Preparation of Dithioformato, Thioformamido and Formamido Derivatives of Iron(II)†

Gabriele Albertin,* Stefano Antoniutti, Elena Del Ministro and Emilio Bordignon*
Dipartimento di Chimica dell'Università di Venezia, Dorsoduro 2137, 30123 Venice, Italy

Dithioformato $[Fe(S_2CH)L_4]BPh_4$ **1**, *N*-ethyl- and *N*-*p*-tolyl-thioformamido $[Fe(RN\cdots CH\cdots S)L_4]BPh_4$ (R = Et or *p*-MeC_6H_4) **2** and **3**, and phenylformamido $[Fe(PhN\cdots CH\cdots O)L_4]BPh_4$ **4** derivatives [L = $P(OEt)_3$ or $PPh(OEt)_2$] were prepared by treating the hydrides $[FeH(H_2)L_4]^+$ with the appropriate heteroallenes CS_2, RNCS and PhNCO. Substitution reactions with CO and isocyanides were studied and the synthesis of $[Fe(RN\cdots CH\cdots S)(CO)L_3]BPh_4$ **5** and **6**, $[Fe(RN\cdots CH\cdots S)(p\text{-}MeC_6H_4NC)L_3]BPh_4$ **7** and **8**, $[Fe(PhN\cdots CH\cdots O)(CO)\{P(OEt)_3\}_3]BPh_4$ **9** and $[Fe(p\text{-}MeC_6H_4NC)_3L_3][BPh_4]_2$ **10** complexes achieved. Their characterization and stereochemistry were established using infrared, ^1H, ^{31}P and ^{13}C NMR spectroscopy.

A large number of studies have been reported on the insertion reactions of heteroallenes such as carbon disulfide, isothiocyanate, aryl isocyanate and carbodiimide into metal–hydride bonds to produce 'formato', 'formamido' and 'formamidinato' complexes.[1–4] These reactions are often seen as models for analogous, but less readily available, reactions of carbon dioxide and may help in the development of transition-metal-mediated conversion of CO_2 into organic products.

The insertion of X=C=Y (X, Y = O, S or NR) into metal–hydride bonds is believed to proceed by a mechanism involving a four-centred intermediate[1b] which does not require an open co-ordination site for the reaction to occur. However, a mechanism involving direct co-ordination of the heteroallene to the metal centre prior to insertion may also be proposed[3b,4] for some metal hydrides, and in these cases the presence of an open co-ordination site should favour the insertion reaction. The reaction products are in any case 'formato' and 'formamido' complexes with the $X\cdots CH\cdots Y$ bonded to the metal in either a bidentate[2–4] or monodentate fashion.[1]

Despite the number of studies reported on several transition metals, very few are concerned with the reactivity of iron hydrides toward heteroallenes and, apart from a brief note[5] on the reaction of $[FeH(\eta^5\text{-}C_5H_5)(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with carbon disulfide, no other data are available on the insertion of X=C=Y into hydride complexes of iron(II). As part of our studies on the properties of classical and non-classical iron(II) hydrides,[6] we now report an investigation on the reactivity of $[FeH(H_2)L_4]BPh_4$ complexes [L = $P(OEt)_3$ or $PPh(OEt)_2$] with CS_2, RNCS (R = Et or *p*-MeC_6H_4) and PhNCO, allowing the synthesis of new dithioformato, thioformamido and formamido iron derivatives.

Experimental

General Comments.—All operations were performed under an inert atmosphere (argon), using standard Schlenk techniques or a Vacuum Atmosphere dry-box. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Diethoxy(phenyl)-phosphine was prepared by the method of Rabinowitz and Pellon;[7] triethyl phosphite was an Ega Chemie product purified by distillation under nitrogen. The heteroallenes CS_2, *p*-MeC_6H_4NCS, EtNCS and PhNCO were Aldrich products, used without further purification. *p*-Tolyl isocyanide was prepared by the phosgene ($COCl_2$) method of Ziehn and co-workers.[8] Other reagents were obtained from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer model 683 spectrophotometer, NMR spectra (^1H, ^{13}C, ^{31}P) on a Bruker AC 200 spectrometer at temperatures between −85 and +34 °C, unless otherwise noted. The ^1H and ^{13}C spectra are referred to internal tetramethylsilane; $^{31}P\text{-}\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in nitromethane or acetone at 25 °C were measured on a Radiometer CDM 83 instrument. Solution susceptibilities were determined by the Evans method.[9]

Synthesis of Complexes.—Molecular hydrogen complexes $[FeH(H_2)L_4]BPh_4$ were prepared by the method previously reported.[6a]

$[Fe(S_2CH)L_4]BPh_4$ **1** [L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. An excess of carbon disulfide (7 mmol, 0.5 cm^3) was slowly added to a dichloromethane solution (15 cm^3) of the appropriate hydride $[FeH(H_2)L_4]BPh_4$ (0.7 mmol) at room temperature and the resulting reaction mixture was stirred for 30 min. The solvent was removed at reduced pressure giving a brown oil which was treated with ethanol (15 cm^3). The orange solid forming after 20–30 min of stirring was filtered off and crystallized from CH_2Cl_2 (5 cm^3)–ethanol (20 cm^3); yield ⩾80%.

$[Fe(EtN\cdots CH\cdots S)L_4]BPh_4$ **2** [L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. An excess of EtNCS (5 mmol, 0.44 cm^3) was added to a dichloromethane solution (10 cm^3) of $[FeH(H_2)L_4]BPh_4$ (0.5 mmol) cooled to −80 °C. The reaction mixture was brought to 0 °C in about 15 min and then stirred for 30 min. Removal of the solvent at reduced pressure gave a brown oil which was treated with ethanol (15 cm^3). The yellow solid which separated out after 30 min of stirring was filtered off and crystallized from CH_2Cl_2 (5 cm^3)–ethanol (20 cm^3); yield ⩾70%.

$[Fe(p\text{-}MeC_6H_4N\cdots CH\cdots S)L_4]BPh_4$ **3** [L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. These compounds were prepared exactly like the related compounds **2**, using *p*-MeC_6H_4NCS as reagent; yield ⩾80%.

$[Fe(PhN\cdots CH\cdots O)\{P(OEt)_3\}_4]BPh_4$ **4a**. An excess of phenyl isocyanate (2.5 mmol, 0.27 cm^3) was added to a dichloromethane solution (10 cm^3) of $[FeH(H_2)\{P(OEt)_3\}_4]BPh_4$ (0.5 mmol, 0.52 g) cooled to −80 °C. The reaction mixture was brought to 0 °C in about 15 min and then stirred for 40 min. The solvent was evaporated under reduced pressure giving a brown oil which was treated with ethanol (10 cm^3). The resulting solution

---

† *Non-SI unit employed:* atm = 101 325 Pa.

was vigorously stirred at 0 °C until a yellow solid separated after about 2 h. This was filtered off and crystallized from CH_2Cl_2 ($4\ cm^3$)–ethanol ($15\ cm^3$); yield ⩾70%.

$[Fe(EtN{\cdots}CH{\cdots}S)(CO)\{P(OEt)_3\}_3]BPh_4$ **5a** *and* $[Fe(p\text{-}MeC_6H_4N{\cdots}CH{\cdots}S)(CO)\{P(OEt)_3\}_3]BPh_4$ **6a**. A dichloromethane solution ($7\ cm^3$) of the appropriate thioformamido complex $[Fe(RN{\cdots}CH{\cdots}S)\{P(OEt)_3\}_4]BPh_4$ (R = Et or *p*-MeC_6H_4) (0.4 mmol) was stirred under CO (1 atm) at room temperature for 2 h. Removal of the solvent at reduced pressure gave a brown oil which was triturated with ethanol ($15\ cm^3$). The pale yellow solid obtained was filtered off and crystallized from CH_2Cl_2 ($5\ cm^3$)–ethanol ($20\ cm^3$); yield ⩾60%.

fac-$[Fe(EtN{\cdots}CH{\cdots}S)(CO)\{PPh(OEt)_2\}_3]BPh_4$ **5b**. A sample of $[Fe\{(EtN{\cdots}CH{\cdots}S)\}\{PPh(OEt)_2\}_4]BPh_4$ (0.4 mmol, 0.52 g) was dissolved in $ClCH_2CH_2Cl$ ($7\ cm^3$) under CO (1 atm) at room temperature. The reaction mixture was stirred for 3 h and the solvent then removed under reduced pressure. The oil obtained was treated with ethanol ($10\ cm^3$) giving, after 4 h of stirring, a pale yellow solid which was filtered off and crystallized from ethanol; yield ⩾65%.

mer-$[Fe(EtN{\cdots}CH{\cdots}S)(CO)\{PPh(OEt)_2\}_3]BPh_4$ **5b′**. A solution of *fac*-$[Fe(EtN{\cdots}CH{\cdots}S)(CO)\{PPh(OEt)_2\}_3]BPh_4$ (0.4 mmol, 0.43 g) in 1,2-dichloroethane ($15\ cm^3$) was refluxed for 80 min and the solvent then removed under reduced pressure. The resulting oil was treated with ethanol ($10\ cm^3$), affording a yellow solid which was filtered off and crystallized from CH_2Cl_2 ($5\ cm^3$)–ethanol ($15\ cm^3$); yield ⩾90%.

$[Fe(EtN{\cdots}CH{\cdots}S)(p\text{-}MeC_6H_4NC)L_3]BPh_4$ **7** [L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. An excess of *p*-tolyl isocyanide (1.6 mmol, $0.19\ cm^3$) was added to a solution of the appropriate thioformamido derivative $[Fe(EtN{\cdots}CH{\cdots}S)L_4]BPh_4$ (0.4 mmol) in $7\ cm^3$ of CH_2Cl_2 (**7a**) or $ClCH_2CH_2Cl$ (**7b**). The reaction mixture was stirred at room temperature for 24 h and the solvent then evaporated under reduced pressure giving a brown oil which was treated with ethanol ($10\ cm^3$). The yellow solid obtained by stirring was filtered off and crystallized from ethanol; yield ⩾65%.

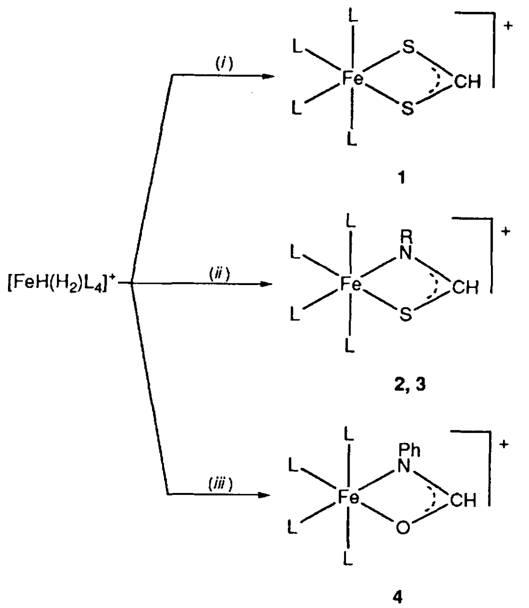
$[Fe(p\text{-}MeC_6H_4N{\cdots}CH{\cdots}S)(p\text{-}MeC_6H_4NC)L_3]BPh_4$ **8** [L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. These compounds were prepared exactly like the related compounds **7**, but oily products were obtained.

$[Fe(PhN{\cdots}CH{\cdots}O)(CO)\{P(OEt)_3\}_3]BPh_4$ **9a**. This compound was prepared like the related **5a** and **6a**, starting from $[Fe(PhN{\cdots}CH{\cdots}O)\{P(OEt)_3\}_4]BPh_4$, with a reaction time of 45 min; yield ⩾40%.

$[Fe(p\text{-}MeC_6H_4NC)_3\{P(OEt)_3\}_3][BPh_4]_2$ **10a**. An excess of *p*-tolyl isocyanide (1.7 mmol, $0.2\ cm^3$) was added to a dichloromethane solution ($10\ cm^3$) of $[Fe(PhN{\cdots}CH{\cdots}O)\{P(OEt)_3\}_4]BPh_4$ (0.4 mmol, 0.46 g) and the reaction mixture was stirred for 45 min. Removal of the solvent at reduced pressure gave an oil which was treated with ethanol ($10\ cm^3$) containing a slight excess of $NaBPh_4$ (0.6 mmol, 0.21 g). The white solid which separated after 90 min of stirring was filtered off and crystallized from ethanol; yield ⩾80%.

Results and Discussion

Carbon disulfide reacts with molecular hydrogen complexes $[FeH(H_2)L_4]BPh_4$ to produce the orange dithioformato derivatives $[Fe(S_2CH)L_4]^+$ **1** shown in Scheme 1. Evolution of H_2 was observed during the reaction, which proceeds at room temperature either in neat CS_2 or in another solvent such as CH_2Cl_2 or tetrahydrofuran (thf) with CS_2 added in stoichiometric amounts. The substitution lability of the dihydrogen ligand[6a] suggests that the formation of dithioformate involves co-ordination of the CS_2 group, by substitution of H_2, prior to insertion in the Fe–H bond. In order to test this hypothesis we treated hydrides $[FeH(CO)L_4]^+$ and $[FeH_2L_4]$,[10,11] which are known to be quite inert to ligand substitution, with CS_2 and observed no formation of dithioformato complexes, even after several hours in boiling thf or benzene. An open co-ordination site for the reaction to occur therefore seems necessary in our hydrides, in contrast with other complexes[1b–d,3b,4] in which the insertion reaction seems to exclude a dissociation process.



Scheme 1 L = $P(OEt)_3$ **a** or $PPh(OEt)_2$ **b**; R = Et **2** or *p*-MeC_6H_4 **3**. (*i*) CS_2; (*ii*) RNCS; (*iii*) PhNCO

Some spectroscopic properties of the dithioformato complexes $[Fe(S_2CH)L_4]BPh_4$ **1**, which are stable orange solids, diamagnetic and 1 : 1 electrolytes,[12] are reported in Tables 1–4. The infrared spectra do not allow all the bands characteristic of the dithioformate (S_2CH) ligand[1,2g,4] to be unambiguously assigned, because the regions of the symmetric and asymmetric $\nu(CS_2)$ bands, at 950–900 and 800–700 cm^{-1} respectively, are partially masked by the vibration of phosphite ligands. However, the bands attributable to $\delta(HCS)$ of the S_2CH ligand are present at 1227 cm^{-1} for **1a** and 1222 cm^{-1} for **1b**.

Strong support for the formulation of **1** as dithioformato complexes comes from the ^1H, ^{31}P and ^{13}C NMR data. In particular, between −80 and +30 °C, the $^{31}P\text{-}\{^1H\}$ spectra appear as symmetrical A_2B_2 multiplets, easily simulable using the parameters reported in Table 2. Furthermore, in the low-field region of the ^1H NMR spectra, multiplets appear at δ 11.11 (**1a**) and 9.97 (**1b**), attributed to the proton resonance of the S_2CH ligand. These multiplets are due to coupling of the dithioformate proton with the phosphorus atoms, as confirmed by the simulation (Fig. 1) of the multiplets with an A_2B_2X model using the parameters reported. The good agreement between theoretical and experimental spectra clearly confirms the symmetrical structure (Scheme 1) for our dithioformate ligand. Lastly, the ^{13}C NMR spectra also confirm the presence of the S_2CH ligand, showing a triplet at δ 237.9 for **1a**, which is split into a doublet of triplets in the coupled ^{13}C spectrum, as expected for the CH resonance of the dithioformate ligand ($^1J_{CH}$ = 185 Hz). The multiplicity of this signal (triplet) is due to coupling with the four phosphorus atoms, as confirmed by a computer simulation using an A_2B_2X (X = ^{13}C) model which revealed that the two $^3J_{CP}$ are different, with values of J_{AX} = 8.9 and J_{BX} = 1.6 Hz, respectively. It may be noted that few ^{13}C NMR data[1c,13] are available for dithioformato complexes, although they show the characteristic high-frequency resonance of the S_2CH ligand between δ 230 and 240. Spectroscopic properties similar to those of our dithioformato complexes **1** have also been observed for the two known iron(II) derivatives $[Fe(S_2CH)(C_5H_5)(dppe)]$[5] and $[Fe(S_2CH)(depe)_2]BPh_4$ (depe = $Et_2PCH_2CH_2PEt_2$),[14] the latter obtained by $NaBH_4$ reduction of $[Fe(S_2CPEt_3)(depe)][BPh_4]_2$.

Table 1 Physical, analytical and selected IR data for the complexes

Complex[a]		M.p./ °C	Λ_M[b]/S cm^2 mol^{-1}	Analysis[c] (%) C	H	N	IR[d]/cm^{-1}
1a	$[Fe(S_2CH)\{P(OEt)_3\}_4]^+$	132	92.3[e]	52.65 (52.70)	7.45 (7.30)		1227w δ(HCS)
1b	$[Fe(S_2CH)\{PPh(OEt)_2\}_4]^+$	107	48.5	62.60 (62.70)	6.60 (6.55)		1222w δ(HCS)
2a	$[Fe(EtN\cdots CH\cdots S)\{P(OEt)_3\}_4]^+$	130	49.8	54.00 (54.30)	7.70 (7.70)	1.15 (1.25)	
2b	$[Fe(EtN\cdots CH\cdots S)\{PPh(OEt)_2\}_4]^+$	100	52.3	63.90 (64.05)	6.85 (6.90)	1.10 (1.10)	
3a	$[Fe(p\text{-}MeC_6H_4N\cdots CH\cdots S)\{P(OEt)_3\}_4]^+$	135	54.3	56.55 (56.50)	7.50 (7.45)	1.15 (1.20)	
3b	$[Fe(p\text{-}MeC_6H_4N\cdots CH\cdots S)\{PPh(OEt)_2\}_4]^+$	110	48.7	65.35 (65.60)	6.75 (6.75)	1.00 (1.05)	
4a	$[Fe(PhN\cdots CH\cdots O)\{P(OEt)_3\}_4]^+$	90	56.1	56.70 (56.95)	7.45 (7.45)	1.10 (1.20)	
5a	$[Fe(EtN\cdots CH\cdots S)(CO)\{P(OEt)_3\}_3]^+$	132	61.5	55.75 (55.80)	7.20 (7.25)	1.50 (1.40)	2010s ν(CO) [2016s]
5b	*fac*-$[Fe(EtN\cdots CH\cdots S)(CO)\{PPh(OEt)_2\}_3]^+$	142	85.9[e]	63.90 (64.15)	6.65 (6.60)	1.25 (1.30)	2008s ν(CO) [2017s]
5b′	*mer*-$[Fe(EtN\cdots CH\cdots S)(CO)\{PPh(OEt)_2\}_3]^+$	142	87.2[e]	63.95 (64.15)	6.45 (6.60)	1.20 (1.30)	1970s ν(CO) [1972s]
6a	$[Fe(p\text{-}MeC_6H_4N\cdots CH\cdots S)(CO)\{P(OEt)_3\}_3]^+$	118	59.4	57.95 (58.25)	7.10 (7.00)	1.30 (1.35)	1999s ν(CO) [2021s]
7a	$[Fe(EtN\cdots CH\cdots S)(p\text{-}MeC_6H_4NC)\{P(OEt)_3\}_3]^+$	118	59.4	58.85 (59.00)	7.35 (7.30)	2.50 (2.60)	2135s ν(NC) [2136s]
7b	$[Fe(EtN\cdots CH\cdots S)(p\text{-}MeC_6H_4NC)\{PPh(OEt)_2\}_3]^+$	135	58.1	66.55 (66.45)	6.75 (6.70)	2.40 (2.40)	2128s ν(NC) [2133s]
9a	$[Fe(PhN\cdots CH\cdots O)(CO)\{P(OEt)_3\}_3]^+$	—	58.2	58.65 (58.80)	7.00 (7.00)	1.45 (1.35)	2020s ν(CO)
10a	$[Fe(p\text{-}MeC_6H_4NC)_3\{P(OEt)_3\}_3]^{2+}$	175	123.5	69.85 (70.00)	7.05 (6.90)	2.65 (2.70)	2187s, 2159s ν(NC) [2193s, 2063s]

[a] All compounds are BPh_4^- salts. [b] In nitromethane solution (10^{-3} mol dm^{-3}) at 25 °C. [c] Calculated values in parentheses. [d] In KBr, except for values in square brackets (CH_2Cl_2). [e] In acetone solution (10^{-3} mol dm^{-3}) at 25 °C.

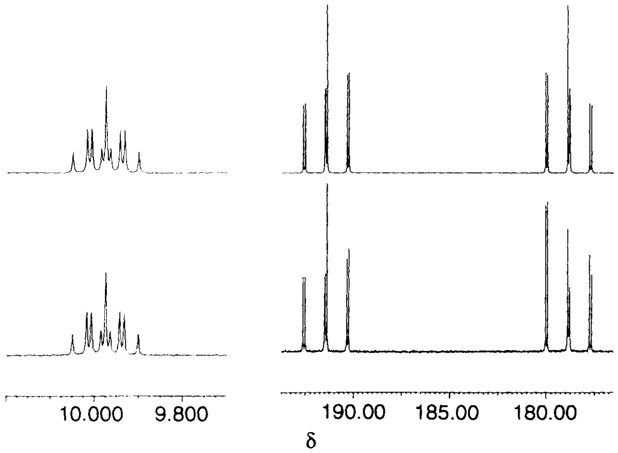


Fig. 1 Observed (bottom) and simulated (top) NMR spectra of $[Fe(S_2CH)\{PPh(OEt)_2\}_4]BPh_4$ **1b** in $(CD_3)_2CO$ at 25 °C. Left: ^1H spectra of dithioformato-proton region. Right: $^{31}P\text{-}\{^1H\}$ spectra. Simulated spectra were obtained using parameters reported in Tables 2 and 3

Both ethyl and *p*-tolyl isothiocyanate RNCS react with non-classical hydrides $[FeH(H_2)L_4]^+$ to give the corresponding *N*-ethyl- and *N*-*p*-tolyl-thioformamido complexes $[Fe\{RNC(H)S\}L_4]^+$ **2** and **3**, as in Scheme 1. In this case too, co-ordination of the RNCS prior to insertion may be proposed, not only in view of the substitution lability of dihydrogen in $[FeH(H_2)L_4]^+$, but also on the basis of the absence of reactivity of $[FeH(CO)L_4]^+$ and $[FeH_2L_4]$ hydrides.

The complexes are yellow-orange solids, diamagnetic 1 : 1 electrolytes,[12] and their formulation as thioformamido complexes is supported not only by elemental analyses and infrared spectra (Table 1) but also by the ^1H, ^{31}P and ^{13}C NMR data reported in Tables 2–4.

The infrared spectra do not give any information on the co-ordination of the RNC(H)S ligand, because the bands of the phosphites and the BPh_4 anion mask the region characteristic of thioformamide ligands, and the only information obtained seems to be the absence[15] of bands attributable to ν(NH) between 3300 and 3500 cm^{-1} and to ν(SH) between 2650 and 2550 cm^{-1}.

Instead, for all thioformamido complexes **2** and **3**, the $^{31}P\text{-}\{^1H\}$ NMR spectra show non-symmetrical multiplets, as expected for the geometry shown (Scheme 1), and may be simulated using an ABC_2 model with the parameters reported in Table 2. Furthermore, in the low-field region of the ^1H NMR spectra of the $P(OEt)_3$ derivatives, multiplets appear at δ 8.24 (**2a**) and 8.43 (**3a**), attributable to the CH proton of the RNC(H)S ligand. These multiplets are due to coupling with the phosphorus atoms of the $P(OEt)_3$ ligands and, in the case of **3a**, the signal may easily be simulated using an ABC_2X model (X = H) as shown in Fig. 2. In the spectra of the related *N*-ethylthioformamido complex **2a**, the signal of the ethyl group of the EtNC(H)S ligand appears as a quartet at δ 3.34 and a triplet at δ 1.12, while the resonance of the central proton of the formamide ligand is complicated by coupling, not only with the phosphorus atoms but also with the same ethyl protons of the ethyl substituent. However, selective homodecoupling gave the CH resonance as an ABC_2X multiplet, easily simulable with the parameters reported in Tables 2 and 3.

These data confirm the presence of the chelate thioformamide ligand as shown. Further support for this formulation comes from the $^{13}C\text{-}\{^1H\}$ NMR spectrum of complex **3a** which, in the low-field region, shows a multiplet at δ 182.7 attributable to the formamide carbon atom. This signal is replaced by two multiplets in the coupled ^{13}C spectrum ($^1J_{CH}$ = 180 Hz), as expected for a CH resonance.

In the ^1H NMR spectra of the formamido complexes containing $PPh(OEt)_2$, **2b** and **3b**, the multiplet attributed to the central proton of the RNC(H)S ligand is difficult to identify, being partially masked by the resonance of the phenyl protons. However, the resonance of the substituent groups at N (Et for **2b** and $p\text{-}MeC_6H_4$ for **3b**) of the RNC(H)S chelate ligand are present in the spectra as a singlet at δ 1.94 for Me of $p\text{-}MeC_6H_4$ and a triplet at δ −0.31 and a quartet at 2.35 for Et, thus confirming the presence of the formamide ligand.

Phenyl isocyanate PhNCO quickly reacts with non-classical iron(II) hydrides $[FeH(H_2)L_4]^+$ to yield the formamido complexes $[Fe\{RNC(H)O\}L_4]BPh_4$ **4**, analogous to the thioformamido complexes described above. However, a pure

Table 2 Proton and phosphorus-31 NMR spectral data

	^{1}H NMR[b,c]			
Complex[a]	δ	Assignment	Spin system	^{31}P-{^{1}H} NMR, δ[b,d]
1a	11.11 (m)	CH	A_2B_2	δ_A 161.5, δ_B 148.9
	4.14 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 123.5]
	1.28 (t)	$\mathrm{POCH_2C}H_3$		
1b	9.97 (m)	CH	A_2B_2	δ_A 189.2, δ_B 176.6
	3.91 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 92.7]
	1.40, 1.22 (t)	$\mathrm{POCH_2C}H_3$		
2a	8.24 (m)	CH	ABC_2[e]	δ_A 166.2, δ_B 165.3, δ_C 147.9
	4.04 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 99.2, J(AC) =135.6
	3.34 (q)	$\mathrm{NC}H_2\mathrm{CH_3}$		J(BC) = 114.6]
	1.12 (t)	$\mathrm{NCH_2C}H_3$		
	1.28, 1.26, 1.22 (t)	$\mathrm{POCH_2C}H_3$		
2b	4.09, 3.59, 3.07 (m)[e]	$\mathrm{POC}H_2\mathrm{CH_3}$	ABC_2[e]	δ_A 199.3, δ_B 194.8, δ_C 179.7
	2.35 (q)	$\mathrm{NC}H_2\mathrm{CH_3}$		[J(AB) = 72.5, J(AC) = 80.7,
	1.53, 1.48, 1.22 (t)	$\mathrm{POCH_2C}H_3$		J(BC) = 109.3]
	−0.31 (t)	$\mathrm{NCH_2C}H_3$		
3a	8.43 (m)	CH	ABC_2	δ_A 166.3, δ_B 164.6, δ_C 147.2
	4.25, 4.09, 3.38 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 106.3, J(AC) = 143.6,
	2.28 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$		J(BC) = 112.9]
	1.32, 1.29, 1.13 (t)	$\mathrm{POCH_2C}H_3$		
3b	3.84, 3.56 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	ABC_2	δ_A 193.4, δ_B 193.1, δ_C 175.7
	1.94 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$		[J(AB) = 40.0, J(AC) = 87.0,
	1.31, 1.11, 1.09 (t)	$\mathrm{POCH_2C}H_3$		J(BC) = 107.0]
4a	7.81 (m)	CH	ABC_2	δ_A 167.7, δ_B 167.4, δ_C 147.6
	4.25, 4.03, 3.82 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 130.0, J(AC) = 139.9,
	1.32, 1.26, 1.20 (t)	$\mathrm{POCH_2C}H_3$		J(BC) = 123.7]
5a	8.59 (m)	CH	ABC	δ_A 159.2, δ_B 155.3, δ_C 141.4
	4.24, 4.10 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 113.4, J(AC) = 143.4,
	3.40 (q)	$\mathrm{NC}H_2\mathrm{CH_3}$		J(BC) = 128.4]
	1.36, 1.33, 1.30 (t)	$\mathrm{POCH_2C}H_3$		
	1.21 (t)	$\mathrm{NCH_2C}H_3$		
5b	4.20, 3.85 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	ABC	δ_A 189.1, δ_B 185.5, δ_C 172.8
	2.88, 2.58 (m)	$\mathrm{NC}H_2\mathrm{CH_3}$		[J(AB) = 85.0, J(AC) = 106.2,
	1.55, 1.51, 1.50,			J(BC) = 96.9]
	1.40, 1.37, 1.33 (t)	$\mathrm{POCH_2C}H_3$		
	0.69 (t)	$\mathrm{NCH_2C}H_3$		
5b′	4.04 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	AB_2	δ_A 185.0, δ_B 171.6
	2.70 (q)	$\mathrm{NC}H_2\mathrm{CH_3}$		[J(AB) = 90.7]
	1.35, 1.34 (t)	$\mathrm{POCH_2C}H_3$		
	0.70 (t)	$\mathrm{NCH_2C}H_3$		
6a	8.62 (m)	CH	ABC	δ_A 158.5, δ_B 152.8, δ_C 137.9
	4.31, 4.16, 4.02 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 117.5, J(AC) = 147.0,
	2.29 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$		J(BC) = 132.3]
	1.37, 1.33, 1.14 (t)	$\mathrm{POCH_2C}H_3$		
7a	8.63 (m)	CH	ABC	δ_A 166.5, δ_B 163.1, δ_C 151.4
	4.20 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 114.4, J(AC) = 133.7,
	3.54, 3.37 (m)[f]	$\mathrm{NC}H_2\mathrm{CH_3}$		J(BC) = 122.2]
	2.39 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$		
	1.33, 1.31, 1.29 (t)	$\mathrm{POCH_2C}H_3$		
	1.26 (t)	$\mathrm{NCH_2C}H_3$		
7b	8.95 (br m)	CH	ABC	δ_A 195.5, δ_B 192.3, δ_C 181.3
	4.18 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 85.0, J(AC) = 99.0,
	2.96, 2.62 (m)[g]	$\mathrm{NC}H_2\mathrm{CH_3}$		J(BC) = 98.6]
	2.33 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$		
	1.54, 1.52, 1.48			
	1.40, 1.38, 1.37 (t)	$\mathrm{POCH_2C}H_3$		
	0.66 (t)	$\mathrm{NCH_2C}H_3$		
9a	7.76 (m)	CH	ABC	δ_A 157.6, δ_B 156.3, δ_C 135.4
	4.30, 4.08 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		[J(AB) = 130.8, J(AC) = 148.6,
	1.38, 1.36, 1.20 (t)	$\mathrm{POCH_2C}H_3$		J(BC) = 148.1]
10a	4.43 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	A_3	142.3 (s)
	2.38 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$		
	1.39 (t)	$\mathrm{POCH_2C}H_3$		

[a] All complexes are $\mathrm{BPh_4}^-$ salts. [b] At room temperature in $\mathrm{(CD_3)_2CO}$. [c] Aryl-proton resonances are omitted. [d] Coupling constants in Hz; positive shift downfield from 85% $\mathrm{H_3PO_4}$. [e] In $\mathrm{CD_2Cl_2}$. [f] By decoupling of $\mathrm{CH_3}$: spin system AB, δ_A 3.45, δ_B 3.37, J(AB) = 11.6 Hz. [g] By decoupling of $\mathrm{CH_3}$: spin system AB, δ_A 2.73, δ_B 2.53, J(AB) = 14.5 Hz.

orange microcrystalline solid was isolated only with L = $\mathrm{P(OEt)_3}$, whereas an oily product which decomposes on attempted crystallization is always obtained with $\mathrm{PPh(OEt)_2}$. The spectroscopic properties of this complex support the proposed formulation. In particular, the ^{31}P-{^{1}H} NMR spectrum shows an ABC_2 multiplet, whereas the ^{1}H NMR spectrum, apart from phenyl and ethyl protons, shows a multiplet at δ 7.81 attributed to the central proton of the

Table 3 Proton NMR data for CH group in iron complexes

Complex[a]	Spin system[b] (X = H)	δ_X	Coupling constant, J/Hz AX	BX	CX
1a	A_2B_2X	11.11	−8.76	6.85	
1b	A_2B_2X	9.97	−8.50	6.42	
2a	ABC_2X[c,d]	8.24	2.95	7.25	6.33
3a	ABC_2X	8.43	3.15	6.45	6.06
4a	ABC_2X	7.81	5.30	5.32	3.91
5a	ABCX[c]	8.59	8.25	6.22	2.10
6a	ABCX	8.62	6.14	7.19	2.64
7a	ABCX[c,d]	8.63	8.22	6.09	2.21
9a	ABCX	7.76	4.65	6.40	3.31

[a] All complexes are BPh_4^- salts. [b] At room temperature in $(CD_3)_2CO$. [c] Methylene decoupled. [d] At room temperature in CD_2Cl_2.

Table 4 Carbon-13 NMR spectral data for selected iron complexes[a]

Complex[b]	δ	Assignment	Coupling constant, $^1J_{CH}$/Hz
1a[c]	237.9 (dt)	S_2CH	185 9[d]
	63.3, 62.4 (tm)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	15.9 (qm)	$\mathrm{POCH_2}C\mathrm{H_3}$	
2b[c]	177.1 (dm)	NCHS	172
	65.6 (tm)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	49.8 (tm)	$\mathrm{N}C\mathrm{H_2CH_3}$	
	16.7 (qm)	$\mathrm{POCH_2}C\mathrm{H_3}$	
	10.4 (qm)	$\mathrm{NCH_2}C\mathrm{H_3}$	
3a	182.7 (dm)	NCHS	180
	63.8, 63.0, 62.5 (tm)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	20.7 (q)	$C\mathrm{H_3C_6H_4}$	
	16.3, 16.1, 15.8 (qm)	$\mathrm{POCH_2}C\mathrm{H_3}$	
4a	168.1 (dm)	NCHO	189
	62.2, 62.0 (m)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	15.3 (m)	$\mathrm{POCH_2}C\mathrm{H_3}$	
5a	214.5 (m)	CO	
	183.3 (dm)	NCHS	183
	64.2 (m)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	53.8 (tm)	$\mathrm{N}C\mathrm{H_2CH_3}$	140
	16.1 (m)	$\mathrm{POCH_2}C\mathrm{H_3}$	
	15.7 (qm)	$\mathrm{NCH_2}C\mathrm{H_3}$	127
6a	214.6 (m)	CO	
	185.8 (dm)	NCHS	183
	64.6 (m)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	21.0 (qm)	$C\mathrm{H_3C_6H_4}$	
	16.3 (m)	$\mathrm{POCH_2}C\mathrm{H_3}$	
7a	181.2 (dm)	NCHS	179
	63.3 (m)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	53.7 (tm)	$\mathrm{N}C\mathrm{H_2CH_3}$	140
	21.2 (m)	$\mathrm{POCH_2}C\mathrm{H_3}$	
	16.5 (qm)	$\mathrm{NCH_2}C\mathrm{H_3}$	
7b[c]	179.2 (dm)	NCHS	172
	65.7 (m)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	50.5 (tm)	$\mathrm{N}C\mathrm{H_2CH_3}$	140
	21.5 (qm)	$C\mathrm{H_3C_6H_4}$	
	16.9 (m)	$\mathrm{POCH_2}C\mathrm{H_3}$	
	14.6 (qm)	$\mathrm{NCH_2}C\mathrm{H_3}$	127
9a[c]	171.1 (dm)	NCHO	180
	64.3 (m)	$\mathrm{PO}C\mathrm{H_2CH_3}$	
	16.4 (m)	$\mathrm{POCH_2}C\mathrm{H_3}$	

[a] Aryl-carbon resonances are omitted. In $(CD_3)_2CO$. [b] All complexes are BPh_4^- salts. [c] In CD_2Cl_2. [d] $^3J_{CP}$.

PhNC(H)O ligand. The multiplicity of the signal is due to coupling with the P atoms of $P(OEt)_3$, as confirmed by simulation of the spectrum using an ABC_2X model (X = H). Furthermore, the presence of the chelate formamide ligand (Scheme 1) is also confirmed by the $^{13}C-\{^1H\}$ NMR spectrum, which shows the central C atom of the PhNC(H)O ligand as a low-field signal at δ 168.1, split into a doublet of multiplets ($^1J_{CH}$ = 189 Hz) in the proton-coupled spectrum.

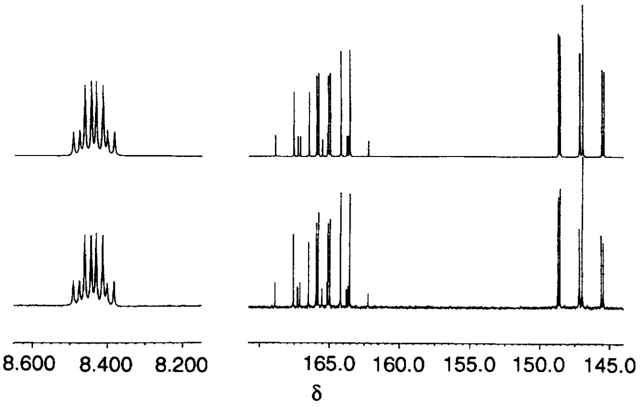


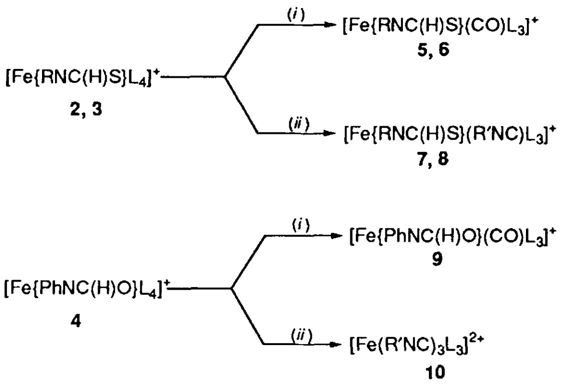
Fig. 2 Observed (bottom) and simulated (top) NMR spectra of [Fe{p-$MeC_6H_4NC(H)S$}{$P(OEt)_3$}$_4$]BPh_4 **3a** in $(CD_3)_2CO$ at 25 °C. Left: ^1H spectra of RNC(H)S proton. Right: $^{31}P-\{^1H\}$ spectra. Simulated spectra were obtained as in Fig. 1

Reactivity.—The dithioformato derivatives [$Fe(S_2CH)L_4$]BPh_4 **1a** and **1b** are quite robust complexes, and neither ligand substitution nor formation of the σ-S_2CH complex were observed even after long reaction times (48 h at 20 °C or 5–8 h in refluxing $ClCH_2CH_2Cl$) with CO, RCN, RNC and X^- (X = Cl or Br, R = aryl). Compounds **1** were also treated with a phosphite and complete substitution of the L ligands was unexpectedly observed. For example, the substitution of all four $PPh(OEt)_2$ in **1b** was observed when the complex was treated for 10 min at reflux with a slight excess of $P(OEt)_3$. Since complexes **1** seem to be inert towards ligand substitution, the above result may be explained on the basis of nucleophilic attack of the $P(OEt)_3$ or $PPh(OEt)_2$ on the carbon atom of the S_2CH ligand, to give phosphonium adducts [Fe{$S_2C(H)$-$P(OEt)_3$}{$PPh(OEt)_2$}$_4$]$^+$ or [Fe{$S_2C(H)PPh(OEt)_2$}{$P(OEt)_3$}$_4$]$^+$. The formation of such adducts, which are not isolable, may alter the ligand-substitution pattern resulting in easy phosphite substitution, as previously observed in related ruthenium derivatives.[16]

In order to confirm this hypothesis, we treated dithioformato complexes **1** with p-tolyl isocyanide in the presence of the same phosphite, varying the Fe:RNC:L molar ratio between 1:1:1 and 1:5:5. Monitoring the reaction by IR spectra, we observe, substitution of phosphite with isocyanide after 5–10 min of reflux in dichloroethane, in contrast with the non-reactivity of **1** in the absence of phosphite. We also attempted to isolate pure samples of the resulting mixed-ligand phosphite–isocyanide dithioformato complexes, but were frustrated by the formation of oily products containing a mixture of mono-, di- and tri-isocyanide derivatives (according to IR and NMR spectra) which, even after chromatographic purification, did not separate as solid products. However, the influence of free phosphite on the ligand substitution of dithioformato complexes **1** seems to be confirmed.

In contrast with the properties shown by the dithioformato compounds, the N-ethyl- and N-p-tolyl-thioformamido derivatives **2** and **3** react at room temperature with carbon monoxide and isocyanides to give monosubstituted complexes **5**–**8**, as shown in Scheme 2. Further substitution of phosphite in **2** and **3** to give disubstituted derivatives does not take place even when using an excess of ligand or reflux conditions: the only result in boiling dichloroethane is *fac*–*mer* isomerization of [Fe{EtNC(H)S}(CO){$PPh(OEt)_2$}$_3$]BPh_4.

The related formamido PhNC(H)O compound **4** also reacts with CO to give the corresponding monocarbonyl **9** as the only substituted product, whereas the reaction with isocyanides proceeds with substitution of formamide ligand, giving [Fe(p-

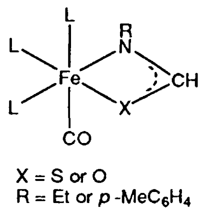


Scheme 2 L = P(OEt)$_3$ or PPh(OEt)$_2$; R = Et **5**, **7** or *p*-MeC$_6$H$_4$ **6**, **8**; R′ = *p*-MeC$_6$H$_4$. (*i*) CO; (*ii*) R′NC

MeC$_6$H$_4$NC)$_3$L$_3$]$^{2+}$ **10** as final product. The reaction of thioformamido derivatives [Fe{RNC(H)S}L$_4$]$^+$ **2** and **3** with phosphite was also studied and showed gradual substitution of all four phosphite ligands, affording a mixture of products of the type [Fe{RNC(H)S}L′$_n$L$_{4-n}$]$^+$ [L,L′ = P(OEt)$_3$ or PPh(OEt)$_2$, *n* = 1–4], as may be deduced from the ^{1}H and ^{31}P NMR spectra of the reaction product. Instead, in the related formamido complexes **4** the reaction with phosphite proceeds with substitution of the formamide RNC(H)O ligand.

The infrared spectra of the monocarbonyl complexes [Fe{RNC(H)S}(CO)L$_3$]BPh$_4$ **5** and **6** and [Fe{PhNC(H)O}(CO)L$_3$]BPh$_4$ **9** show only one ν(CO) band at 1990–2020 cm^{-1}, in both the solid state and CH$_2$Cl$_2$ solution. Furthermore, in the temperature range from −80 to +30 °C, the ^{31}P-{^{1}H} NMR spectra of all the compounds are ABC multiplets which can be simulated with the parameters in Table 2. Finally, the ^{1}H NMR spectra indicate the presence of thioformamide or formamide ligands and, apart from signals due to *N*-bonded substituents, show only one multiplet at δ 8.59–7.76, attributable to the CH resonance of the RNC(H)X ligand (X = S or O), as confirmed by the easy simulation of the spectra using an ABCX model (X = H) (Table 3).

Further support for the proposed formulation of the carbonyl complexes comes from the ^{13}C NMR spectra (Table 4), which show multiplets at δ 214.5 and 214.6 for **5a** and **6a**, respectively, attributable to the carbonyl carbon atom, and at δ 183.3 and 185.8, respectively, replaced by a doublet in the ^{1}H-coupled spectra ($^1J_{CH}$ = 183 Hz), characteristic of the CH resonance of the RNC(H)S chelate ligands. For the formamido derivative **9a**, the CH resonance appears at δ 171.1 with $^1J_{CH}$ = 180 Hz. According to these data, it therefore seems plausible to propose a *fac* geometry in solution for our monocarbonyl derivatives.



These monocarbonyls are all very stable in solution, except [Fe{EtNC(H)S}(CO){PPh(OEt)$_2$}$_3$]BPh$_4$ **5b**, which isomerizes when the solution is heated, affording the *mer* derivative **5b′**. The IR spectrum of the latter shows ν(CO) at 1970 cm^{-1}, while the ^{31}P-{^{1}H} spectrum is an AB$_2$ multiplet instead of an ABC. These data do not allow us to assign one of the two possible *mer* geometries to the complexes; only a crystal structure determination could resolve this.

The isocyanide derivatives **7** are yellow diamagnetic solids which can be obtained only with the *N*-ethylthioformamide ligand, because the related [Fe{*p*-MeC$_6$H$_4$NC(H)S}(4-MeC$_6$H$_4$NC)L$_3$]BPh$_4$ **8** are oily products which crystallize only with difficulty. The spectroscopic properties support the proposed formulation for **7a** and **7b** and, like carbonyls **5**, **6** and **9**, suggest a *fac* geometry in solution. In fact, the infrared spectra display only one band at 2128–2136 cm^{-1} attributable to ν(CN), whereas the ^{31}P-{^{1}H} NMR spectra comprise ABC multiplets, in agreement with three non-equivalent phosphorus atoms.

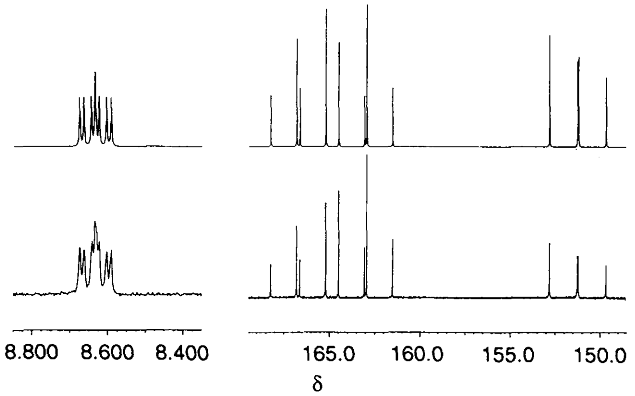
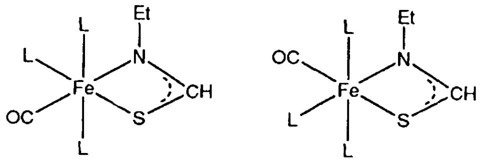
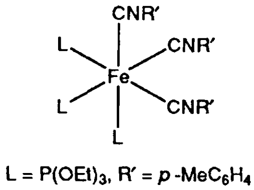


Fig. 3 Observed (bottom) and simulated (top) NMR spectra of [Fe{EtNC(H)S}(*p*-MeC$_6$H$_4$NC){P(OEt)$_3$}$_3$]BPh$_4$ **7a** in (CD$_3$)$_2$CO at 25 °C. Left: ^{1}H spectra of EtNC(H)S proton, selectively homodecoupled from NC*H*$_2$CH$_3$ protons. Right: ^{31}P-{^{1}H} spectra. Simulated spectra were obtained as in Fig. 1



In the low-field region of the ^{1}H NMR spectra the CH resonance of the thioformamide EtNC(H)S ligand appears as a complicated multiplet which, after selective homodecoupling from the CH$_2$ protons of the NEt, can be simulated using an ABCX model (Fig. 3). Furthermore, the prochiral nature of the two methylene protons of the NEt group is evidenced by the appearance of two multiplets at δ 3.54 and 3.37 for **7a** and at δ 2.96 and 2.62 for **7b**. Selective decoupling of these protons from CH$_3$ results in an AB quartet with proton–proton coupling constants $^2J_{AB}$ of 11.6 (**7a**) and 14.5 Hz (**7b**), characteristic of prochiral CH$_2$ protons.[17,18] Lastly, in the coupled ^{13}C NMR spectra, the CH resonance of the EtNC(H)S ligand appears as a doublet of multiplets at δ 179.2 ($^1J_{CH}$ = 172 Hz) for **7b**, while the methyl and methylene carbon atoms of the NEt group appear as a quartet of multiplets (δ 14.6) and a triplet of multiplets (δ 50.5, J_{CH} = 140 Hz), in agreement with the proposed formulation.

The chelate formamide ligand was also substituted in [Fe{PhNC(H)O}{P(OEt)$_3$}$_4$]BPh$_4$ by *p*-tolyl isocyanide, affording [Fe(*p*-MeC$_6$H$_4$NC)$_3${P(OEt)$_3$}$_3$][BPh$_4$]$_2$ **10a** the spectroscopic properties of which seem to indicate the *fac* structure shown. The ^{31}P-{^{1}H} NMR spectrum showed a sharp singlet in the temperature range −80 to +30 °C, indicating the presence of three magnetically equivalent phosphorus atoms, whereas in the ν(CN) region of the infrared spectrum only two bands at 2193 and 2063 cm^{-1} (CH$_2$Cl$_2$) are present, as expected for the structure shown.



Acknowledgements

The financial support of Ministero dell'Università e della Ricerca Scientifica e Tecnologica and Consiglio Nazionale delle Ricerche, Rome, is gratefully acknowledged. We thank Daniela Baldan for technical assistance.

References

1 (*a*) G. Jia and D. W. Meek, *Inorg. Chem.*, 1991, **30**, 1953; (*b*) S. J. Schauer, D. P. Eyman, R. J. Bernhardt, M. A. Wolff and L. M. Mallis, *Inorg. Chem.*, 1991, **30**, 570 and refs. therein; (*c*) W. D. Jones, V. L. Chandler and F. J. Feher, *Organometallics*, 1990, **9**, 164; (*d*) D. P. Klein, G. M. Kloster and R. G. Bergman, *J. Am. Chem. Soc.*, 1990, **112**, 2022; (*e*) C. Bianchini, D. Masi, C. Mealli, A. Meli and M. Sabat, *Organometallics*, 1985, **4**, 1014.

2 (*a*) A. Mishra and U. C. Agarwala, *Inorg. Chim. Acta*, 1988, **145**, 191; (*b*) J. F. Leboeuf, J. C. Leblanc and C. Moise, *J. Organomet. Chem.*, 1987, **335**, 331; (*c*) M. I. Bruce, M. G. Humphrey, A. G. Swincer and R. C. Wallis, *Aust. J. Chem.*, 1984, **37**, 1747; (*d*) D. J. Darensbourg, A. Rakicki and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1981, **103**, 3223; (*e*) R. D. Adams, N. M. Golembeski and J. P. Selegue, *J. Am. Chem. Soc.*, 1981, **103**, 546; (*f*) H. Werner and W. Bertleff, *Chem. Ber.*, 1980, **113**, 267; (*g*) G. Gattow and W. Behrendt, in *Topics in Sulfur Chemistry*, ed. A. Senning, Georg Thieme, Leipzig, 1977, p. 2; (*h*) P. V. Yaneff, *Coord. Chem. Rev.*, 1977, **23**, 183.

3 (*a*) S. Komiya and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 748; (*b*) A. Albinati, A. Musco, G. Carturan and G. Strukul, *Inorg. Chim. Acta*, 1976, **18**, 219; (*c*) F. G. Mores, R. W. M. Tenhoedt and J. P. Langhout, *J. Organomet. Chem.*, 1974, **63**, 93; (*d*) I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, 1974, **66**, 161; (*e*) R. O. Harris, L. S. Sadavoy, S. C. Nyburg and F. H. Pickhard, *J. Chem. Soc., Dalton Trans.*, 1973, 2646; (*f*) A. Gusev, A. Kalinin and Y. Struchkov, *J. Struct. Chem. (Engl. Transl.)*, 1973, **14**, 804; (*g*) F. W. Einstein, E. Enwall, N. Flitcroft and J. M. Leach, *J. Inorg. Nucl. Chem.*, 1972, **34**, 885; (*h*) A. Palazzi, L. Busetto and M. Graziani, *J. Organomet. Chem.*, 1971, **30**, 273; (*i*) V. G. Albano, P. L. Bellon and G. Ciani, *J. Organomet. Chem.*, 1971, **31**, 75; (*j*) D. Commereuc, I. Douec and G. Wilkinson, *J. Chem. Soc. A*, 1970, 1771.

4 A. Sahajpal and S. D. Robinson, *Inorg. Chem.*, 1979, **18**, 3572; S. D. Robinson and A. Sahajpal, *Inorg. Chem.*, 1977, **16**, 2718, 2722; L. D. Brown, S. D. Robinson, A. Sahajpal and J. A. Ibers, *Inorg. Chem.*, 1977, **16**, 2728; A. D. Harris, S. D. Robinson, A. Sahajpal and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 1327.

5 P. M. Treichel and D. C. Molzahn, *Inorg. Chim. Acta*, 1979, **36**, 267.

6 (*a*) G. Albertin, S. Antoniutti and E. Bordignon, *J. Am. Chem. Soc.*, 1989, **111**, 2072; (*b*) G. Albertin, S. Antoniutti and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1992, 1111; (*c*) G. Albertin, S. Antoniutti, E. Del Ministro and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1992, 3203.

7 R. Rabinowitz and J. Pellon, *J. Org. Chem.*, 1961, **26**, 4623.

8 R. Appel, R. Kleinstück and K. D. Ziehn, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 132.

9 D. F. Evans, *J. Chem. Soc.*, 1959, 2003; R. A. Bailey, *J. Chem. Educ.*, 1972, **49**, 297.

10 G. Albertin, S. Antoniutti, M. Lanfranchi, G. Pelizzi and E. Bordignon, *Inorg. Chem.*, 1986, **25**, 950.

11 F. N. Tebbe, P. Meakin, J. P. Jesson and E. L. Muetterties, *J. Am. Chem. Soc.*, 1970, **92**, 1068.

12 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

13 D. Miguel, V. Riera, J. A. Miguel, F. Diego, C. Bois and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, 1990, 2719.

14 C. Bianchini, P. Innocenti, A. Meli, A. Orlandini and G. Scapacci, *J. Organomet. Chem.*, 1982, **233**, 233.

15 R. M. Silverstein, C. G. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1974.

16 T. V. Ashworth, E. Singleton and M. Laing, *J. Chem. Soc., Chem. Commun.*, 1976, 875; T. V. Ashworth, D. J. A. DeWaal and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 1981, 78.

17 F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1969.

18 R. J. Abraham and P. Loftus, *Proton and Carbon-13 NMR Spectroscopy*, Heyden, London, 1980.

Received 14*th January* 1994; *Paper* 4/00233D