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Preliminary Communication

Carbene complexes of Fe^{II} prepared from a precursor complex containing a remote nucleophilic heteroatom

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Abstract

The complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl]$ reacts with isothiazol-5-yllithium to form $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{CCHCHNS})]$ (1). Treatment of 1 with CF_3SO_3H or CF_3SO_3Me gives the cationic organo(thio)carbene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{CCHCHN(R)S})][SO_3CF_3]$ (R = H(2); Me(3)). Determination of the crystal structure of complex 3 has revealed an Fe–carbene carbon bond length of 1.952(3) Å.

Key words: Iron; Carbene; Crystal structure; Thiazolinylidene

It has previously been shown that lithiated thiazoles readily react with suitable transition metal complexes to give thiazolyl complexes that, upon protonation or alkylation of the N-atom give stable amino(thio)carbene complexes [1–3]. In these thiazolinylidene complexes the N-atom is in an α-position with respect to the coordinated carbene carbon (Scheme 1), as is typical for known cyclic and acyclic aminocarbene complexes [4,5].

We have found that isothiazole, prepared as previously described [6] react analogously to give heterocarbene complexes. However, the carbene complexes derived from isothiazolyl complexes [7*] differ in two important respects from those derived from thiazolyl complexes (Scheme 1): (i) the nucleophilic N-atom is in the β- rather than α-position with respect to the coordinated carbon atom [8*], and (ii) organo(thio)- instead of amino(thio)carbene complexes are obtained. Öfele and co-workers [9] have prepared similar carbene complexes by the interaction of 1,2-dimethyl-4-pyrazolium iodide with anionic Group 6 metal complexes, but their approach was different in that the β-nitrogen was already alkylated before the reaction with the metal species and furthermore the ligand contains a stabilizing alkylated N-atom in the α-position, which is the case in known heterocyclic-carbene compounds.

The reaction of $[(\eta\text{-}C_5H_5)Fe(CO)_2Cl]$ with one molar equivalent of isothiazole-5-yllithium [7*] in THF at −78°C gives the neutral complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{CCHCHNS})]$ (1) in 52% yield (Scheme 2). Complex 1 was obtained as a brown oil after purification by column chromatography (Florisil; diethyl ether–hexane; −10°C) and has been fully characterised spectroscopically (Table 1). The oil decomposes slowly and was not analyzed.

The isothiazolyl complex 1 readily reacts with one equivalent of CF_3SO_3H or CF_3SO_3Me in CH_2Cl_2 at 0°C to give the organo(thio)carbene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{CCHCHN(R)S})][SO_3CF_3]$ (R = H (2) or Me (3)), which to our knowledge are the first examples of heterocarbene complexes formed from a precursor in which the nucleophilic heteroatom (N in this case) is not directly bonded to the coordinated carbon. After filtration through anhydrous $MgSO_4$ the solutions were concentrated, pentane was added, and the solutions were kept at −25°C to deposit dark brown, analytically pure (C, H, N S), crystals of the isothiazolinyl complexes 2 and 3 in 36 and 41% yields, respectively.

The $^{13}C\text{-}\{^1H\}$ NMR data (Table 1) for compounds 2 and 3 show that the C^5 carbene carbon resonances appear at δ 189.1 and 189.9, respectively, and are shifted downfield with respect to the C^5 resonance for compound 1. This downfield shift of the C^5 resonances is similar to that found for the analogous thiazolinylidene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{CNHCMeCHS})][SO_3CF_3]$ [3], and is indicative of carbene formation. Also indicative of carbene formation are the positions of the ν(CO) absorption bands of complexes 2 and 3 which appear at higher energies than those observed for complex 1 [3].

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* Reference number with asterisk indicates a note in the list of references.

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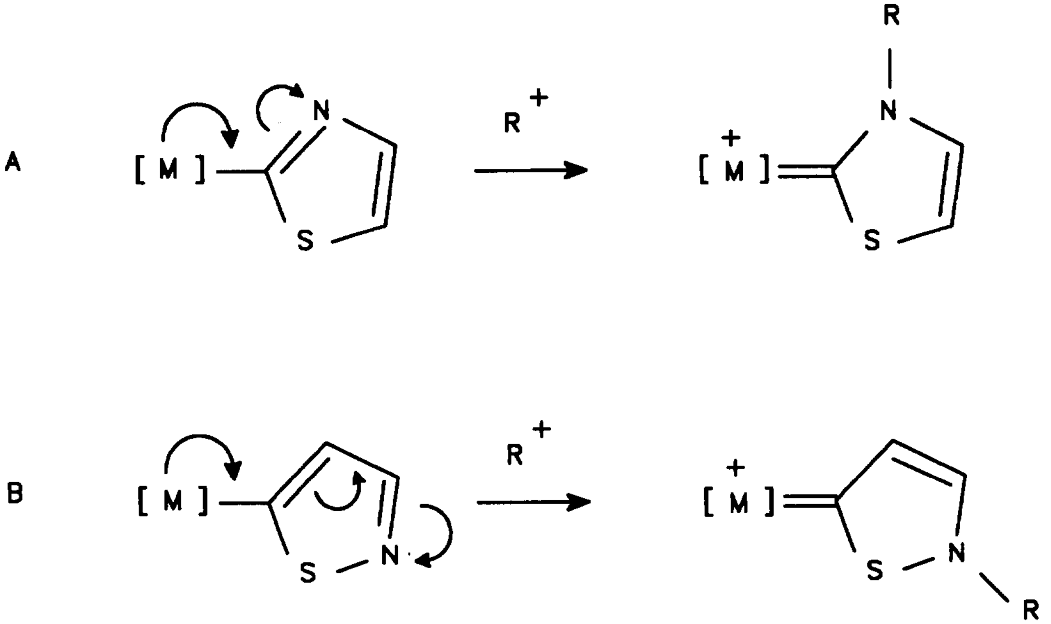


Scheme 1. Formation of a carbene complex from (A) a thiazolyl complex and (B) an isothiazolyl complex. [M] = suitable transition metal complex; $R^+ = H^+$ or Me^+.

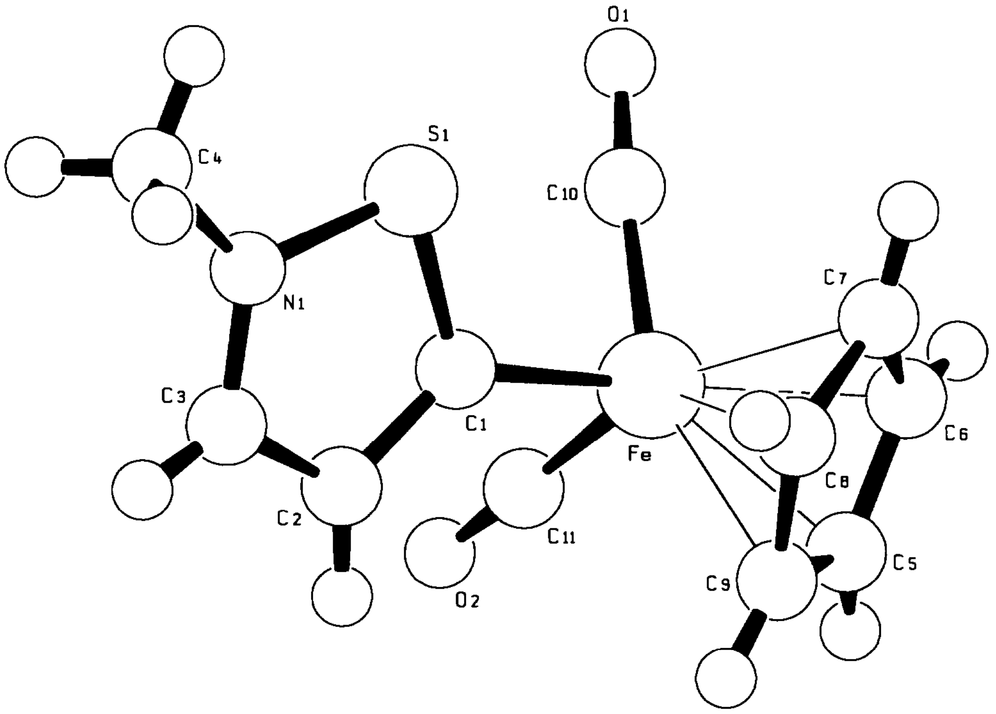
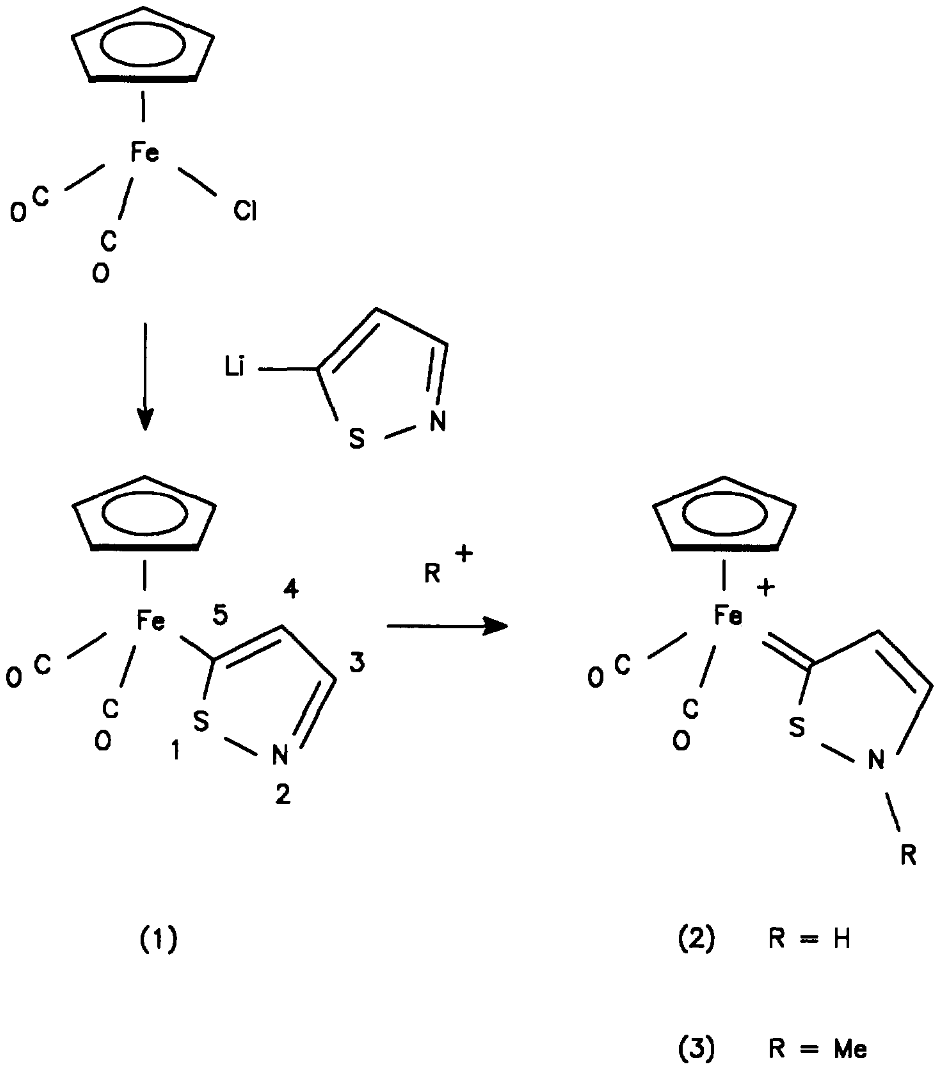


Fig. 1. Molecular structure of the cation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{CCHCHN(Me)S})][SO_3CF_3]$ (3) (SCHAKAL 88 [11]). Selected bond lengths (Å) and angles (°): Fe–C(1) 1.952(3), Fe–C(10) 1.778(4), Fe–C(11) 1.773(3), Fe–C_5H_5 (average) 2.089, C(1)–C(2) 1.388(4), C(2)–C(3) 1.400(5), C(3)–N(1) 1.311(5), N(1)–S(1) 1.674(3), S(1)–C(1) 1.680(3); Fe–C(1)–S(1) 120.5(2), Fe–C(1)–C(2) 131.4(2), S(1)–C(1)–C(2) 108.0(2).

The X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{\text{CCHCHN(Me)S}})][SO_3CF_3]$ (3) (Fig. 1) unambiguously shows the N-atom (N(1)) to be in the β-position with respect to the carbene carbon (C(1)) [10*]. The Fe–C(1) bond length of 1.952(3) Å is similar to that of 1.947(3) Å observed in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{\text{CNHCMeCHS}})][SO_3CF_3]$ [3].

We are currently investigating the preparation of carbene complexes in which the remote nucleophilic heteroatom (O, N or S) in the precursor complex, obtained after trans metallation, is (i) part of an acyclic ligand, (ii) located outside a coordinated ring system, and (iii) separated from the coordinated carbon by several bonds.



Scheme 2. Route to complexes 1–3.

TABLE 1. Spectroscopic and physical data for complexes 1–3

Compound	M.p./°C [a]	NMR [b]		MS [c]		ν_{CO} [d]/cm^{-1}
		^1H	^{13}C-{^1H}	m/z	Fragment ion	
1	(oil)	8.61 (s, 1H, H^3),	214.4 (CO),	261	$[CpFe(CO)_2(\overline{CCHCHNS})]^+$	2036
		6.99 (s, 1H, H^4),	164.0 (C^5),	233	$[CpFe(CO)(\overline{CCHCHNS})]^+$	1986
		4.16 (s, 5H, C_5H_5)	157.3 (C^3),	205	$[CpFe(\overline{CCHCHNS})]^+$	
			134.9 (C^4)	178	$[CpFe(C_2HS)]^+$	
			85.6 (C_5H_5)	121	$[CpFe]^+$	
				56	$[Fe]^+$	
2	91–92	14.48 (br. s, 1H, NH),	211.5 (CO)	261	$[CpFe(CO)_2(\overline{CCHCHNS})]^+$	2046
		8.56 (d, 1H, $J(H^3$-$H^4)$2.0, H^3),	189.1 (C^5),	233	$[CpFe(CO)(\overline{CCHCHNS})]^+$	2001
		7.41 (d, 1H, $J(H^4$-$H^3)$1.9, H^4),	150.4 (C^3),	205	$[CpFe(\overline{CCHCHNS})]^+$	
		5.22 (s, 5H, C_5H_5)	134.5 (C^4),	178	$[CpFe(C_2HS)]^+$	
			87.1 (C_5H_5)	121	$[CpFe]^+$	
				56	$[Fe]^+$	
3	85–86	8.56 (d, 1H, $J(H^3$–$H^4)$2.6, H^3),	211.4 (CO),	276	$[CpFe(CO)_2(\overline{CCHCHN(CH_3)S})]^+$	2046
		7.31 (d, 1H, $J(H^4$–$H^3)$2.6, H^4),	189.9 (C^5),	261	$[CpFe(CO)_2(\overline{CCHCHNS})]^+$	2004
		5.25 (s, 5H, C_5H_5),	153.6 (C^3),	233	$[CpFe(CO)(\overline{CCHCHNS})]^+$	
		4.17 (s, 3H, NCH_3)	134.7 (C^4),	205	$[CpFe(\overline{CCHCHNS})]^+$	
			87.2 (C_5H_5),	186	$[Cp_2Fe]^+$	
			40.5 (NCH_3)	121	$[CpFe]^+$	
				56	$[Fe]^+$	

[a] Recorded on a standardised Büchi 535 apparatus.

[b] All spectra recorded on a Varian VXR 200 FT at 298 K; ^1H NMR at 200.6 MHz and ^{13}C-{^1H} at 50.3 MHz; 1 in C_6D_6, 2 and 3 in CD_2Cl_2.

[c] Mass spectra recorded on a Finnigan Mat 8200 instrument (70 eV); Cp = $C_5H_5^-$.

[d] Solution spectra recorded in hexachlorobutadiene on a Perkin-Elmer 841 spectrophotometer.

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8 The N-atom in the precursor 1 could also be considered to be in a γ-position with respect to the coordinated carbon if one takes account the formal electron movement in the conjugated carbon chain upon reaction with an electrophile (Scheme 1).

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10 *Crystal data for 3*: $C_{12}H_{10}F_3NO_5S_2Fe$, $M = 425.18$, $P2_1/c$ (no. 14), $a = 8.5188(6)$, $b = 14.211(2)$, $c = 13.345(12)$ Å, $\beta = 91.69(68)°$, $V = 1613.50$ Å^3, $Z = 4$, $F(000) = 856$, $R = 0.053$ for 3916 reflections with $F_o > 4\sigma(F_o)$, $R = 0.063$ for all 4678 reflections (Enraf-Nonius CAD-4 diffractometer Mo Kα). The structure was refined using the program SHELXL-93 by G.M. Sheldrick, University of Göttingen, Germany, 1993. All crystal data may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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