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Preparation and characterization of carbene complexes of iron from azolyl and thienyl precursors

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Azolyl and thienyl iron(II) complexes have been synthesized by the addition of 1-phenylpyrazol-5-yllithium, 5-(4,5-dihydro-4,4-dimethyloxazolin-2-yl)-2-thienyllithium, 2-(4,5-dihydro-4,4-dimethyloxazolin-2-yl)-3-thienyllithium or 5-(2-pyridyl)-2-thienyllithium to $[Fe(cp)(CO)_2Cl]$ (cp = η-C_5H_5). Protonation or alkylation of these precursor complexes yielded the corresponding amino(organo)-, organo(thio)- or heterometallacyclic alkoxy(amino)- and hydroxy(amino)-carbene complexes as well as compounds in which the ligand shows more pyridinium character. The molecular structures of the pyrazolyl complex $[Fe(cp)(CO)_2(\overline{C{=}CHCH{=}N\text{N}}Ph)]$ and the pyrazolinylidene complex $[Fe(cp)(CO)_2(\overline{CCH{=}CHNH\text{N}}Ph)][CF_3SO_3]$ have iron–carbon bond lengths of 1.981(2) and 1.969(5) Å respectively.

In previous papers we have described the synthesis of carbene complexes of iron by the addition of thiazolyl- or isothiazolyllithium to $[Fe(cp)(CO)_2Cl]$ (cp = η-cyclopentadienyl) and subsequent alkylation or protonation of the products formed.[1,2] The isothiazolinylidene complexes are unique in that they have been prepared from a precursor in which the nucleophilic heteroatom is situated γ to the co-ordinated carbon atom and not α as in the thiazolinylidene compounds and most other typical Fischer-type carbene complexes.[1,3,4] In this paper we describe the synthesis of a series of compounds *via* an analogous method but using different ligands. Utilizing this procedure we have been able to synthesize carbene complexes in which the nucleophilic heteroatom in the precursor complex is located outside the co-ordinated ring system and separated from the co-ordinated carbon by several bonds. The compounds 1-phenylpyrazole, 4,5-dihydro-4,4-dimethyl-2-(2-thienyl)oxazole or 2-(2-thienyl)pyridine were lithiated and treated with the compound $[Fe(cp)(CO)_2Cl]$ to form precursor iron compounds which were then alkylated or protonated with CF_3SO_3Me or CF_3SO_3H to form amino(organo)-, organo(thio)-, alkoxy(amino)- or hydroxy(amino)-carbene complexes as well as compounds which can be described as pyridinium iron complexes.

In the pyrazolyl complex the active nucleophilic nitrogen atom is situated γ to the metal-bonded carbon as is the case in the isothiazolyl complexes. The crystal and molecular structures of the neutral precursor 1-phenylpyrazolyl complex and the cationic pyrazolinylidene complex were determined by X-ray single-crystal diffraction methods and by comparing the bond lengths of the two compounds we could ascertain whether protonation and thus carbene formation had any effect on the ligand.

The bifunctional 4,5-dihydro-4,4-dimethyl-2-(2-thienyl)oxazole can be lithiated in either the 3 or 5 position of the thienyl ring.[5] Lithiation in the 5 position, at −80 °C with lithium diisopropylamide, transmetallation and subsequent protonation afforded an organo(thio)carbene complex whereas lithiation in the 3 position of the thienyl ring, at 0 °C in diethyl ether, gave an unexpected chelate aminoacyl product which after alkylation or protonation afforded metallacyclic carbene complexes. A ^1H NMR study of the protonated carbene complex suggested the presence of two conformational isomers. The reaction of the cyclic alkoxy(amino)carbene complex with diethylamine reformed the precursor chelate complex. Transmetallation of the 2-(oxazolin-2-yl)-3-thienyllithium compound with $[Fe(cp)(CO)(PPh_3)Br]$ afforded a nitrogen-co-ordinated heterometallacycle.

Reactions with 2-(2-pyridyl)-5-thienyllithium afforded, after protonation or alkylation, complexes which should be formulated as pyridinium salts rather than carbene complexes.

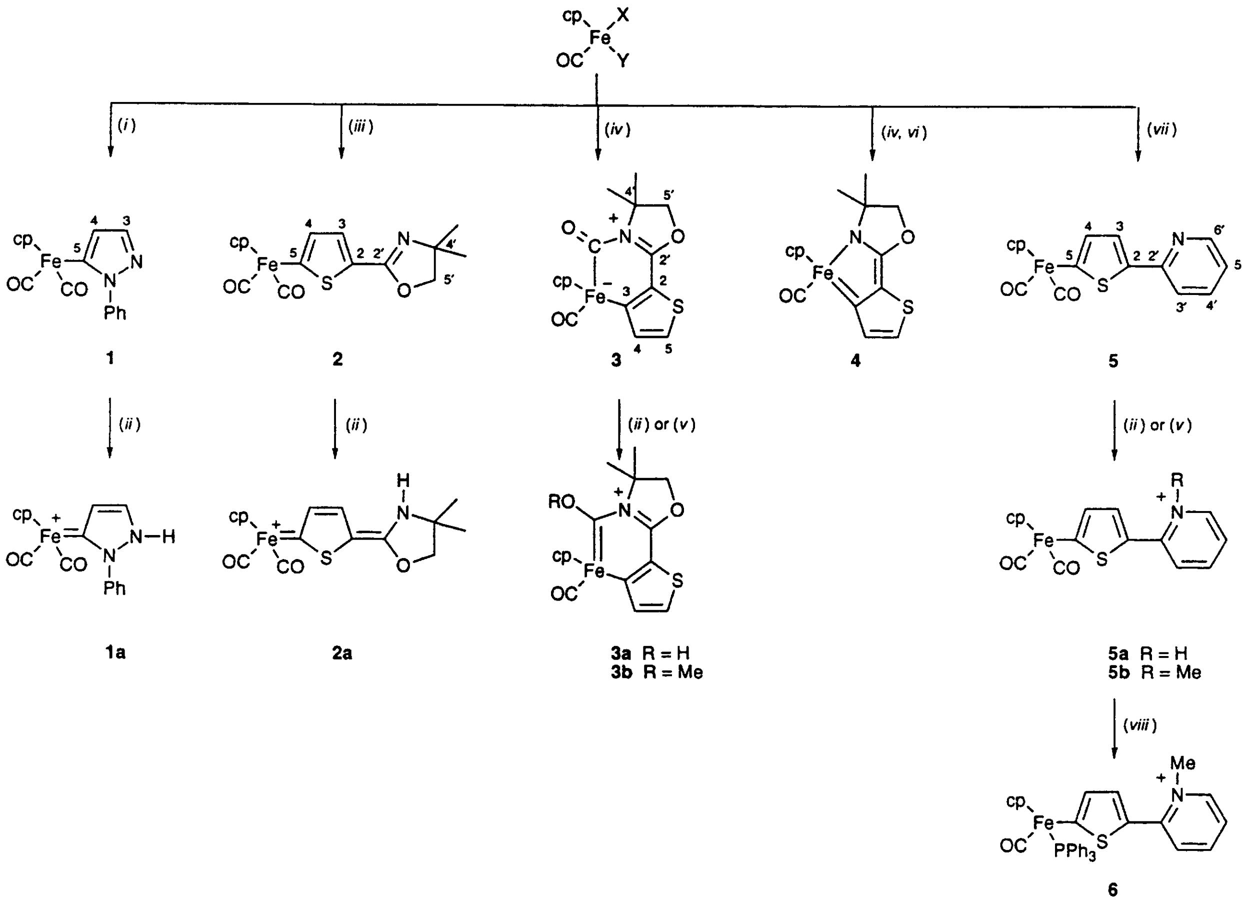
Results and Discussion

Analytical and physical, as well as spectroscopic, data for all the new compounds described are collected in Tables 1–3 and are discussed where relevant. To simplify the drawings in the schemes the counter ion $CF_3SO_3^-$ is not included when cationic complexes are formed. In Scheme 1 the resonance forms depicted do not necessarily represent the true structure of the compounds. The reason for the resonance forms chosen, however, will become evident later in the text. The spectroscopic data are discussed with respect to the numbering scheme in Scheme 1.

Preparation of 1-phenylpyrazolyl and 1-phenylpyrazolinylidene iron complexes

The reaction of $[Fe(cp)(CO)_2Cl]$ with 1 equivalent of 1-phenylpyrazol-5-yllithium in thf (tetrahydrofuran) at −80 °C gave the neutral complex $[Fe(cp)(CO)_2(\overline{C{=}CHCH{=}N\text{N}}Ph)]$ **1** in 85% yield (Scheme 1). Complex **1** was purified by column chromatography and crystallized from diethyl ether–hexane to give large cubic orange crystals. The pyrazolyl complex **1** readily reacts with 1 equivalent of CF_3SO_3H in CH_2Cl_2 at −40 °C to give the cationic amino(organo)carbene complex $[Fe(cp)(CO)_2(\overline{CCH{=}CHNH\text{N}}Ph)][CF_3SO_3]$ **1a** (Scheme 1). Crystallization from CH_2Cl_2–diethyl ether afforded orange crystals of **1a**. The crystals from both the precursor pyrazolyl complex and the carbene complex were suitable for X-ray crystallographic investigations and we were able to compare the two structures.

Complex **1** is soluble in diethyl ether, hexane and pentane while **1a** is soluble in CH_2Cl_2 and thf. Both may be handled in air as solids. The ^{13}C-$\{^1H\}$ NMR data (Table 3) for the pyrazolinylidene complex **1a** show that the carbene carbon resonates at δ 164.7 and that it is shifted downfield with respect to the co-ordinated carbon of the neutral pyrazolyl complex **1**, which resonates at δ 145.6 ($\Delta\delta$ = 19.1 ppm). This downfield shift is similar to that found for the analogous thiazolyl/thiazolinylidene[1] and isothiazolyl/isothiazolylinylidene[2] complexes,



Scheme 1 X = Br or Cl; Y = CO or PPh$_3$. (*i*) Li(C=CHCH=NNPh); (*ii*) CF$_3$SO$_3$H; (*iii*) Li[C=CHCH=C(C=NCMe$_2$CH$_2$O)S]; (*iv*) Li[C=C(C=NCMe$_2$CH$_2$O)SCH=CH]; (*v*) CF$_3$SO$_3$Me; (*vi*) −PPh$_3$; (*vii*) Li[C=CHCH=C(C=NCH=CHCH=CH)S]; (*viii*) PPh$_3$, *h*ν

Table 1 Analytical, physical and infrared spectroscopic data for the new complexes

Complex	M.p./°C	Yield (%)	Analysis[a] (%) C	H	N	ṽ(CO)[b]/cm^{-1}
1 [Fe(cp)(CO)$_2$(C=CHCH=NNPh)]	153–154	85.6	59.9 (60.05)	3.8 (3.8)	8.9 (8.75)	2031, 1979[c]
1a [Fe(cp)(CO)$_2$(CCH=CHNHNPh)][CF$_3$SO$_3$]	110–111	53.0	43.4 (43.45)	2.6 (2.8)	6.1 (5.95)	2048, 1989[c]
2 [Fe(cp)(CO)$_2${C=CHCH=C(C=NCMe$_2$CH$_2$O)S}]	143–144	75.8	54.0 (53.8)	4.2 (4.25)	3.8 (3.9)	2014, 1956
2a [Fe(cp)(CO)$_2${CCH=CHC(=CNHCMe$_2$CH$_2$O)S}][CF$_3$SO$_3$]	> 126 (decomp.)	74.8	40.1 (40.25)	3.2 (3.2)	2.7 (2.75)	2041, 1991
3 [Fe(cp)(CO){C=C[CN(C=O)CMe$_2$CH$_2$O]SCH=CH}]	159	50.8	54.0 (53.8)	4.2 (4.25)	3.7 (3.9)	1915
3a [Fe(cp)(CO){C=C[CN(COH)CMe$_2$CH$_2$O]SCH=CH}][CF$_3$SO$_3$]	> 64	53.1	40.1 (40.25)	3.2 (3.2)	2.6 (2.75)	1976
3b [Fe(cp)(CO){C=C[CN(COMe)CMe$_2$CH$_2$O]SCH=CH}][CF$_3$SO$_3$]	> 154 (decomp.)	56.2	41.3 (41.45)	3.4 (3.5)	2.7 (2.7)	1980
4 [Fe(cp)(CO){CC(=CNCMe$_2$CH$_2$O)SCH=CH}]	133–134	45.6	54.6 (54.75)	4.6 (4.6)	4.3 (4.25)	1912
5 [Fe(cp)(CO)$_2${C=CHCH=C(C=NCH=CHCH=CH)S}]	116–117	69.8	56.8 (57.0)	3.3 (3.3)	4.0 (4.15)	2044, 1960
5a [Fe(cp)(CO)$_2${C=CHCH=C(C=NHCH=CHCH=CH)S}][CF$_3$SO$_3$]	> 90 (decomp.)	35.7	41.7 (41.9)	2.3 (2.5)	2.9 (2.85)	2026, 1968
5b [Fe(cp)(CO)$_2${C=CHCH=C(C=NMeCH=CHCH=CH)S}][CF$_3$SO$_3$]	105–106	67.3	43.0 (43.15)	2.6 (2.8)	2.8 (2.8)	2022, 1983
6 [Fe(cp)(CO)(PPh$_3$){C=CHCH=C(C=NMeCH=CHCH=CH)S}][CF$_3$SO$_3$]	162–163	59.8	57.0 (57.15)	4.0 (3.95)	1.8 (1.9)	1952

[a] Required values given in parentheses. [b] Recorded as KBr discs unless stated otherwise. [c] In hexachlorobutadiene.

where comparable shifts of 25.1 and 24.4 ppm are found, respectively. The carbene carbon in the pyrazolinylidene complex appears upfield from the carbene carbons found in most other azolinylidene compounds, but this can be ascribed to the relatively small chemical shift of the C^5 carbon atom in both free 1-phenylpyrazole and the pyrazolyl complex **1**. There is little change in the chemical shifts of the remaining carbons in the precursor complex **1** and **1a**. The ν(CO) infrared absorption

Table 2 Proton NMR data [δ, J(HH)/Hz] in CH_2Cl_2

Complex	H^3	H^4	H^5	$H^{5'}$	CMe_2	cp	Other
1	7.60 (1 H, br s)	6.25 (1 H, br s)	—	—	—	4.73 (5 H, s)	7.43 (5 H, m, Ph)
1a	7.87 (1 H, d, 2.48)	6.65 (1 H, d, 2.06)	—	—	—	4.89 (5 H, s)	14.14 (1 H, br s, NH), 7.65 (3 H, m, Ph), 7.44 (2 H, m, Ph)
2	7.39 (1 H, d, 3.46)	6.81 (1 H, d, 3.50)	—	4.00 (2 H, s)	1.29 (6 H, s)	5.01 (5 H, s)	—
2a	8.12 (1 H, d, 4.08)	7.16 (1 H, d, 4.00)	—	4.58 (2 H, s)	1.58 (6 H, s)	5.06 (5 H, s)	11.30 (1 H, br s, NH)
3	—	7.11 (1 H, d, 5.08)	7.42 (1 H, d, 5.06)	4.25 (1 H, d, 8.48) 4.20 (1 H, d, 8.44)	1.33 (3 H, s) 1.26 (3 H, s)	4.48 (5 H, s)	—
3a	—	7.49 (1 H, d, 4.82)	7.73 (1 H, d, 5.12)	4.46 (1 H, d, 9.12) 4.31 (1 H, d, 8.60)	1.56 (3 H, s) 1.19 (3 H, s)	4.88 (5 H, s)	—
3b	—	7.45 (1 H, d, 5.14)	7.78 (1 H, d, 5.12)	4.53 (1 H, d, 8.60) 4.42 (1 H, d, 8.78)	1.53 (3 H, s) 1.05 (3 H, s)	4.92 (5 H, s)	4.82 (3 H, s, OMe)
4	—	7.34 (1 H, d, 4.48)	7.61 (1 H, d, 4.62)	4.35 (1 H, d, 8.34) 4.32 (1 H, d, 8.38)	1.28 (3 H, s) 1.27 (3 H, s)	4.62 (5 H, s)	—

	H^3	H^4	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$	cp	Other
5	7.50 (2 H, m)	6.86 (1 H, d, 3.50)	7.50 (2 H, m)	7.61 (1 H, td, 1.74, 7.32)	7.01 (1 H, ddd, 1.28, 5.00, 7.18)	8.45 (1 H, d, 4.44)	5.03 (5 H, s)	—
5a	8.00 (1 H, d, 3.86)	7.11 (1 H, d, 3.72)	7.83 (1 H, d, 8.36)	8.20 (1 H, t, 7.71)	7.42 (1 H, t, 6.47)	8.48 (1 H, d, 5.48)	5.00 (5 H, s)	13.99 (1 H, br s, NH)
5b	7.60 (1 H, d, 3.66)	7.13 (1 H, d, 3.66)	7.97 (1 H, d, 8.06)	8.25 (1 H, t, 7.78)	6.98 (1 H, t, 6.98)	8.73 (1 H, d, 6.40)	5.10 (5 H, s)	4.42 (1 H, s, NMe)
6	7.36 (17 H, m)	7.00 (1 H, d, 2.68)	7.79 (1 H, d, 8.19)	8.08 (1 H, t, 7.56)	7.36 (17 H, m)	8.56 (1 H, d, 5.62)	4.67 (5 H, s)	7.36 (17 H, m, Ph), 4.20 (3 H, s, NMe)

Table 3 Carbon-13 NMR data[a]

Compound	C^2	C^3	C^4	C^5	$C^{2'}$	$C^{4'}$	$C^{5'}$	CMe_2	C^{10}	cp	CO	Other
1	—	140.7	120.9	145.6	—	—	—	—	—	86.2	215.1	138.8, 128.9, 128.4 and 127.9 (Ph)
1a	—	132.7	123.3	164.7	—	—	—	—	—	86.5	212.5	138.1, 131.7, 130.3 and 128.5 (Ph)
2	136.1	131.4	139.3	148.1	157.5	67.7	79.2	28.5	—	86.4	214.7	—
2a	124.3	142.9	139.3	177.4	162.5	63.1	83.2	26.5	—	86.8	213.3	—
3	130.8	149.7	130.5	121.4	164.4	72.0	80.6	27.8 27.2	271.6	83.9	220.7	—
3a[b]	139.4	150.0	133.8	119.3	165.2	73.3	80.8	27.2 25.8	—	86.3	215.2	—
3b	137.7	151.7	133.2	119.6	164.8	72.3	80.7	27.1 27.7	331.2	86.2	214.9	69.0 (OMe)
4	122.7	192.4	139.6	129.9	168.7	66.0	83.4	28.5 25.8	—	80.6	220.4	—

	C^2	C^3	C^4	C^5	$C^{2'}$	$C^{3'}$	$C^{4'}$	$C^{5'}$	$C^{6'}$	cp	CO	Other
5	144.1	127.4	140.4	151.0	154.0	118.1	137.2	121.1	150.0	87.3	216.1	—
5a[b]	138.0	132.9	141.2	163.4	146.5	124.0	143.0	122.9	147.1	87.7	215.1	—
5b	136.2	135.4	141.4	161.1	149.8	128.9	144.1	123.9	146.2	86.6	213.9	48.1 (NMe)
6	135.4	134.5	142.7	183.6 (26.7)[c]	149.3	128.0	143.0	122.5	145.9	85.5	220.4 (29.8)[c]	133.6 (9.6),[c] 130.7 (2.3)[c] and 128.7 (9.9)[c] (Ph), 48.5 (NMe)

[a] Measured in CH_2Cl_2 unless otherwise stated. [b] Measured in $(CD_3)_2CO$. [c] J(PC) in Hz.

Table 4 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Fe–C(1)	1.771(2)	Fe–C(2)	1.762(2)
Fe–C(3)	2.110(2)	Fe–C(4)	2.084(2)
Fe–C(5)	2.090(2)	Fe–C(6)	2.100(2)
Fe–C(7)	2.108(3)	Fe–C(8)	1.981(2)
N(1)–N(2)	1.377(2)	N(1)–C(8)	1.372(3)
N(1)–C(11)	1.428(3)	N(2)–C(10)	1.323(3)
C(8)–C(9)	1.381(3)	C(9)–C(10)	1.394(3)
C(1)–Fe–C(2)	92.2(1)	C(1)–Fe–C(8)	96.10(9)
C(2)–Fe–C(8)	87.5(1)	Fe–C(8)–N(1)	130.1(1)
Fe–C(8)–C(9)	126.1(2)	N(1)–C(8)–C(9)	103.7(2)

bands of the cationic complex **1a** (2048 and 1989 cm^{-1}), however, appear at higher energy than those observed for the neutral complex **1** (2031 and 1979 cm^{-1}). A similar effect was observed for the analogous thiazolyl/thiazolinylidene[1] and isothiazolyl/isothiazolinylidene[2] complexes. The downfield shift of the co-ordinated carbon in the $^{13}C-\{^1H\}$ NMR spectrum and the higher-energy absorption of the ν(CO) bands in the IR spectrum upon going from the precursor complex to the protonated counterpart indicate that carbene formation has taken place. However the cation formation could also be held responsible for the decreasing metal to CO back donation.

Structures of [Fe(cp)(CO)$_2$(C=CHCH=NNPh)] 1 and [Fe(cp)(CO)$_2$(CCH=CHNHNPh)][CF$_3$SO$_3$] 1a

The molecular structures of complexes **1** and **1a** are shown in Figs. 1 and 2 respectively. Selected bond lengths and angles are given in Tables 4 and 5.

The iron atom in both molecules is pseudo-octahedrally surrounded by a cyclopentadienyl group, two carbonyl ligands and a pyrazole ligand in **1** or a pyrazolinylidene ligand in **1a**. The essentially similar and normal Fe–C (cyclopentadienyl) distances have an average length of 2.098(2) Å in **1** and 2.094(6) Å in **1a**. The average Fe–CO bond lengths are similar in **1** and **1a**

Table 5 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **1a**

Fe–C(1)	1.767(5)	Fe–C(2)	1.779(7)
Fe–C(3)	2.089(6)	Fe–C(4)	2.104(7)
Fe–C(5)	2.091(6)	Fe–C(6)	2.095(6)
Fe–C(7)	2.090(6)	Fe–C(8)	1.969(5)
N(1)–N(2)	1.379(5)	N(1)–C(8)	1.371(6)
N(1)–C(11)	1.421(6)	N(2)–C(10)	1.298(7)
N(2)–H(11)	0.979(4)	C(8)–C(9)	1.365(6)
C(9)–C(10)	1.390(8)		
C(2)–Fe–C(8)	88.9(2)	Fe–C(8)–N(1)	127.8(3)
Fe–C(8)–C(9)	127.4(4)	N(1)–C(8)–C(9)	104.8(4)
C(1)–Fe–C(2)	91.5(3)		

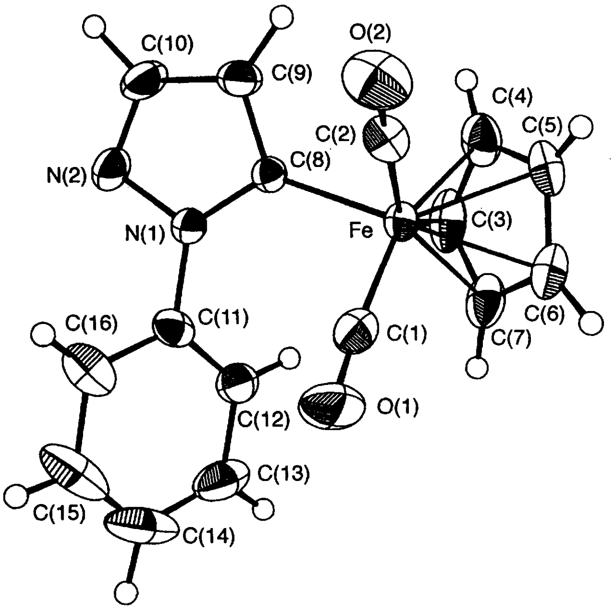


Fig. 1 View of the molecular structure of $[Fe(cp)(CO)_2(C{=}CHCH{=}NNPh)]$ **1**, with the atomic numbering scheme. The ellipsoids enclose 50% probability

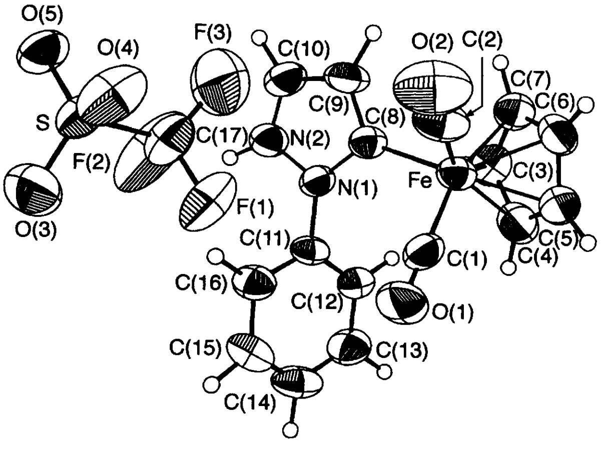


Fig. 2 View of the molecular structure of $[Fe(cp)(CO)_2\{CCH{=}CHNHNPh\}][CF_3SO_3]$ **1a**. Details as in Fig. 1

and are also consistent with values obtained previously for other compounds containing $Fe(cp)(CO)_2$ units.[6]

The aim of the X-ray study of compounds **1** and **1a** was to ascertain whether any significant change in the bond lengths could be observed upon carbene ligand formation. A slight change was found in the Fe–C(8) bond length, showing a difference of 0.012 Å. This bond is only slightly shorter in **1a** [1.969(5) Å] than in **1** [1.981(2) Å]. The Fe–C (carbene) bond length of complex **1a** is only slightly longer than the 1.952(3) Å observed in $[Fe(cp)(CO)_2(CCH{=}CHNMeS)][CF_3SO_3]$[2] and the 1.947(3) Å for $[Fe(cp)(CO)_2\{CN(H)CCMe{=}CHS\}][CF_3SO_3]$.[1] An investigation, using information from the Cambridge Structural Database, revealed that typical σ Fe–C(sp^2) bond distances fall within the range 1.97–2.00 Å with an average of 1.98 Å, while Fe–C (carbene) bond lengths of known carbene complexes are most typically in the range 1.72–2.00 Å with an average of 1.86 Å.[7–9]

Other bond-length deviations between the pyrazolyl/pyrazolinylidene ligands of the two compounds are relatively small with a maximum difference of 0.025 Å observed for the C(10)–N(2) bond distance.

In both compounds the C (co-ordinated carbon)–N(1) bond length is longer than N(2)–C(10) ($\Delta = 0.049$ in **1** and 0.073 Å in **1a**). There is less π bonding from nitrogen to carbon than one would expect. This is in contrast to the thiazolinylidene complex $[Fe(cp)(CO)_2\{CN(H)C(Me){=}CHS\}][CF_3SO_3]$[1] in which the C (carbene)–N bond length of 1.328(3) Å is significantly shorter than the corresponding N–C(sp^2) bond distance of 1.395 Å.

In conclusion there are no large differences between the two compounds and none is large enough to draw any conclusions from.

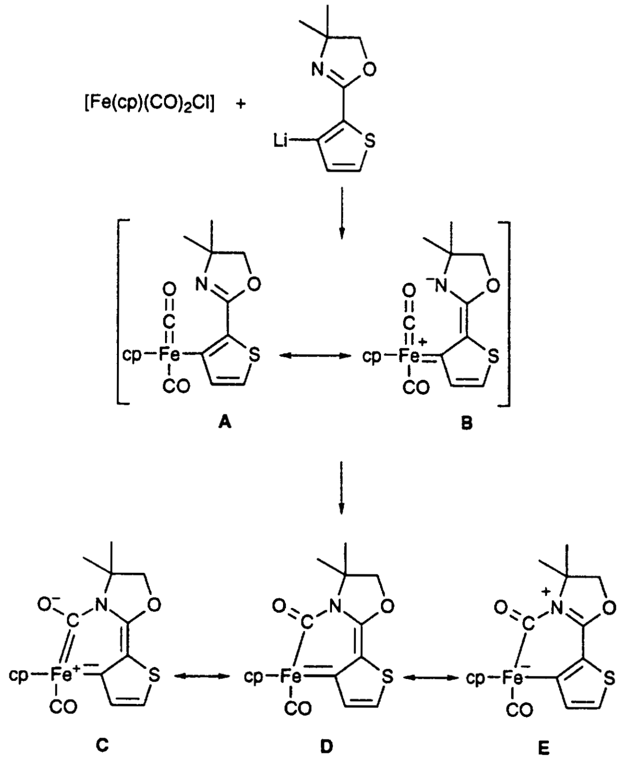
Preparation of a 5-thienyl and an organo(thio)carbene complex of iron

The neutral thienyl complex **2** (Scheme 1) was prepared by treating $[Fe(cp)(CO)_2Cl]$ with 5-(4,5-dihydro-4,4-dimethyloxazolin-2-yl)-2-thienyllithium in thf at −78 °C. The solvent was removed under vacuum and the residue extracted with diethyl ether before filtration through Florisil. Crystallization from diethyl ether–hexane afforded orange crystals. The neutral thienyl complex **2** was readily protonated with CF_3SO_3H in CH_2Cl_2 at −20 °C to form the cationic organo(thio)carbene complex **2a** (Scheme 1). After filtration through anhydrous $MgSO_4$, the solution was concentrated and pentane slowly added. Upon standing at −25 °C orange, needle-like crystals were obtained. This represents the first carbene complex prepared from a precursor in which the nucleophilic heteroatom (N in this case) is located outside the co-ordinated ring system and is separated from the co-ordinated carbon by several bonds.

The $^{13}C\text{-}\{^1H\}$ NMR data (Table 3) show that the carbene carbon (δ 177.4) of complex **2a** resonates at a much lower field than that of the precursor **2** (δ 148.1). This constitutes a downfield shift of 29.3 ppm which is even larger than the corresponding shifts observed for the thiazolinylidene complex (25.1 ppm),[1] isothiazolinylidene[2] complex (24.4 ppm) and pyrazolinylidene complex **1a** (19.1 ppm). It could lead one to conclude that true carbene formation, not only protonation of the nitrogen atom, occurred. Furthermore, the IR spectrum (Table 1) shows that the ν(CO) absorption bands of complex **2a** occur at 27 and 35 cm^{-1} higher than for the neutral complex **2** from which it was prepared. This could be ascribed to both an increase in positive charge and to metal–ligand back donation to the formed carbene carbon atom.

Preparation of a 3-thienyl chelate, cyclic carbene complexes and a nitrogen co-ordinated metallacycle of iron

The reaction of 2-(4,5-dihydro-4,4-dimethyloxazolin-2-yl)-3-thienyllithium with $[Fe(cp)(CO)_2Cl]$ at −65 °C in diethyl ether afforded, after purification by column chromatography and crystallization, the unexpected heterometallacyclic complex **3** (Scheme 1). It is clear from the product formed that the nucleophilic nitrogen atom attacked one of the carbonyl ligands intramolecularly to form a chelate complex. Evidence for this



Scheme 2

intramolecular reaction is found in the presence of a single metal carbonyl absorption band in the IR spectrum at 1915 cm^{-1} and by the additional absorption at 1558 cm^{-1} assigned to the acyl function. Futhermore, the mass spectrum as well as the elemental analysis confirmed that two CO entities are present. The observation of two resonances for the CMe_2 group and a typical AB pattern for the OCH_2 group of the oxazoline ring in the ^1H NMR spectra indicated that the oxazoline ring is no longer able to rotate as would be the case in the absence of heterometallacyclic ring formation.

There are only a few literature examples of intramolecular attack on a carbonyl ligand and also examples where this leads to the formation of a complex in which a metal–carbene bond is part of the ring.[10,11] However, to our knowledge, these complexes are anionic with an active negative charge on the C, N or O atom which attacks the carbonyl group in contrast to complex **3** which is neutral. We conclude that resonance structure **B** (Scheme 2), in which the co-ordinated carbon has carbene character, should be involved alongside A, to explain the chelation reaction. There is, however, no evidence, as discussed below, that the carbene character of the co-ordinated carbon persists in the final complex and its structure, therefore, is probably best represented by **E** in Scheme 2.

The ^{13}C NMR resonance (Table 3) of the co-ordinated carbon of the thienyl ring appears at δ 149.7 and is shifted 19.6 ppm downfield with respect to C^3 of the free ligand. In comparison, the co-ordinated carbon of the thiazolinylidene[1] complex published previously shifts downfield by 46.1 ppm relative to the sp^2 C^2 carbon in the free thiazole. Similar comparisons show that for isothiazolinylidene[2] this difference is 40.2 ppm, for pyrazolinylidene it is 37.7 ppm and for complex **2a** discussed above the difference is 48.0 ppm. The shift of 19.6 ppm exhibited by complex **3**, therefore, is not large and it thus appears that the co-ordinated carbon has less carbene character than in the other complexes mentioned above and one should be hesitant to call **3** a carbene complex. The FeC(O) carbon resonates at δ 271.6 which is comparable to those of other iron acyl compounds *e.g.* δ 277.2 for $[Fe\{C(O)Me\}(CO)_4]^-$[12] and δ 254.4 for $[Fe(cp)(CO)_2\{C(O)Me\}]$.[13]

Acidification or alkylation of complex **3** with CF_3SO_3H or CF_3SO_3Me produced the cationic cyclic carbene complexes **3a** and **3b** (Scheme 1), which were purified by crystallization. These complexes also only exhibit a single ν(CO) absorption band in their IR spectra and two resonances for the CMe_2 group as well as an AB pattern for the OCH_2 groups for the oxazoline ring in their ^1H NMR spectra (Table 2). The appearance of an OMe peak at δ 4.82 in the ^1H NMR spectrum and at δ 69.0 in the ^{13}C-$\{^1H\}$ NMR spectrum of complex **3b** indicates that alkylation of the oxygen atom has occurred.

The C^3 co-ordinated carbon signal for the alkoxy(amino)-carbene complex **3b** appears at δ 151.7 which is similar to the δ 149.7 for **3**, indicating that alkylation has had very little effect on this carbon. In contrast, the C^{10} carbene carbon resonance appears at δ 331.2 and manifests a large downfield shift of 59.6 ppm relative to complex **3**. This value also accentuates the large difference in chemical shifts between typical Fischer-type carbene carbons[14] and those derived from azole rings.[1,2] The ^{13}C-$\{^1H\}$ NMR spectrum of complex **3a** was poorly resolved and as a result the signals are broad and the carbene carbon resonance as well as the C^3 resonance could not unequivocally be assigned.

The ^1H NMR spectrum of compound **3** (Table 2) shows a clearly defined AB system for the OCH_2 protons of the oxazoline ring and the H^5 proton of the thienyl ring gives a clearly defined doublet. In the ^1H NMR spectrum of compound **3b**, however, the peak of one of the OCH_2 protons is broad whereas that for the other proton is sharp. Furthermore, when the ^1H NMR spectrum is run in $(CD_3)_2CO$ even further broadening of this peak occurs and the H^5 proton resonance of the thienyl ring broadens as well (one can no longer distinguish it as a doublet). A possible explanation for this phenomenon is the existence of two conformers of compound **3b** that exchange at a rate comparable to the NMR excitation time-scale.

The reaction of complex **3b** with hydrous $NHEt_2$ led to the reformation of **3**, and not the expected aminocarbene complex. The mechanism probably involves a simple hydrolysis reaction on a Michael-type substrate.

The reaction of $[Fe(cp)(CO)(PPh_3)Br]$ with 1 equivalent of 2-(4,5-dihydro-4,4-dimethyloxazolin-2-yl)-3-thienyllithium in diethyl ether at −78 °C gave the neutral nitrogen co-ordinated metal chelate complex $[Fe(cp)(CO)\{CC(=COCH_2CMe_2N)SCH{=}CH\}]$ **4** (Scheme 1) and involved loss of the PPh_3 ligand. Complex **4** was purified by column chromatography and crystallized from diethyl ether–hexane to give large red crystals. A similar reaction using $[Fe(cp)(CO)(CNC_6H_{11})Cl]$ gave the same compound. The ^{13}C resonance of the co-ordinated carbon of the thienyl ring of compound **4** appears at δ 192.4 and is shifted 62.3 ppm downfield with respect to C^3 of the free azole. This is a large shift and it thus appears that the co-ordinated carbon in **4** exhibits carbene character. A single ν(CO) absorption band is present at 1912 cm^{-1}.

Preparation of pyridyl-5-thienyl and thienylpyridinium complexes of iron

The reaction of 1 molar equivalent of 5-(2′-pyridyl)-2-thienyllithium with $[Fe(cp)(CO)_2Cl]$ at −55 °C afforded the neutral thienyl iron complex **5** (Scheme 1). The solvent was removed under vacuum and the residue extracted with diethyl ether before filtration through Florisil. Crystallization from diethyl ether–hexane afforded orange-brown crystals. Protonation or alkylation of **5**, at −20 °C with CF_3SO_3H or CF_3SO_3Me, produced yellow solids of the cationic complexes **5a** and **5b**, respectively. These were purified by crystallization from CH_2Cl_2–hexane mixtures. The neutral complex **5** is soluble in diethyl ether while the cationic complexes **5a** and **5b** are soluble in CH_2Cl_2 and thf.

The ^{13}C-{^{1}H} NMR data for the cationic thienyl compounds **5a** and **5b** show that the resonances of the co-ordinated carbons appear at δ 163.4 and 161.1 respectively and that they are shifted downfield with respect to the C^5 resonance for **5** at δ 151.0. This downfield shift, however, is much smaller than that observed upon formation of the carbene complex **2a**. Furthermore, one of the ν(CO) absorption bands of complexes **5a** and **5b** appears at lower energy than that observed for **5** whereas the other appears at higher energy. This is not indicative of carbene formation. Both the ^{13}C-{^{1}H} NMR and the IR spectra suggest that protonation or alkylation on the nitrogen atom occurred to form more typical pyridinium salts rather than true carbene complexes.

Photolysis of the iron thienyl compound **5b** in the presence of triphenylphosphine generated red crystals of complex **6** (Scheme 1). This experiment was undertaken unambiguously to assign the C^5 and C$^{2'}$ carbons of complex **5b**, since the signal of the co-ordinated carbon splits into a doublet for **6**. The co-ordinated carbon shifted downfield from δ 161.1 for **5b** to δ 183.6 for **6** with a coupling constant of 26.7 Hz, while the C$^{2'}$ carbon appeared at δ 149.3 for **6** compared to δ 149.8 for **5b**.

Experimental

Materials

The iron compounds [Fe(cp)(CO)$_2$Cl][15] and [Fe(cp)(CO)(PPh$_3$)Br][16] well as 2-(2-thienyl)pyridine[17] and 4,5-dihydro-4,4-dimethyl-2-(2-thienyl)oxazole[5] were prepared according to literature methods. 1-Phenylpyrazole, CF$_3$SO$_3$Me and CF$_3$SO$_3$H were obtained from Aldrich and *n*-butyllithium from Merck. Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium diphenylketyl and CH$_2$Cl$_2$, hexane and pentane from CaH$_2$.

Physical methods

All reactions involving organometallic reagents were performed under an atmosphere of nitrogen using standard vacuum-line and Schlenk techniques. Chromatographic purifications were performed under nitrogen using silica gel or Florisil as the stationary phase in double-layered columns at temperatures lower than −10 °C. Melting points were determined on a standardized Buchi 535 apparatus. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument at *ca.* 70 eV (1.12 × 10^{-17} J) and NMR spectra on a Varian 200 FT spectrometer. Elemental analyses were carried out by the Division of Energy Technology, Council for Scientific and Industrial Research, Pretoria, South Africa.

Preparations

[Fe(cp)(CO)$_2$(C=CHCH=NNPh)] 1. The complex [Fe(cp)(CO)$_2$Cl] (0.70 g, 3.30 mmol) was dissolved in thf (15 cm^3) and slowly treated with 1-phenylpyrazol-5-yllithium, prepared from 1-phenylpyrazole (0.44 cm^3, 3.3 mmol) and *n*-butyllithium (1.6 mol dm^{-3}, 2.08 cm^3, 3.33 mmol) at −80 °C. The reaction mixture was stirred for 30 min and the solvent removed under vacuum. The residue was dissolved in diethyl ether and purified by column chromatography on Florisil with hexane–diethyl ether as eluent. Concentration of the filtrate, slow addition of hexane and cooling to −20 °C afforded orange crystals of complex **1**. Mass spectrum: *m*/*z* 320 (9, *M*$^+$), 292 (6, [*M* − CO]$^+$), 264 (100, [*M* − 2CO]$^+$), 144 (10, [CH=CHCH=NNPh]$^+$), 121 {30, [(cp)Fe]$^+$} and 56 (70%, [Fe]$^+$).

[Fe(cp)(CO)$_2$(CCH=CHNHNPh)][CF$_3$SO$_3$] 1a. A solution of complex **1** in CH$_2$Cl$_2$ (30 cm^3) was cooled to −20 °C and treated dropwise with CF$_3$SO$_3$H (0.13 cm^3, 1.488 mmol). The mixture was stirred at this temperature for 40 min and at room temperature for 30 min. The reaction mixture was filtered through anhydrous MgSO$_4$. Concentration of the orange filtrate, slow addition of hexane and cooling to −20 °C afforded orange needle-like crystals of complex **1a**. Mass spectrum: *m*/*z* 320 (5, [*M* − 1]$^+$), 292 (3, [*M* − 1 − CO]$^+$), 264 (18, [*M* − 1 − 2CO]$^+$), 186 {13, [Fe(cp)$_2$]$^+$}, 144 (100, [CH=CHCH=NNPh]$^+$), 77 (56, [Ph]$^+$), 66 (38, [C=CHCH=NN]$^+$) and 56 (39%, [Fe]$^+$).

[Fe(cp)(CO)$_2${C=CHCH=C(C=NCMe$_2$CH$_2$O)S}] 2. The complex [Fe(cp)(CO)$_2$Cl] (0.26 g, 1.24 mmol) was dissolved in thf (20 cm^3) and slowly treated with 5-(4,5-dihydro-4,4-dimethyloxazolin-2-yl)-2-thienyllithium, prepared from 4,5-dihydro-4,4-dimethyl-2-(2-thienyl)oxazole (0.26 g, 1.44 mmol) and a lithium diisopropylamide solution, at −80 °C. The mixture was stirred for 30 min at −80 °C, then for 30 min at −30 °C, for 30 min at − 20 °C and at − 10 °C for 30 min before warming to room temperature. The solvent was removed under vacuum, the residue extracted with ether and purified by column chromatography on Florisil. Concentration of the filtrate, slow addition of hexane and cooling to −20 °C afforded orange crystals of complex **2**. Mass spectrum: *m*/*z* 357 (32, *M*$^+$), 329 (67, [*M* − CO]$^+$), 301 (100, [*M* − 2CO]$^+$), 286 (34, [*M* − 2CO − Me]$^+$), 271 (19, [*M* − 2CO − 2Me]$^+$), 229 (15, [(cp)Fe{CCH=CHC(C=N)S}]$^+$), 121 {54, [(cp)Fe]$^+$} and 56 (31%, [Fe]$^+$).

[Fe(cp)(CO)$_2${CCH=CHC(=CNHCMe$_2$CH$_2$O)S}][CF$_3$SO$_3$] 2a. The orange complex **2a** was prepared in the same way as **1a** with **2** (0.46 g, 1.29 mmol) and CF$_3$SO$_3$H (0.13 cm^3, 1.488 mmol). The filtrate yielded needle-like crystals of complex **2a**. Mass spectrum: *m*/*z* 357 (5, [*M* − 1]$^+$), 329 (12, [*M* − 1 − CO]$^+$), 301 (20, [*M* − 1 − 2CO]$^+$), 286 (10, [*M* − 1 − 2CO − Me]$^+$), 229 {25, [(cp)Fe{CCH=CHC(C=N)S}]$^+$}, 181 {20, [CH=CHCH=C(C=NCMe$_2$CH$_2$O)S]$^+$}, 166 (100, [CH=CHCH=C(C=NCMeCH$_2$O)S]$^+$}, 151 (20, [CH=CHCH=C(C=NCCH$_2$O)S]$^+$} and 121 {15%, [(cp)-Fe]$^+$}.

[Fe(cp)(CO){C=C[CN(C=O)CMe$_2$CH$_2$O]SCH=CH}] 3. A solution of 4,5-dihydro-4,4-dimethyl-2-(2-thienyl)oxazole (0.76 g, 4.2 mmol) in diethyl ether (20 cm^3) was cooled to −78 °C and treated with *n*-butyllithium (1.6 mol dm^{-3}, 1.06 cm^3, 1.70 mmol). The solution was stirred at −78 °C for 15 min and at 0 °C for 30 min. A solution of [Fe(cp)(CO)$_2$Cl] (0.31 g, 1.47 mmol) in diethyl ether (50 cm^3) was added dropwise at −65 °C. The mixture was stirred for 30 min at −65 °C and for 1 h at −20 °C before warming to room temperature. The reaction mixture was purified by filtration through Florisil. Concentration of the green filtrate, slow addition of hexane and cooling to −20 °C afforded green crystals of complex **3**. Mass spectrum: *m*/*z* 357 (10, *M*$^+$), 329 (21, [*M* − CO]$^+$), 301 (100, [*M* − 2CO]$^-$), 121 {29, [(cp)Fe]$^+$} and 56 (6%, [Fe]$^+$).

[Fe(cp)(CO){C=C[CN(COH)CMe$_2$CH$_2$O]SCH=CH}]-[CF$_3$SO$_3$] 3a. A solution of complex **3** (0.30 g, 0.84 mmol) in diethyl ether (15 cm^3) was cooled to −20 °C and treated with CF$_3$SO$_3$H (0.09 cm^3, 1.00 mmol). The solution was stirred at −20 °C for 1.5 h and at room temperature for 4 h, then filtered to give a black-green solid which was washed several times with diethyl ether. This product was purified by crystallization from CH$_2$Cl$_2$–diethyl ether to give black-green crystals of complex **3a**. Mass spectrum: *m*/*z* 358 (5, *M*$^+$), 343 (4, [*M* − Me]$^+$), 329 (7, [*M* − 1 − CO]$^+$), 315 (10, [*M* − CO − Me]$^+$), 301 (15, [*M* − 1 − 2CO]$^+$), 166

Table 6 Crystal data, collection and refinement details for complexes **1** and **1a** *

	1	**1a**
Formula	$C_{16}H_{12}FeN_2O_2$	$C_{17}H_{13}F_3FeN_2O_5S$
Space group	$P2_1/c$	$P2_1/n$
a/Å	8.5441(9)	12.2989(25)
b/Å	15.3513(16)	9.8777(18)
c/Å	10.9076(15)	16.7194(24)
β/°	104.365(6)	104.212(16)
U/Å^3	1385.94(29)	1968.99(63)
D_c/g cm^{-3}	1.534	1.586
μ/cm^{-1}	11.22	9.52
F(000)	656	952
Scan angle, ω/°	0.93–1.12	0.36–0.49
hkl Ranges	−12 to 12, −1 to 21, −1 to 15	−14 to 14, −1 to −11, −1 to 20
Reflections measured	4910	4435
Unique reflections used	4025	3555
Parameters refined	226	262
Absorption correction	83.35–99.96	89.28–99.92
Difference map peaks/e Å^{-3}	0.08 (0.1 Å from Fe)	0.13 (0.4 Å from Fe)
R, R'	0.037, 0.034	0.055, 0.048

* Details in common: monoclinic; $Z = 4$; scan type ω–2θ; scan range θ 2–30°; maximum scan rate 5.5° min^{-1}; maximum scan time per reflection 60 s; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2$.

{100, $[CH{=}CHCH{=}C(C{=}NCMeCH_2O)S]^+$} and 151 {40%, $[CH{=}CHCH{=}C(C{=}NCCH_2O)S]^+$}.

$[Fe(cp)(CO)\{C{=}C[CN(COMe)CMe_2CH_2O]SCH{=}CH\}]$-$[CF_3SO_3]$ 3b. The green complex **3b** was prepared in the same way as **3a** with **3** (0.34 g, 0.94 mmol) and CF_3SO_3Me (0.11 cm^3, 0.95 mmol). The solution yielded black-green crystals of complex **3b**. Mass spectrum: m/z 416 (7, $[\{C{=}C[C{=}N(C{=}O)CMe_2CH_2O]SCH{=}CH\}_2]^+$), 301 {13, $[(cp)Fe\{C{=}C(C{=}NCMe_2CH_2O)SCH{=}CH\}]^+$}, 223 {25, $[C{=}C\{C{=}N(COMe)CMe_2CH_2O\}SCH{=}CH]^+$}, 208 {40, $[C{=}C\{C{=}N(C{=}O)CMe_2CH_2O\}SCH{=}CH]^+$}, 186 {76, $[Fe(cp)_2]^+$}, 136 {100, $[C{=}CHCH{=}C(C{=}NCO)S]^+$}, 121 {36, $[(cp)Fe]^+$} and 56 (19%, $[Fe]^+$).

$[Fe(cp)(CO)\{CC({=}CNCMe_2CH_2O)SCH{=}CH\}]$ 4. A solution of 4,5-dihydro-4,4-dimethyl-2-(2-thienyl)oxazole (0.31 g, 1.7 mmol) in diethyl ether (15 cm^3) was cooled to −78 °C and treated with n-butyllithium (1.6 mol dm^{-3}, 1.06 cm^3, 1.70 mmol). The solution was stirred at −78 °C for 15 min and at 0 °C for 30 min. A solution of $[Fe(cp)(CO)(PPh_3)Br]$ (0.73 g, 1.50 mmol) in thf (15 cm^3) was added dropwise at −10 °C. The mixture was stirred for 1 h at −10 °C before warming to room temperature. The solvent was removed under vacuum and the residue purified by column chromatography at −10 °C on Florisil with diethyl ether–hexane (5% diethyl ether) as eluent. Concentration of the collected orange filtrate, slow addition of hexane and cooling to −20 °C afforded red crystals of complex **4**. Mass spectrum: m/z 329 (15, M^+), 301 (100, $[M - CO]^+$), 121 {17, $[(cp)Fe]^+$} and 56 (16%, $[Fe]^+$).

$[Fe(cp)(CO)_2\{C{=}CHCH{=}C(C{=}NCH{=}CHCH{=}CH)S\}]$ 5. A solution of 2-(2-thienyl)pyridine (0.96 g, 5.80 mmol) in thf (15 cm^3) was cooled to −10 °C and treated with n-butyllithium (1.6 mol dm^{-3}, 3.66 cm^3, 5.85 mmol). The red solution was stirred at −10 °C for 30 min and at room temperature for 5 min. A solution of $[Fe(cp)(CO)_2Cl]$ (1.23 g, 5.78 mmol) in thf (15 cm^3) was added dropwise at −55 °C. The mixture was stirred for 45 min at this temperature and for 30 min at room temperature. The solvent was removed under vacuum, the residue extracted with diethyl ether and filtered through Florisil. Concentration of the yellow filtrate, slow addition of hexane and cooling to −20 °C afforded dark orange crystals of complex **5**. Mass spectrum: m/z 337 (6, M^+), 309 (6, $[M - CO]^+$), 281 (100, $[M - 2CO]^+$), 216 (51, $[M - 2CO - cp]^+$), 161 (9, $[M - 2CO - cp - Fe]^+$), 121 {8, $[(cp)Fe]^+$} and 56 (16%, $[Fe]^+$).

$[Fe(cp)(CO)_2\{C{=}CHCH{=}C(C{=}NHCH{=}CHCH{=}CH)S\}]$-$[CF_3SO_3]$ 5a. A solution of complex **4** (0.47 g, 1.41 mmol) in diethyl ether (25 cm^3) was cooled to −20 °C and treated with CF_3SO_3H (0.14 cm^3, 1.61 mmol). The solution was stirred at −20 °C for 30 min and at room temperature for 2 h. The reaction mixture was filtered giving a yellow solid which was washed several times with diethyl ether. This product was purified by crystallization from a CH_2Cl_2–hexane mixture to give orange crystals of complex **5a**. Mass spectrum: m/z 337 (8, $[M - 1]^+$), 309 (15, $[M - 1 - CO]^+$), 281 (37, $[M - 1 - 2CO]^+$), 186 {55, $[Fe(cp)_2]^+$}, 161 (100, $[M - 1 - 2CO - cp - Fe]^+$), 121 {31, $[(cp)Fe]^+$} and 56 (22%, $[Fe]^+$).

$[Fe(cp)(CO)_2\{C{=}CHCH{=}C(C{=}NMeCH{=}CHCH{=}CH)S\}]$-$[CF_3SO_3]$ 5b. The green complex **5b** was prepared in the same way as **5a** with **5** (0.34 g, 1.02 mmol) and CF_3SO_3Me (0.14 cm^3, 1.22 mmol). The solution yielded black-green crystals of complex **5b**. Mass spectrum: m/z 354 {100%, $[(cp)Fe(CO)_2]_2$}.

$[Fe(cp)(CO)(PPh_3)\{C{=}CHCH{=}C(C{=}NMeCH{=}CHCH{=}CH)S\}]$ $[CF_3SO_3]$ 6. Complex **5b** (0.75 g, 1.5 mmol) and triphenylphosphine (0.42 g, 1.6 mmol) were dissolved in CH_2Cl_2 (15 cm^3) and irradiated in a quartz apparatus. The reaction was monitored by IR (disappearance of carbonyl stretches at 2022 and 1983 cm^{-1} relative to the emergence of carbonyl stretch at 1952 cm^{-1}) and irradiation stopped after 1 h. The reaction mixture was filtered through anhydrous $MgSO_4$ and purified by crystallization from a CH_2Cl_2–diethyl ether mixture to give red crystals of complex **6**. Mass spectrum: m/z 262 (100, $[PPh_3]^+$) and 108 (60%, $[PPh]^+$).

Crystallography

Yellow crystals of complexes **1** and **1a** were mounted on glass fibres and transferred to the diffractometer (Enraf-Nonius CAD4F). Data were collected at 23 °C with graphite-monochromated Mo-Kα radiation (λ = 0.710 73) to $2\theta_{max} = 30°$ and corrected for Lorentz-polarization effects and for absorption using the ψ-scan method. Unique sets of data with $I > 2.0\sigma(I)$ were used to solve the structures by the heavy-atom method. Refinements on F were done using the least-squares method. All non-hydrogen atoms were refined anisotropically. Hydrogen positions were found from a difference map for **1** and placed in idealized positions for **1a**. These were assigned common isotropic thermal parameters ($U = 0.08$ Å^3). In the case of **1** the hydrogen coordinates could be refined successfully. For structure solution and refinement the XTAL 3.2 package was used.[18] Important crystallographic parameters are given in Table 6.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/232.

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