

Synthesis and Crystallographic Characterization of Thiazolyl and Thiazolinylidene Complexes of Cyclopentadienyliron(II) †

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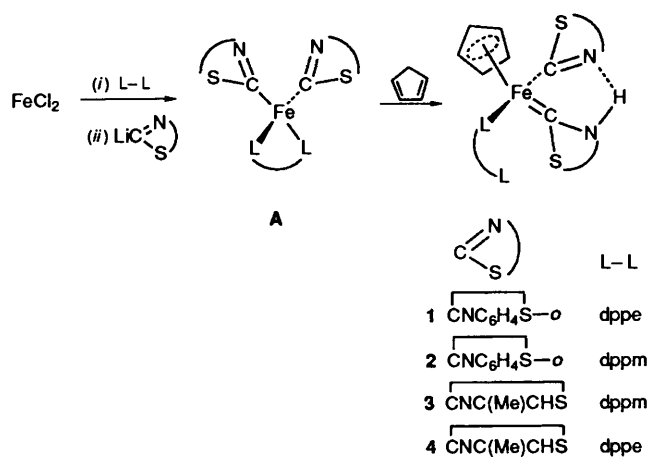
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The consecutive reaction of FeCl₂ with bis(diphenylphosphino)methane or 1,2-bis(diphenylphosphino)ethane, benzothiazol-2-yl lithium or 4-methylthiazolyl lithium and cyclopentadiene affords thiazolinylidene (thiazolyl) complexes which contain only one co-ordinated phosphorus atom. An X-ray crystal structure determination of one of these, [Fe(η⁵-C₅H₅)(CNC₆H₄S-o)(C=NC₆H₄S-o)(dppe)], has revealed a metal-carbene carbon bond length of 1.889(3) Å and a hydrogen bond between the nitrogen atoms in the two neighbouring carbene and benzothiazolyl ligands. Cationic thiazolinylidene complexes form when the products from the reaction between [Fe(η⁵-C₅H₅)(CO)₂Cl] and benzothiazol-2-yl lithium or 4-methylthiazolyl lithium are acidified with trifluoromethanesulfonic acid. A single crystal X-ray structure determination of [Fe(η⁵-C₅H₅)(CO)₂{CNC(Me)=CHS}]CF₃SO₃·0.5H₂O showed a metal-carbene carbon bond length of 1.947(3) Å which is longer than all the Fe-C(carbonyl) distances (average 1.768 Å).

Lithiated compounds of thiazoles have been used to prepare amino(thio)carbene complexes of chromium¹ and gold.² Stone and co-workers³ obtained similar compounds of monosubstituted iron pentacarbonyl by treating 2-chloro-*N*,4-dimethyl-1,3-thiazolium and 2-chloro-*N*-methyl-1,3-benzothiazolium tetrafluoroborate with [Fe(CO)₄]²⁻. Although various cationic cyclopentadienyliron carbene complexes are known, only one amino(thio)carbene compound, [Fe(η⁵-C₅H₅)(CO)₂{CNC(CH₂)₂S}]PF₆, has been reported. Two synthetic pathways, one using the dithiocarbene complex [Fe(η⁵-C₅H₅)(CO)₂{C(SMe)₂}]⁺ and the other employing the thiocarbonyl compound [Fe(η⁵-C₅H₅)(CO)₂(CS)]⁺ as starting material, were used by Angelici and co-workers^{4,5} for its preparation.

Our recent reports have shown that cyclopentadiene can be deprotonated by complexes of the type [Fe(L-L)R₂] [L-L = 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm); R = Me or Ph] to afford stable complexes of the type [Fe(η⁵-C₅H₅)(L-L)R].^{6,7} The four-membered chelates are reactive towards CS₂ and form isomeric dithioacetate-*S,S'* and dithiobenzoate-*C,S,S'* complexes of iron. In the CS₂ insertion reaction a metal-phosphine bond is cleaved.⁷

We embarked on the present study with the dual purpose (i) of using the above-mentioned methodology to prepare carbene complexes from new precursors of the type [Fe(η⁵-C₅H₅)(L-L)R] (R = C=NC₆H₄S-o, or C=NC(Me)=CHS), and (ii) of using [Fe(η⁵-C₅H₅)(CO)₂Cl] and LiR to prepare first the neutral complexes [Fe(η⁵-C₅H₅)(CO)₂R], which could then give cationic carbene complexes upon acidification. This paper reports our results which include the discovery of unexpected [amino(thio)carbene] (thiazolyl) complexes obtained according to the first procedure as well as the first X-ray crystallographic data for amino(thio)carbene complexes of iron.



Scheme 1

Results and Discussion

Preparation and Structural Characterization of the Compounds

[Fe(η⁵-C₅H₅)(CNC₆H₄S-o)(C=NC₆H₄S-o)(L-L)] and [Fe(η⁵-C₅H₅){CNC(Me)=CHS}{C=NC(Me)=CHS}(L-L)].—Compounds 1–4 were prepared in low yields according to Scheme 1. The diphosphine dppe or dppm was added to dry FeCl₂ in tetrahydrofuran (thf) and the mixture then treated with benzothiazol-2-yl lithium or 4-methylthiazolyl lithium presumably to give compounds of type A. The formulation of compounds A is based on the isolation of bulky phosphine-stabilized analogous compounds.⁸ Subsequent reaction with cyclopentadiene, purification by column chromatography and recrystallization afforded the crystalline, analytically pure, neutral carbene complexes 1–3. Compound 4 could not be successfully separated from a thiazolyl complex 5, which still contained a bidentate phosphine ligand. The microcrystalline powder obtained after column chromatography and evaporation of solvent *in vacuo* contained 4 and 5 in a molar proportion

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

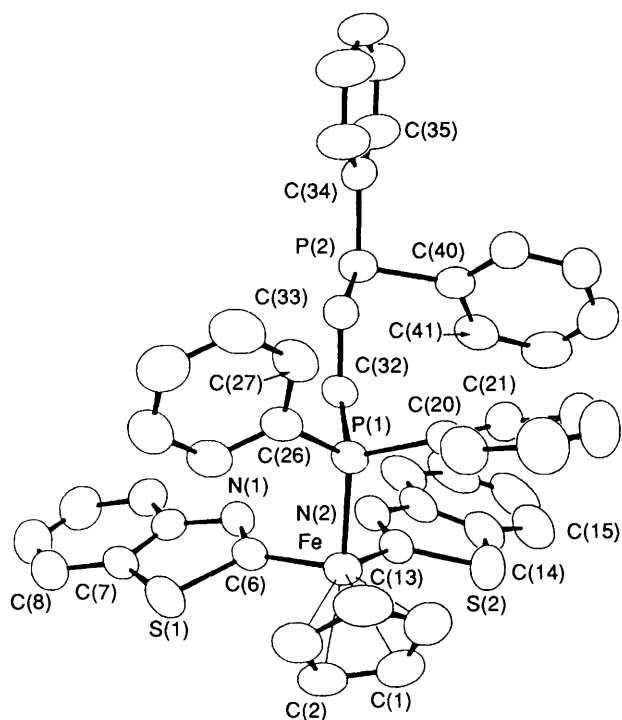
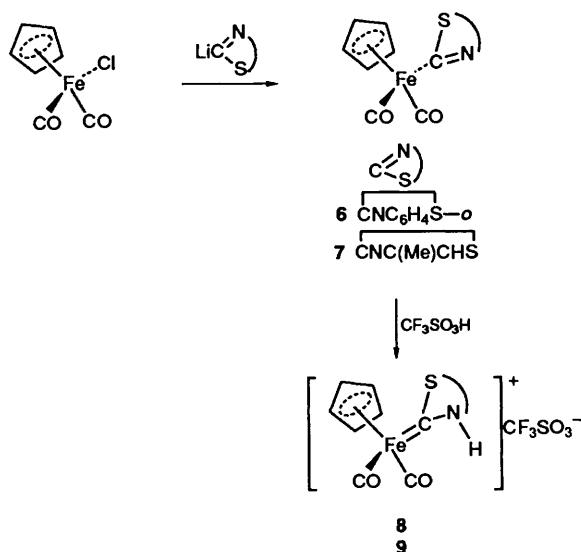


Fig. 1 Perspective view of complex 1 showing the numbering scheme



Scheme 2

of 3:1 (established by ^1H NMR spectroscopy) and in yields of 14 and 5% respectively.

Our results established that the complexes $[\text{Fe}(\text{L-L})\text{R}_2]$ [$\text{R} = \text{C}=\text{NC}_6\text{H}_4\text{S-o}$ or $\text{C}=\text{NC}(\text{Me})=\text{CHS}$], prepared *in situ*, deprotonated cyclopentadiene to facilitate cyclopentadienyl coordination. In the predominant process both four- and five-membered chelates suffered metal-phosphorus bond rupture and, significantly, the proton attached itself to a nitrogen atom of a thiazolyl ligand to form a neutral carbene complex which still contained a thiazolyl ligand. Proton transfer, true to expectation, did occur to a metal-bonded carbon of a thiazolyl group on addition of cyclopentadiene (to give compound 5), but only when the ligands 4-methylthiazolyl and dppe were combined in compound A.

An advantageous feature of our published method for the preparation of complexes of the type $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{L-L})\text{R}]$

($\text{R} = \text{Me}$ or Ph)^{6,7} is the total absence of ferrocene in the product mixture (Lehmkuhl's method of synthesis affords a significant proportion of ferrocene⁹). The formation of the carbene complexes, however, was accompanied by *ca.* 1% ferrocene.

The new compounds were characterized by elemental analysis (not the mixture of 4 and 5), mass spectra (which showed their molecular ions) and nuclear magnetic resonance measurements. The N-H vibrations appeared at 3058–3105 cm^{-1} in the infrared spectra. The NMR spectra (compare the Experimental section) revealed certain characteristic features. The cyclopentadienyl ^1H NMR signals of compounds 1–4 appear as doublets ($J_{\text{PH}} = 1.2\text{--}1.4$ Hz) at δ 4.60–4.85. The CH_2 protons of dppm give a doublet of doublets in line with our previous result for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CS}_2\text{Me})(\text{dppm})]$,⁷ whereas the aliphatic protons of mono co-ordinated dppe resonate as two multiplets; with both phosphorus atoms co-ordinated only one multiplet is found for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Me}(\text{dppe})]$ ¹⁰ and 5. The NH protons involved in hydrogen bonding were significantly deshielded and showed chemical shifts between δ 17.22 and 17.95. The room-temperature NMR measurements allow no differentiation between the thiazolyl and thiazolylidene ligands and the fact that all these signals persisted without change at -50°C indicates that the fluxional process involving the two heterocyclic rings is already fast at this temperature. The doublets in the ^{13}C NMR spectra a δ 231 (for the σ metal-bonded carbons in the benzothiazol-2-yl-derived 1 and 2) and at δ *ca.* 223 (for the 4-methylthiazolyl complexes 3 and 4) are due to coupling with the co-ordinated phosphorus atoms. A similar coupling, to afford a triplet signal, was previously found for the methyl group in the compound $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Me}(\text{dppm})]$,⁷ The metal-bonded carbon in the alkyl-type complex 5 resonates as a singlet at δ 167.4.

Structure of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CNHC}_6\text{H}_4\text{S-o})(\text{C}=\text{NC}_6\text{H}_4\text{S-o})$ (dppe)] 1.—The molecular structure of complex 1 is shown in Fig. 1. Final atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. The C–H bond distances are not tabulated but vary between 0.81 and 1.09 Å with estimated standard deviations (e.s.d.s) of less than 0.05 Å. The iron atom is pseudo-octahedrally⁷ surrounded by a η^5 -cyclopentadienyl group, a carbene (benzothiazolylidene) ligand, a benzothiazolyl group and a phosphine with angles between the legs of the piano stool varying between $91.4(1)$ and $94.1(1)^\circ$. The two essentially flat ligands derived from benzothiazole form a dihedral angle of $31.8(3)^\circ$ and are linked by a hydrogen bond; the hydrogen atom bonded to N(2) [$1.094(21)$ Å] is also in close contact with N(1) [$\text{HN}(2)\cdots\text{N}(1)$ 1.633 Å, $\text{N}(1)\cdots\text{HN}(2)\text{--N}(2)$ 143.1°]. The N \cdots N separation is 2.592 Å. Differentiation between the two σ -bonded carbon ligands is possible in the solid state. Whereas the benzothiazolylidene ligand has a shorter metal-carbon separation than the co-ordinated benzothiazolyl group [1.889(3) against 1.941(2) Å] its C(carbene)–N separation is 0.063 Å longer and its C(carbene)–S separation 0.03 Å shorter. Metal-carbene bond lengths in known neutral cyclopentadienylcarbonyliron(II) compounds vary between 1.863 and 1.932 Å.¹¹

Preparation and Structural Characterization of the σ -Bonded Thiazolyls $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}=\text{NC}_6\text{H}_4\text{S-o})]$ 6 and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{C}=\text{NC}(\text{Me})=\text{CHS})]$ 7 and the Cationic Carbene Complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNHC}_6\text{H}_4\text{S-o})]$ $\text{CF}_3\text{SO}_3\cdot 0.5\text{-H}_2\text{O}$ 8 and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\{\text{CNHC}(\text{Me})=\text{CHS}\}]\text{CF}_3\text{SO}_3\cdot 0.5\text{H}_2\text{O}$ 9.—Reaction of benzothiazol-2-yl- or 4-methylthiazolyl-lithium with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ at -75°C afforded the light-sensitive neutral complexes 6 and 7 (Scheme 2) (together with *ca.* 11% of the well known compound $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}_2]$) which were purified on preparative TLC plates. Acidification of 6 and 7 with trifluoromethanesulfonic acid produced the two cationic amino(thio)carbene

Table 1 Fractional coordinates ($\times 10^4$) for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\overline{\text{CNHC}_6\text{H}_4\text{S-o}})(\overline{\text{C}=\text{NC}_6\text{H}_4\text{S-o}})(\text{dppe})] \mathbf{1}$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Fe	2 662(1)	3 105(1)	1 548(1)	C(39)	1 970(4)	6 586(3)	5 551(2)
C(1)	3 761(4)	3 090(3)	620(2)	C(40)	2 358(3)	7 650(3)	3 598(2)
C(2)	2 853(3)	1 836(3)	671(2)	C(41)	2 096(4)	7 848(3)	2 853(2)
C(3)	3 247(4)	1 568(3)	1 389(2)	C(42)	3 072(5)	8 819(4)	2 557(2)
C(4)	4 401(4)	2 686(4)	1 795(2)	C(43)	4 310(5)	9 615(3)	3 017(3)
C(5)	4 726(3)	3 622(3)	1 309(2)	C(44)	4 600(4)	9 454(3)	3 754(2)
C(6)	697(3)	2 048(2)	1 527(1)	C(45)	3 651(3)	8 472(3)	4 049(2)
S(1)	60(1)	345(1)	1 406(1)	H(1)	3 649(23)	3 596(21)	231(13)
C(7)	-1 637(3)	164(3)	1 392(2)	H(2)	2 052(23)	1 251(21)	301(13)
C(8)	-2 874(4)	-940(3)	1 312(2)	H(3)	2 879(23)	800(21)	1 597(13)
C(9)	-4 093(4)	-810(3)	1 279(2)	H(4)	4 953(23)	2 742(21)	2 318(13)
C(10)	-4 129(3)	342(4)	1 314(2)	H(5)	5 436(23)	4 567(21)	1 441(13)
C(11)	-2 927(3)	1 455(3)	1 418(2)	H(8)	-2 811(23)	-1 740(21)	1 307(13)
C(12)	-1 655(3)	1 346(3)	1 463(1)	H(9)	-4 881(23)	-1 510(21)	1 238(13)
N(1)	-345(2)	2 366(2)	1 561(1)	H(10)	-4 900(23)	484(21)	1 224(13)
C(13)	2 258(3)	4 433(2)	1 220(1)	H(11)	-2 964(23)	2 268(21)	1 418(13)
S(2)	3 372(1)	5 696(1)	809(1)	H(15)	3 120(24)	7 783(21)	169(13)
C(14)	2 179(4)	6 376(3)	685(2)	H(16)	1 136(23)	8 430(21)	181(13)
C(15)	2 254(4)	7 463(3)	376(2)	C(17)	-797(23)	7 299(21)	652(13)
C(16)	1 158(6)	7 772(3)	364(2)	H(18)	-1 012(24)	5 463(21)	1 216(13)
C(17)	-14(5)	7 063(4)	639(2)	HN(2)	180(23)	3 826(21)	1 387(13)
C(18)	-133(3)	5 982(3)	937(2)	H(21)	4 300(23)	6 742(21)	2 724(13)
C(19)	985(3)	5 658(3)	961(2)	H(22)	6 386(24)	8 308(21)	2 906(13)
N(2)	1 066(2)	4 615(2)	1 242(1)	H(23)	8 249(23)	7 877(21)	3 250(13)
P(1)	3 044(1)	3 968(1)	2 775(1)	H(24)	7 956(23)	5 890(21)	3 478(13)
C(20)	4 776(3)	5 314(3)	3 032(1)	H(25)	5 808(24)	4 288(21)	3 368(13)
C(21)	4 979(3)	6 509(3)	2 888(2)	H(27)	4 221(23)	4 355(21)	4 408(13)
C(22)	6 315(3)	7 489(3)	2 987(2)	H(28)	3 965(23)	3 019(21)	5 296(13)
C(23)	7 455(3)	7 255(4)	3 216(2)	H(29)	2 796(23)	951(21)	4 996(13)
C(24)	7 279(3)	6 088(4)	3 363(2)	H(30)	1 797(23)	150(21)	3 758(13)
C(25)	5 957(3)	5 109(3)	3 277(2)	H(31)	1 916(27)	1 320(24)	2 864(14)
C(26)	3 028(3)	2 978(2)	3 517(1)	H(32A)	1 036(26)	4 041(24)	2 913(15)
C(27)	3 681(3)	3 487(3)	4 276(2)	H(32B)	1 949(26)	5 356(24)	2 737(14)
C(28)	3 588(4)	2 718(3)	4 829(2)	H(33A)	1 641(27)	4 584(24)	4 185(14)
C(29)	2 843(4)	1 425(3)	4 639(2)	H(33B)	2 985(26)	5 788(23)	4 107(14)
C(30)	2 203(3)	910(3)	3 900(2)	H(35)	477(29)	8 076(26)	4 761(15)
C(31)	2 291(3)	1 675(3)	3 340(2)	H(36)	678(30)	8 914(26)	5 922(16)
C(32)	1 862(3)	4 670(3)	3 049(2)	H(37)	1 681(28)	8 397(26)	6 923(15)
C(33)	2 015(3)	5 244(3)	3 891(2)	H(38)	2 467(29)	6 876(26)	6 670(15)
P(2)	1 077(1)	6 273(1)	3 924(1)	H(39)	2 261(30)	6 057(26)	5 454(16)
C(34)	1 325(3)	6 911(3)	4 943(2)	H(41)	1 240(27)	7 398(25)	2 603(15)
C(35)	786(4)	7 775(4)	5 130(2)	H(42)	2 827(28)	8 953(25)	2 102(15)
C(36)	907(5)	8 317(4)	5 873(3)	H(43)	4 855(29)	10 237(26)	2 833(16)
C(37)	1 568(4)	7 992(4)	6 456(2)	H(44)	5 420(27)	9 952(25)	4 046(15)
C(38)	2 080(5)	7 129(4)	6 301(2)	H(45)	3 905(26)	8 297(24)	4 549(15)

Table 2 Selected bond lengths (Å) and angles ($^\circ$) for complex **1** with e.s.d.s in parentheses

Fe-C(1)	2.123(4)	Fe-C(4)	2.107(5)
Fe-C(2)	2.114(4)	Fe-C(5)	2.133(4)
Fe-C(3)	2.121(4)	Fe-P(1)	2.215(1)
Fe-C(6)	1.941(2)	Fe-C(13)	1.889(3)
C(6)-S(1)	1.794(3)	C(13)-S(2)	1.760(3)
C(6)-N(1)	1.308(4)	C(13)-N(2)	1.371(4)
C(12)-N(1)	1.392(3)	C(19)-N(2)	1.388(4)
S(1)-C(7)	1.727(3)	S(2)-C(14)	1.751(4)
C(7)-C(12)	1.375(5)	C(14)-C(19)	1.384(4)
N(1)⋯HN(2)	1.633	N(2)-HN(2)	1.094(21)
N(1)⋯N(2)	2.592		
C(6)-Fe-C(13)	91.4(1)	N(2)-HN(2)⋯N(1)	143.1
C(6)-Fe-P(1)	94.1(1)	C(13)-Fe-P(1)	91.6(1)
S(1)-C(6)-N(1)	109.6(2)	S(2)-C(13)-N(2)	106.0(2)

complexes, **8** and **9** (Scheme 2), which were purified by crystallization. The acid was not dried before use with the result that the crystals of both product compounds contained water of crystallization.

Both neutral carbonyl complexes showed molecular ions in the mass spectra (70 eV, *ca.* 1.12×10^{-17} J) and fragmented by

the stepwise loss of two carbonyl groups, but then **6** loses a cyclopentadienyl group whereas in **7** the metal-carbon σ bond breaks first. Similarly, the metal-carbene bond in the cationic complex **9** is only cleaved after loss of a cyclopentadienyl group whereas the reverse occurs in **8**. The two strong carbonyl vibrations of both cationic carbene complexes (compare the Experimental section) occur at 11–21 cm^{-1} higher than for the neutral complexes from which they were prepared. Yamamoto and Yamazaki¹² made a similar observation for their cationic amino(alkyl)carbene complexes compared to the precursors used.

The carbonyl resonances in the ^{13}C NMR spectra of complexes **6** and **7** occur at δ 214. Based on the results of Johnson *et al.*,¹³ the high-field signals of **8** and **9** at δ 210.1 and 199.5 should be assigned to the carbene carbons and those at δ 211.9 and 210.6 to the carbonyl carbon atoms but, based on our previous experience according to which the carbene carbons generally have longer spin-lattice relaxation times than those of the carbonyl atoms in the same compound,^{1,14} we have assigned the higher-intensity peak at δ 210.1 for **8** to the carbonyl carbon atoms and the resonance at δ 211.9 to the carbene carbon atom. The assignment for **9** above is in line with this criterion.

Structure of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\{\overline{\text{CNHC}(\text{Me})=\text{CHS}}\}]\text{CF}_3$ -

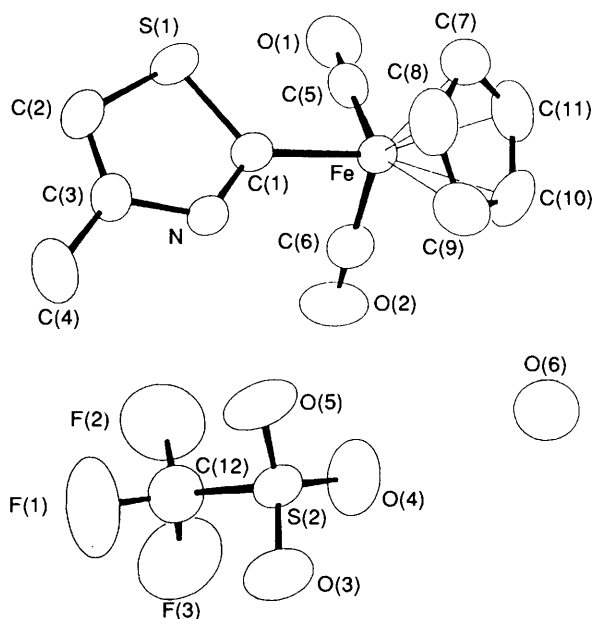


Fig. 2 Perspective view of complex 9 showing the numbering scheme

Table 3 Fractional coordinates ($\times 10^4$) for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{-}\{\text{CNHC}(\text{Me})=\text{CHS}\}]\text{CF}_3\text{SO}_3\cdot 0.5\text{H}_2\text{O}$ 9

Atom	X/a	Y/b	Z/c
Fe	2641(1)	4660(1)	266(1)
C(1)	1481(2)	5294(2)	-353(2)
S(1)	498(1)	4913(1)	-1170(1)
C(2)	-73(2)	5862(2)	-1363(2)
C(3)	467(2)	6435(2)	-826(2)
C(4)	287(3)	7336(2)	-763(3)
N	1325(2)	6094(1)	-261(2)
C(5)	1998(2)	3705(2)	169(2)
O(1)	1622(2)	3082(1)	98(2)
C(6)	2466(2)	4911(2)	1343(2)
O(2)	2357(2)	5079(2)	2043(2)
C(7)	3436(3)	4336(3)	-668(3)
C(8)	3348(3)	5188(3)	-645(3)
C(9)	3781(3)	5459(2)	245(3)
C(10)	4164(3)	4755(3)	769(3)
C(11)	3935(3)	4083(2)	201(3)
S(2)	7596(1)	2516(1)	1962(1)
O(3)	7906(2)	3346(1)	2168(2)
O(4)	8212(2)	1922(2)	2542(2)
O(5)	7337(2)	2312(2)	1019(2)
C(12)	6464(3)	2440(3)	2282(3)
F(1)	5818(2)	2983(2)	1827(2)
F(2)	6036(2)	1734(2)	2077(2)
F(3)	6544(2)	2584(2)	3124(2)
O(6)	0	1004(3)	2500
H(2)	-635(24)	5899(22)	-1787(22)
H(4A)	-293(27)	7468(23)	-1090(26)
H(4B)	760(28)	7604(22)	-992(24)
H(4C)	149(27)	7492(23)	-158(26)
HN	1725(26)	6425(22)	70(22)
H(7)	3159(25)	3981(22)	-1208(23)
H(8)	3060(26)	5470(24)	-1143(24)
H(9)	3793(27)	6000(22)	411(24)
H(10)	4380(26)	4808(24)	1349(24)
H(11)	4170(27)	3601(22)	436(25)
HO(6)	579(22)	1219(20)	2192(20)

$\text{SO}_3\cdot 0.5\text{H}_2\text{O}$ 9.—The structure of compound 9 is the first to be determined for a cationic cyclopentadienyl amino(thio)carbene complex of iron and one of only a few cationic cyclopentadienyl carbene complexes characterized in this manner.¹⁵ The molecular structure is shown in Fig. 2. Final atomic coordinates

Table 4 Selected bond lengths (Å) and angles ($^\circ$) for complex 9 with e.s.d.s in parentheses

Fe—C(7)	2.091(4)	Fe—C(10)	2.085(4)
Fe—C(8)	2.088(4)	Fe—C(11)	2.075(4)
Fe—C(9)	2.071(3)	Fe—C(1)	1.947(3)
Fe—C(5)	1.777(3)	Fe—C(6)	1.758(3)
S(1)—C(1)	1.708(3)	N—C(1)	1.328(3)
C(2)—S(1)	1.723(3)	C(3)—N	1.395(3)
C(2)—C(3)	1.331(4)	C(3)—C(4)	1.488(4)
N—HN	0.840(33)		
C(1)—Fe—C(5)	94.2(1)	C(1)—Fe—C(6)	91.0(1)
C(5)—Fe—C(6)	94.8(1)	S(1)—C(1)—N	107.6(2)

are given in Table 3 and selected bond lengths and distances in Table 4.

The iron atom is pseudo-octahedrally [C(1)—Fe—C(5) 94.2(1), C(1)—Fe—C(6) 91.0(1) and C(5)—Fe—C(6) 94.8(1) $^\circ$] surrounded by a cyclopentadienyl group, two carbonyl ligands and a 2-methylthiazolinylidene ligand. The anion, CF_3SO_3^- , and one half of a water molecule per formula unit crystallize with the cation. The Fe—C(cyclopentadienyl) distances [average 2.082(4) Å] are normal and compare well with similar distances in for example $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\{\text{C}(\text{SMe})_2\}]^+$.¹⁵ The Fe—C(carbonyl) bond lengths differ by 0.02 Å and are significantly shorter (on average 0.18 Å) than the Fe—C(carbene) bond of 1.947(3) Å. The latter bond length falls in the range (1.91–2.02 Å) observed for other cyclopentadienyliron carbene complexes.^{11,15} π -Bonding occurs between the carbene carbon and the neighbouring nitrogen as well as sulfur atoms as shown by the bond lengths respectively of 1.328(3) and 1.708(3) Å which are both shorter than the corresponding heteroatom—C(sp²) bonds: N—C(3) [1.395(3) Å] and S(1)—C(2) [1.723(3) Å]. The N—HN bond length of the protonated nitrogen atom is 0.840(33) Å. The short O(5)···N distance of 2.863 Å [O(5)···HN 2.050 Å] is indicative of the formation of an intermolecular hydrogen bond and also of the close proximity of the cation and anion. There is also an intermolecular hydrogen bond between the water molecule and the anion: the O(6)···O(4) distance is 2.943 Å [HO(6)···O(4) 2.000 Å].

Experimental

Materials.—Anhydrous FeCl_2 was prepared from FeCl_3 ,¹⁶ and cyclopentadiene was obtained by cracking dicyclopentadiene. The phosphine ligands were purchased from Strem Chemicals and the thiazoles, 4-methylthiazole and benzothiazole, from Aldrich and Fluka respectively. Benzothiazole was distilled from P_2O_5 and stored over molecular sieves (4 Å). *n*-Butyllithium was purchased from Merck and $\text{CF}_3\text{SO}_3\text{H}$ (trifluoromethanesulfonic acid) from Fluka. The complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ was prepared from $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}_2]$ (Aldrich).¹⁷ Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium diphenylketyl, CH_2Cl_2 from P_2O_5 and hexane and pentane from CaH_2 .

Physical Methods.—All reactions and manipulations were performed under an argon atmosphere with use of standard vacuum-line and Schlenk techniques. Melting points were determined on a Büchi 535 apparatus and are uncorrected. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument, the infrared spectra on a Perkin-Elmer 841 spectrometer and NMR spectra on a VXR 200 FT spectrometer. Elemental analyses were carried out by the Mikroanalytisches Labor Pascher, Bonn.

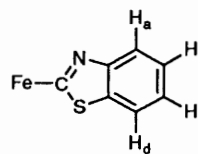
Preparations.— $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CNHC}_6\text{H}_4\text{S}-o)(\text{C}=\text{NC}_6\text{H}_4\text{S}-o)(\text{dppe})]$ 1. The diphosphine dppe (1.3 g, 3.2 mmol) was added to a suspension of FeCl_2 (0.40 g, 3.2 mmol) in thf (20 cm³). The mixture was stirred for 30 min and then added at -78°C to a

solution of benzothiazol-2-yl lithium in thf [prepared from a 1.6 mol dm⁻³ *n*-butyllithium solution in hexane (4.0 cm³, 6.4 mmol) and benzothiazole (0.70 cm³, 6.4 mmol) in thf (20 cm³) at -78 °C; stirred for 10 min¹⁸ before the addition]. After stirring the reaction mixture for 1 h at -78 °C, cyclopentadiene (2.6 cm³, 32 mmol) was injected. Stirring was continued for another hour and the mixture was then allowed to reach room temperature. The solvent was removed *in vacuo*. The residue was extracted with diethyl ether (2 × 60 cm³), the extract filtered through alumina (15 g), and evaporated to dryness. The product was purified by column chromatography at -10 °C on SiO₂ with diethyl ether-hexane (1:10) as eluent. Red crystals suitable for the crystal structure determination were obtained from a diethyl ether-pentane (1:1) solution at -20 °C. Yield 173 mg (7%), m.p. 111 °C (decomp.) (Found: C, 68.7; H, 4.9; N, 3.6. C₄₅H₃₈FeN₂P₂S₂ requires C, 68.5; H, 4.9; N, 3.55%); $\nu_{\max}/\text{cm}^{-1}(\text{NH})$ 3064w (hexachlorobutadiene); $\delta_{\text{H}}(200.6 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 1.73 (2 H, m, CH₂P), 2.36 (2 H, m, FePCH₂), 4.66 [5 H, d, *J*(PH) 1.2, C₅H₅], 6.60–7.80 [28 H, m, P(C₆H₅), C₆H₄S], and 17.95 (1 H, br s, NH); $\delta_{\text{C}}(50.3 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 24.1 (m, PCH₂CH₂P), 85.1 (s, C₅H₅), 114.6–138.8 [m, C₆H₅, NC(CH)₄CS], 150.3 (s, NC), and 230.7 [d, *J*(PC) 30.2, SCN]; $\delta_{\text{P}}(80.98 \text{ MHz, solvent C}_6\text{D}_6, \text{ external standard 85\% H}_3\text{PO}_4)$ -10.7 [d, *J*(PP) 33.0, PhPCH₂] and 75.0 [d, *J*(PP) 33.0 Hz, FeP]; *m/z* 788 (M⁺, 1) and 654 (96%, M - C₆H₄S).

[Fe(η⁵-C₅H₅)(C₆H₄S-o)(C=NC₆H₄S-o)(dppm)] **2**. The yellow complex **2** was prepared and purified similarly as described for **1**, from FeCl₂ (0.35 g, 2.2 mmol), dppm (1.1 g, 2.8 mmol), 1.6 mol dm⁻³ *n*-butyllithium (3.5 cm³, 5.6 mmol), benzothiazole (0.60 cm³, 5.5 mmol) and cyclopentadiene (0.25 cm³, 3.0 mmol). Yield 35 mg (2%), m.p. 118 °C (decomp.) (Found: C, 68.3; H, 4.6; N, 3.7. C₄₄H₃₆FeN₂P₂S₂ requires C, 68.2; H, 4.7; N, 3.6%); $\nu_{\max}/\text{cm}^{-1}(\text{NH})$ 3058w (hexachlorobutadiene); $\delta_{\text{H}}(200.6 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 3.36 [2 H, dd, *J*(PH), 10.5, 2.5, PCH₂P], 4.85 [5 H, d, *J*(PH) 1.2, C₅H₅], 6.70–7.60 [28 H, m, P(C₆H₅), C₆H₄S], and 17.69 (1 H, br s, NH); $\delta_{\text{C}}(50.3 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 28.5 (m, PCH₂P), 85.3 (s, C₅H₅), 114.4–141.0 [m, C₆H₅, NC(CH)₄CS], 150.5 (s, NC), and 231.3 [d, *J*(PC) 31.4, NCS]; $\delta_{\text{P}}(80.98 \text{ MHz, solvent C}_6\text{D}_6, \text{ external standard 85\% H}_3\text{PO}_4)$ -25.6 [d, *J*(PP) 70.3, PhPCH₂] and 72.7 [d, *J*(PP) 70.3 Hz, FeP]; *m/z* 639 (<1, M - C₆H₄S) and 505 (12%, M - C₆H₄S - C=NC₆H₄S).

[Fe(η⁵-C₅H₅){C₆H₄S-o}{C=NC(Me)=CHS}]{C=NC(Me)=CHS}-(dppm)] **3**. Complex **3** was prepared in the same way as **1** from FeCl₂ (0.34 g, 2.7 mmol), dppm (1.0 g, 2.7 mmol), 1.6 mol dm⁻³ *n*-butyllithium (3.4 cm³, 5.4 mmol), 4-methylthiazole (0.49 cm³, 5.4 mmol) and cyclopentadiene (0.22 cm³, 2.7 mmol). The extract was filtered through Florisil (9 g) and diethyl ether-hexane (1:5–2:1) eluent was used for the column chromatography. Evaporation of the eluent yielded orange, microcrystalline **3**. Yield 74 mg (4%), m.p. 120 °C (decomp.) (Found: C, 65.1; H, 5.25; N, 4.6. C₃₈H₃₆FeN₂P₂S₂ requires C, 65.0; H, 5.2; N, 4.0%); $\nu_{\max}/\text{cm}^{-1}(\text{NH})$ 3105w and 3056w (hexachlorobutadiene); $\delta_{\text{H}}(200.6 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 1.97 [6 H, d, *J*(HH) 0.8, Me], 3.31 [2 H, dd, *J*(PH) 9.2, 2.9, PCH₂P], 4.77 [5 H, d, *J*(PH) 1.2, C₅H₅], 6.36 (2 H, br s, HCS), 6.80–7.30 [20 H, m, P(C₆H₅)], and 17.22 (1 H, br s, NH); $\delta_{\text{C}}(50.3 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 14.6 (s, Me), 29.9 (m, PCH₂P), 83.4 (s, C₅H₅), 115.4 (s, SC), 125.9–141.0 (m, C₆H₅), 146.0 (s, NC), and 223.0 [d, *J*(PC) 31.0, SCN]; $\delta_{\text{P}}(80.98 \text{ MHz, solvent C}_6\text{D}_6, \text{ external standard 85\% H}_3\text{PO}_4)$ -24.6 [d, *J*(PP) 63.2, PhPCH₂] and 75.0 [d, *J*(PP) 63.2 Hz, FeP]; *m/z* 702 (M⁺, <1) and 603 (3%, M - C₆H₄S).

[Fe(η⁵-C₅H₅){C₆H₄S-o}{C=NC(Me)=CHS}]{C=NC(Me)=CHS}-(dppe)] **4** and [Fe(η⁵-C₅H₅){C=NC(Me)=CHS}]{C=NC(Me)=CHS}-(dppe)] **5**. Complexes **4** and **5** were obtained in a similar way as **1** from



FeCl₂ (0.63 g, 5.0 mmol), dppe (2.0 g, 4.9 mmol), 1.6 mol dm⁻³ *n*-butyllithium (6.2 cm³, 9.9 mmol), 4-methylthiazole (0.90 cm³, 9.9 mmol) and cyclopentadiene (4.1 cm³, 50 mmol). The diethyl ether extract was filtered through Florisil (9 g) and diethyl ether-hexane (1:4–3:1) eluent was used for the column chromatography to give an orange solution which was stripped of solvent to afford 636 mg of residue. NMR analysis allowed the yields of **4** and **5** to be determined as 14 and 5% respectively.

Complex **4**: $\nu_{\max}/\text{cm}^{-1}(\text{NH})$ 3059w (hexachlorobutadiene); $\delta_{\text{H}}(200.6 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 1.95 (2 H, m, PhPCH₂), 2.03 [6 H, d, *J*(HH) 0.6, Me], 2.36 (2 H, m, FePCH₂), 4.60 [5 H, d, *J*(PH) 1.4, C₅H₅], 6.32 (2 H, br s, CH), 6.80–7.50 (20 H, m, C₆H₅), and 17.48 (1 H, br s, NH); $\delta_{\text{C}}(50.3 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 14.8 (s, Me), 24.3 (m, PCH₂CH₂P), 83.2 (s, C₅H₅), 115.3 (s, CS), 126.1–139.3 (m, C₆H₅), 145.9 (s, NC), and 222.3 [d, *J*(PC) 31.0, SCN]; $\delta_{\text{P}}(80.98 \text{ MHz, solvent C}_6\text{D}_6, \text{ external standard 85\% H}_3\text{PO}_4)$ -10.8 [d, *J*(PP) 34.8, PhPCH₂] and 77.2 [d, *J*(PP) 34.8 Hz, FeP]; *m/z* 617 [100, M - C₆H₄S] and 520 [11%, M - C₆H₄S - C=NC(Me)=CHS].

Complex **5**: $\delta_{\text{H}}(200.6 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 1.99 [3 H, d, *J*(HH) <1 Hz, Me], 2.20 (4 H, m, PCH₂CH₂P), 4.63 (4 H, s, C₅H₅), 6.28 (1 H, br s, CH), and 6.80–7.50 (20 H, m, C₆H₅); $\delta_{\text{C}}(50.3 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 14.8 (s, Me), 31.9 (m, PCH₂CH₂P), 83.0 (s, C₅H₅), 115.3 (s, SC), 126.1–139.3 (m, C₆H₅), 145.9 (s, NC), and 167.4 (s, SCN); $\delta_{\text{P}}(80.98 \text{ MHz, solvent C}_6\text{D}_6, \text{ external standard 85\% H}_3\text{PO}_4)$ 79.8 (s); *m/z* 617 (M⁺, 100) and 520 [11, M - C=NC(Me)=CHS].

[Fe(η⁵-C₅H₅)(CO)₂(C=NC₆H₄S-o)] **6**. The complex [Fe(η⁵-C₅H₅)(CO)₂Cl] (0.71 g, 3.3 mmol) was dissolved in thf (20 cm³) and treated with benzothiazol-2-yl lithium, prepared from benzothiazole (0.36 cm³, 3.3 mmol) and 1.6 mol dm⁻³ *n*-butyllithium (2.1 cm³, 3.4 mmol), at -78 °C. The mixture was stirred for 1 h at 0 °C and evaporated to dryness. The residue was extracted with diethyl ether (2 × 60 cm³), the extract filtered through alumina (15 g) and evaporated to dryness. The product was purified by chromatography with ether-hexane (1:4) on silica gel preparative plates (Merck) and yielded yellow crystals of complex **6** (0.30 g, 29%), m.p. 68 °C (decomp.) (Found: C, 54.7; H, 2.9; N, 4.5. C₁₄H₉FeNO₂S requires C, 54.0; H, 2.9; N, 4.5%); $\nu_{\max}/\text{cm}^{-1}(\text{CO})$ 2035s, 2029s, 1975s (Nujol); 2036s and 1986s (hexachlorobutadiene); $\delta_{\text{H}}(200.6 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 4.18 (5 H, s, C₅H₅), 7.00 [1 H, dt, *J*(H_cH_b) 7.6, *J*(H_cH_d) 7.6, *J*(H_cH_a) 1.2, H_c], 7.15 [1 H, dt, *J*(H_aH_b) 7.6, *J*(H_cH_b) 7.6, *J*(H_dH_b) 1.22, H_b], 7.65 [1 H, dd, H_cH_d], 7.6, *J*(H_bH_d) 1.2, H_d], and 8.11 [1 H, dd, *J*(H_aH_b) 7.6, *J*(H_cH_a) 1.2 Hz, H_a]; $\delta_{\text{C}}(50.3 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 86.1 (s, C₅H₅), 120.6 (s, H_cC), 122.3 (s, H_bC), 119.8 (s, H_dC), 124.7 (s, H_aC), 140.7 (s, SC), 157.6 (s, NC), 184.5 (s, NCS) and 213.8 (s, CO); *m/z* 311 (M⁺, 30) and 283 (8%, M - CO).

[Fe(η⁵-C₅H₅)(CO)₂(C=NC(Me)=CHS)] **7**. Complex **7** was prepared in the same way as **6** from [Fe(η⁵-C₅H₅)(CO)₂Cl] (0.77 g, 3.6 mmol), 1.6 mol dm⁻³ *n*-butyllithium (2.3 cm³, 3.7 mmol) and 4-methylthiazole (0.33 cm³, 3.6 mmol). Chromatography on preparative plates yielded yellow crystals of **7** (0.44 g, 44%), m.p. 58 °C (decomp.) (Found: C, 48.4; H, 3.3; N, 5.0. C₁₁H₉FeNO₂S requires C, 48.0; H, 3.3; N, 5.1%); $\nu_{\max}/\text{cm}^{-1}(\text{CO})$ 2014s, 1984s, 1953s (Nujol); 2038s and 1983s (hexachlorobutadiene); $\delta_{\text{H}}(200.6 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 2.48 [3 H, d, *J*(HH) 0.8, Me], 4.15 (5 H, s, C₅H₅), and 6.65 [1 H, br s, *J*(HH) 1.2 Hz, SCH]; $\delta_{\text{C}}(50.3 \text{ MHz, solvent C}_6\text{D}_6, \text{ standard SiMe}_4)$ 17.4 (s,

Me), 85.9 (s, C₅H₅), 117.4 (s, SCH), 155.4 (s, NC), 175.1 (s, SCN) and 214.4 (s, CO); *m/z* 275 (*M*⁺, 18) and 247 (31%, *M* - CO).

[Fe(η⁵-C₅H₅)(CO)₂(CNHC₆H₄S-*o*)]CF₃SO₃·0.5H₂O **8**. A mixture of CH₂Cl₂ (20 cm³) and CF₃SO₃H (0.25 cm³, 2.8 mmol) was added slowly at 0 °C to a solution of complex **6** (0.87 g, 2.8 mmol) in CH₂Cl₂ (20 cm³). The reaction mixture was stirred for 1 h and filtered through anhydrous MgSO₄ (12 g). The filtrate was concentrated. The concentrate yielded red crystals of complex **8** (0.29 g, 22%) at -20 °C, m.p. 78 °C (decomp.) (Found: C, 38.35; H, 2.3; N, 3.0. C₁₅H₁₁F₃FeNO_{5.5}S₂ requires C, 38.3; H, 2.4; N, 3.0%); *v*_{max}/cm⁻¹(CO) 2055s, 2015s; (NH) 3134w and 3110w (hexachlorobutadiene); δ_H(200.6 MHz, solvent CD₂Cl₂, standard SiMe₄) 5.34 (5 H, s, C₅H₅), 7.47 (2 H, m, H_b, H_c), 7.79 [1 H, d, *J*(H_cH_d), 7.6 Hz, H_d], 8.06 [1 H, d, *J*(H_aH_b), 7.6 Hz, H_a], and 14.03 (1 H, br s, NH); δ_C(50.3 MHz, solvent CD₂Cl₂, standard SiMe₄) 87.7 (s, C₅H₅), 115.8 (s, H_aC), 121.2 (s, H_cC), 126.1 (s, H_bC), 128.1 (s, H_aC), 135.8 (s, SC), 146.1 (s, NC), 210.1 (s, CO) and 211.9 (s, NCS)]; *m/z* 311 (19, *M* - CF₃SO₃·0.5H₂O) and 282 (9%, *M* - CF₃SO₃·0.5H₂O - CO).

[Fe(η⁵-C₅H₅)(CO)₂{(CNHC(Me)=CHS)}]CF₃SO₃·0.5H₂O **9**. The orange complex **9** was prepared in the same way as **8** with **7** (0.22 g, 0.79 mmol) and CF₃SO₃H (0.10 cm³, 1.1 mmol). The concentrate yielded orange crystals of **9** (0.23 g, 67%), m.p. 127 °C (Found: C, 33.2; H, 2.3; N, 2.2. C₁₂H₁₁F₃FeNO_{5.5}S₂ requires C, 33.2; H, 2.55; N, 2.2%); *v*_{max}/cm⁻¹(CO) 2058s, 2002s, (NH) 3145w and 3111w (hexachlorobutadiene); δ_H(200.6 MHz, solvent CD₂Cl₂, standard SiMe₄) 2.55 [3 H, d, *J*(HH) < 1 Hz, Me], 5.30 (5 H, s, C₅H₅), 7.05 (1 H, br s, SCH), and 13.51 (1 H, s, NH); δ_C(50.31 MHz, solvent CD₂Cl₂, SiMe₄) 13.5 (s, Me), 87.3 (s, C₅H₅), 121.0 (s, SCH), 148.6 (s, NC), 199.5 (s, SCN) and 210.6 (s, CO); *m/z* 275 (79, *M* - CF₃SO₃·0.5H₂O) and 247 (42%, *M* - CF₃SO₃·0.5H₂O - CO).

Crystallography.—**Crystal data for** [Fe(η⁵-C₅H₅)(CNHC₆H₄S-*o*)(C≡NC₆H₄S-*o*)(dppe)] **1**. C₄₅H₃₈FeN₂P₂S₂, *M* = 788.7, triclinic, space group *P* $\bar{1}$, *a* = 10.633(2), *b* = 11.625(2), *c* = 17.702(3) Å, α = 95.92(1), β = 96.57(2), γ = 113.93(2)°, *U* = 1960(1) Å³ (based on the least-squares refinement of the diffractometer angles for 25 centred reflections with 16 ≤ θ ≤ 17°, using Mo-Kα (λ = 0.7107 Å), *Z* = 2, *D*_c = 1.34 g cm⁻³. Brown-red needle, crystal dimensions 0.27 × 0.55 × 0.19 mm, μ(Mo-Kα) 55.4 cm⁻¹, *F*(000) = 820.

Data collection and processing. CAD4 diffractometer, graphite-monochromated Mo-Kα radiation, ω-2θ scan mode with ω = 0.50 + 0.35 tanθ, variable ω scan rate 5.49° s⁻¹, max scan time 60 s per reflection, 11 376 unique reflections (*h* 0-14, *k* -16 to 16, *l* -24 to 24) with 3 ≤ θ ≤ 30° measured. Data corrected for Lorentz polarization and absorption using empirical absorption corrections (maximum, minimum, average correction factors = 1.000, 0.977 and 0.990) yielding 7388 reflections with *I* > 4σ(*I*) used for the analysis and refinement. Decay 0.5% (uncorrected).

Structure analysis and refinement. Direct methods (SHELX 86), followed by conventional Fourier-difference techniques using SHELX 76. Full-matrix least-squares refinement (in two blocks for final cycles) with all non-hydrogen atoms anisotropic, all hydrogen atoms refined in experimental positions with a common isotropic thermal parameter that converged to *U*_{iso} = 0.067(1) Å² using σ(*F*)⁻² weights and refining 586 parameters. Final *R*, *R'* are 0.050, 0.036. See ref. 19 for programs used and general procedures.

Crystal data for [Fe(η⁵-C₅H₅)(CO)₂{(CNHC(Me)=CHS)}]CF₃SO₃·0.5H₂O **9**. C₁₂H₁₁F₃FeNO_{5.5}S₂, *M* = 434.2, monoclinic, space group *C*2/*c* (no. 15), *a* = 14.105(1), *b* =

16.181(1), *c* = 15.128(2) Å, β = 105.44(9)°, *U* = 3330(1) Å³ [based on the least-squares refinement of the diffractometer angles for 25 centred reflections with 18 < θ < 22° using Mo-Kα (λ = 0.7107 Å) radiation], *Z* = 8, *D*_c = 1.73 g cm⁻³. Orange crystals with irregular shape, approximate dimensions 0.25 × 0.27 × 0.33 mm, μ(Mo-Kα) 11.3 cm⁻¹, *F*(000) = 1752.

Data collection and processing. CAD4 diffractometer, graphite-monochromated Mo-Kα radiation, ω-2θ scan mode with ω = 0.49 + 0.35 tanθ, variable ω-scan rate 5.49° s⁻¹, maximum scan time 60 s per reflection, 6114 unique reflections (*h* 0-21, *k* 0-24, *l* -22 to 22) with 3 ≤ θ ≤ 30° measured. Data corrected for Lorentz and polarisation, yielding 3754 reflections with *I* > 3σ(*I*) used for the analysis and refinement. Decay 2.2% (uncorrected).

Structure analysis and refinement. Direct methods (SHELX 86) followed by conventional Fourier difference techniques using SHELX 76. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic except the oxygen atom of the water of crystallization, which was refined isotropically in the special position 0, *y*, ½, with a site occupancy of 50%. The hydrogen atoms were all located and refined in experimental positions with a common isotropic thermal parameter that converged to *U*_{iso} = 0.100(4) Å². A weighting scheme [weights σ⁻²(*F*)] was used and 253 parameters were refined. Final *R*, *R'* are 0.048, 0.032. See ref. 19 for programs used and general procedures.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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