly, and C. J. Winscom, *J. Chem. Soc.* (*A*), 1969, 2242.

For the species $[Fe(CO)_2(CNR)\{S_2C_2(CF_3)_2\}]$ and $[Fe(CNR)_3\{S_2C_2(CF_3)_2\}]$, the order of decreasing $\nu_{CN}$ was $R = Bu^t > p\text{-}ClC_6H_4$, which was consistent with the view that the aryl isonitrile is a better $\pi$-acceptor than its alkyl analogue.

Oxidation of $[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]^0$ to the corresponding monocations was accompanied by the expected increase in $\nu_{NO}$, of 120 cm$^{-1}$.

Unfortunately, assignment of the perturbed C=C stretching frequency associated with the sulphur ligand proved to be impossible because of the complexity of bands due to the Lewis bases in the region 1600—1350 cm$^{-1}$; in $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$ this vibration has been reported[3] to occur at 1481 cm$^{-1}$, which is low in comparison with the values for $\nu_{C=C}$ obtained from species believed to contain the ligand in its ethylenedithiolato, rather than dithioketonic, form.

From the majority of the i.r. spectral data, no useful information concerning the likely structures of these complexes could be obtained. However, the species $[Fe(CNR)_3\{S_2C_2(CF_3)_2\}]$ exhibited two strong and one weak CN stretching frequencies in solution, and in the solid state.

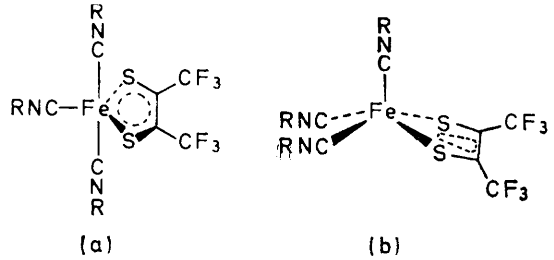

FIGURE 2

Assuming that the metal is five-co-ordinate, the most likely structures will be as shown in Figure 2(a) ($C_{2v}$) and 2(b) ($C_s$). Both of these would give rise to three i.r.-active CN stretching frequencies, and so, on the basis of the available data, we can draw no definite structural conclusions. However, one isomer of $[Ru(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}]$ is known[3] to have a square-pyramidal structure (with equatorial CO), and, in our opinion, this geometry seems the more reasonable for our compounds.

*Voltammetric Studies.*—The new complexes were examined voltammetrically in dichloromethane using a rotating platinum electrode, and the results are summarised in Table 5.

The majority of the compounds exhibited an ill-defined oxidation process appearing to correspond to a multiple-electron step. The half-wave potentials for the processes could not be measured accurately, and only the position of the beginning of the oxidation wave was noted. Although no meaningful information can be drawn from these electrochemical data, there is a rough correlation between the potential of the beginning of the oxidation processes and the $\pi$-acceptor ability of the Lewis base ligand. Thus, those complexes containing good $\pi$-acceptor ligands were oxidised at higher potentials than those containing less good $\pi$-acceptors. Surprisingly, $[Fe(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}]$ exhibited a well defined one-electron oxidation process.

TABLE 5

Electrochemical data obtained from new iron–sulphur complexes

| Complex | $E_{\frac{1}{2}}$ [a] | $R$ [b] | $D$ [c] | CV [d] |
|---|---|---|---|---|
| $[Fe(CO)_2(PPh_3)\{S_2C_2(CF_3)_2\}]$ | +1·2 [e] | | | I |
| $[Fe(CO)_2(p\text{-}ClC_6H_4NC)\{S_2C_2(CF_3)_2\}]$ | +1·0 [e] | | | I |
| $[Fe(CO)_2\{P(OEt)_3\}\{S_2C_2(CF_3)_2\}]$ | +0·95 [e] | | | I |
| $[Fe(CO)(Ph_2PCH{:}CHPPh_2)\text{-}\{S_2C_2(CF_3)_2\}]$ | +0·90 [e] | | | I |
| $[Fe(CO)(Ph_2PCH_2CH_2PPh_2)\text{-}\{S_2C_2(CF_3)_2\}]$ | +0·87 [e] | | | I |
| $[Fe(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}]$ | +0·69 | 53 | 8·1 | QR |
| $[Fe(NO)(Ph_2PCH{:}CHPPh_2)\text{-}\{S_2C_2(CF_3)_2\}]$ | +0·28 | 57 | 7·9 | R |
| $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)\text{-}\{S_2C_2(CF_3)_2\}]$ | +0·23 | 56 | 7·6 | R |

[a] In V, in $CH_2Cl_2$ *vs.* SCE using rotating Pt electrode. [b] $R = E_{\frac{3}{4}} - E_{\frac{1}{4}}$, in mV; for reversible one-electron transfer $R = 56$. [c] $D = i_d/c$ in $\mu$A/mM; for standard couple $[Ni\{S_2C_2(CN)_2\}_2]^{2-} \rightleftharpoons [Ni\{S_2C_2(CN)_2\}]_2^- + e^-$, under same conditions, $D = 7·1$. [d] Cyclic voltammetry; from shape of the cyclic voltammograms the waves were classified as (*a*) reversible (R), (*b*) quasi-reversible (QR) having a couple chemical reaction or (*c*) irreversible (I); further, peak separation for a reversible couple [see (*c*)] in dichloromethane was 120 mV. [e] Beginning of wave (multiple-electron step).

The neutral nitrosyl complexes, $[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]^0$ (LL' = *cis*-$Ph_2PCH{:}CHPPh_2$ or $Ph_2PCH_2CH_2PPh_2$) readily underwent electrochemical oxidation in a well defined one-electron transfer reaction. The $E_{\frac{1}{2}}$-value for the complex containing *cis*-$Ph_2PCH{:}CHPPh_2$ was *ca.* 60 mV more positive than that of the species containing its saturated analogue, again consistent with the greater $\pi$-acceptor ability of the conjugated diphosphine. The oxidation potentials for the couple

$$[Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]^0 \rightleftharpoons [Fe(NO)(LL')\{S_2C_2(CF_3)_2\}]^+ + e^-$$

were such that chemical oxidation using $Ag^+$ was easily achieved.

We thank the S.R.C. for studentships (C. J. J. and D. G. O.), the Royal Society for funds to purchase the Beckman Electroscan Polarograph, and Mr. G. A. Wright, Mr. S. Jones, Mr. G. Mettam, and Mrs. J. Bray for technical and experimental assistance.

[1/2329 *Received, 6th December*, 1971]