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The cleavage of coordinated organoisothiocyanates to give heteronuclear clusters containing organoisocyanides as ligands

Preparation, spectra and structure of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)\{\mu_3\text{-}CNC(O)C_6H_5\}]$, $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)(CNC_6H_4Me\text{-}4)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CO)]$, and related complexes[1]

Anthony R. Manning [a,*], Liam O'Dwyer [a], Patrick A. McArdle [b], Desmond Cunningham [b]

[a] *Department of Chemistry, University College, Belfield, Dublin 4, Ireland*
[b] *Department of Chemistry, University College, Galway, Ireland*

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Abstract

Two equivalents of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ cleave the coordinated C–S bond of $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}SCNR)]$ complexes to give clusters having the general formulae $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(S)(CNR)]$, I. Those where RNC = (a) MeNC and (b) $4\text{-}Me_2NC_6H_4NC$ exist in both the solid state and in solution as the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)(CNR)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CO)]$ isomer, I^I. Those where R = (f) MeC(O)NC, (g) $4\text{-}Me_2NC_6H_4C(O)NC$ and (h) $C_6H_5C(O)NC$ exist as the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ isomer, I^{II}, and those where RNC = (c) $4\text{-}MeC_6H_4NC$, (d) C_6H_5NC and (e) $4\text{-}ClC_6H_4NC$ exist as a mixture of I^I and I^{II} in fluxional equilibrium in solution with the proportion of I^{II} increasing with increasing electron-withdrawing ability of R. Variable temperature ^{1}H-NMR spectroscopy shows that apart from the $I^I = I^{II}$ interconversion ($\Delta G^* =$ ca. 77–88 kJ mol^{-1}), the I^I isomer undergoes a further fluxional process which inverts the configuration at Fe ($\Delta G^* =$ ca. 65 kJ mol^{-1}). All I react with $MeOSO_2CF_3$ to give salts of the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)R\}]^+$ cations except for Ig which is alkylated at the NMe_2 group to give $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CNC(O)C_6H_4NMe_3]^+$. The new complexes are characterized by IR and NMR spectroscopy, and by X-ray crystallography for $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)(CNC_6H_4Me\text{-}4)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CO)]$, Ic, and $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)\{\mu_3\text{-}CNC(O)C_6H_5\}]$, Ih. In both the structure is based on a $FeCo_2$ triangle capped on one face by a μ_3-S ligand and on the other by a μ_3-CNC(O)Ph (Ih) or μ_3-CO (Ic) ligand with S and CO are disordered in Ic. In both cases the C ligand acts as a 2e donor in these 48e complexes. The bridging isocyanide ligand is bent at N indicating that it is acting as a strong electron acceptor, unlike the μ_3-CNMe ligand in $[Ni_3(Ph_2PCH_2PPh_2)_2(CNMe)_2(\mu_3\text{-}I)(\mu_3\text{-}CNMe)]^+$ which is almost linear and probably only a weak acceptor but a strong donor. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organoisothiocyanates; Heteronuclear clusters; Organoisocyanides; Fluxionality; μ_3-Isocyanides

1. Introduction

The suggestion that a coordinated η^2-CS_2 ligand could be cleaved by a metal complex which is potentially electron-deficient to give a $MM'_2(\mu_3\text{-}S)(\mu_3\text{-}CS)$ cluster has been confirmed by the reaction of $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}$

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* Corresponding author. Fax: +353 1 7062127; e-mail: armannin@ollamh.ucd.ie

[1] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday.

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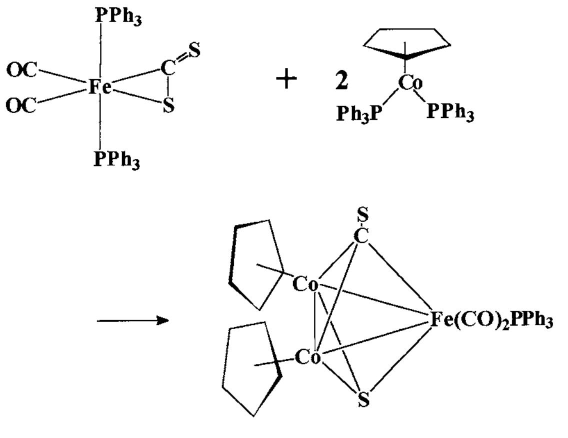
Table 1
Analytical data for the compounds described in the text

Compound	Analyses[a]				
R	Mp (°C)[b]	%C	%H	%N	%S
$[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)(CNR)\}(\mu_3\text{-}S)]$					
Me, (Ia)	dec. 159	55.1 (55.3)	4.0 (4.0)	1.8 (2.0)	4.6 (4.6)
4-$Me_2NC_6H_4$, (Ib)	dec. 72	57.8 (58.5)	4.6 (4.5)	3.5 (3.5)	3.7 (4.0)
4-$CH_3C_6H_4$, (Ic)	dec. 179	58.6 (59.1)	4.3 (4.2)	1.8 (1.8)	4.6 (4.2)
C_6H_5, (Id)	dec. 172	58.5 (58.6)	4.0 (4.0)	2.0 (1.9)	4.0 (4.2)
4-ClC_6H_4, (Ie)	dec. 207	56.2 (56.1)	3.8 (3.7)	1.8 (1.8)	3.8 (4.0)
MeC(O)[c], (If)	—				
4-$Me_2NC_6H_4C(O)$, (Ig)	>250	57.9 (58.0)	4.2 (4.2)	3.1 (3.4)	3.3 (3.9)
$C_6H_5C(O)$, (Ih)	>250	58.6 (58.1)	4.0 (3.9)	1.9 (1.8)	4.2 (4.1)
$[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2\ PPh_3\}\{\mu_3\text{-}CN(Me)R\}][SO_3CF_3]$					
Me, $[IIa]^+$	>250	46.6 (47.5)	3.6 (3.6)	1.5 (1.6)	7.8 (7.5)
4-$Me_2NC_6H_4$ (+C_6H_6[d]), $[IIb]^+$	>250	53.7 (54.3)	4.8 (4.7)	2.9 (2.8)	6.0 (6.4)
4-$CH_3C_6H_4$, $[IIc]^+$	>250	52.0 (51.3)	3.8 (3.7)	1.5 (1.5)	7.2 (6.8)
C_6H_5, $[IId]^+$	>250	49.6 (50.8)	3.5 (3.6)	1.5 (1.5)	7.6 (7.0)
4-ClC_6H_4 (+$2H_2O$), $[IIe]^+$	>250	47.3 (47.1)	3.7 (3.6)	1.2 (1.4)	
4-$Me_3NC_6H_4C(O)$[e], $[IIg]^+$	>250	68.4 (67.1)	4.9 (5.0)	3.0 (2.4)	3.1 (2.8)
$C_6H_5C(O)$, $[IIh]^+$	>250	49.9 (49.8)	3.6 (4.4)	1.4 (1.5)	7.1 (6.7)

[a] Found (calculated).
[b] dec., decomposes without melting.
[c] Compound too unstable to analyze.
[d] Confirmed by NMR spectroscopy.
[e] $[BPh_4]^-$ salt with methylation at NMe_2 (see text).

SCS)] with two moles of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ to give $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ (*i*) [1].



(*i*)

As an extension of this reaction, a $Fe^0\{\eta^2\text{-}(C\text{–}S)\text{-}SCNR\}$ complex would be expected to give a related cluster containing CNR ligand in place of the CS. The present paper confirms this prediction. It gives the spectroscopic properties of the resultant $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)(S)(CNR)\}]$ clusters including a study of their fluxional behavior, describes their reactions with electrophiles, and reports the structures of two typical examples as determined by X-ray diffraction. There has been a preliminary communication of this work [2].

2. Experimental details

Literature methods or variants thereof were used to prepare MeC(O)NCS [3], $C_6H_5C(O)NCS$ [3], 4-$Me_2NC_6H_4C(O)NCS$ [3], $[Fe(PPh_3)_3(CO)_2]$ [4], $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}SCNR)]$ {RNCS = (a) MeNCS, (b) 4-$Me_2NC_6H_4NCS$, (c) 4-MeC_6H_4NCS, (d) C_6H_5NCS, (e) 4-ClC_6H_4NCS, (f) MeC(O)NCS, (g) 4-$Me_2NC_6H_4C(O)NCS$, (h) $C_6H_5C(O)NCS$} [5], and $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ [6]. Other chemicals were purchased.

All reactions were carried out at room temperature in dried and deoxygenated solvents under an atmosphere of nitrogen unless it is stated otherwise. They were monitored by IR spectroscopy where appropriate.

IR spectra were run on a Perkin Elmer 1720 or a Mattson Galaxy FTIR 3000 spectrometer, and NMR spectra on a JEOL JNM-GX 270 spectrometer. Elemental analyses were determined by the Microanalytical Laboratory at University College Dublin.

2.1. Reaction of $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}SCNR)]$ with $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$

Solid $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}SCNR)]$ (3.86 mmol) was added to a solution of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ (5 g, 7.72 mmol) in benzene (100 cm^3). The mixture was stirred for 5 h, during which time its color changed from red to green. It was filtered, its volume reduced to 10 cm^3 at

Table 2
IR spectra (1000–2200 cm^{-1}) of the [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)(CNR)}(μ_3-S)] compounds described in the text

	Absorption bands[a]					
	ν(CN)	ν(CO)	Others[b]	ν(CN)[c]	ν(CO)[c]	ν(μ_3-CO)[c]
[{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)(CNR)}(μ_3-S)]						
Me, (Ia)	2143 (6.2)	1919 (10)	1640 (6.1)	2135 (10)	1914 (10)	1642 (6.5)
4-Me$_2$NC$_6$H$_4$, (Ib)	2083 (9.4)	1892 (10)	1672 (6.5)	2092 (10)	1973 (sh)	1643 (6.0, br)
				2041 (sh)	1913 (9.4)	
4-CH$_3$C$_6$H$_4$, (Ic)	2063 (7.1)	1898 (10)	1676 (6.6)	2081 (10)	1981 (sh)	1674 (4.3, br)
	2035 (5.5)		1658 (5.8)	2044 (4.6)	1904 (8.3)	
C$_6$H$_5$, (Id)	2069 (0.9)[d]	1967 (7.4)	1622 (2.0)	2077 (10)	1973 (sh)	1654 (4.4, br)
		1901 (10)	1562 (4.2)	2037 (sh)	1914 (6.8)	
4-ClC$_6$H$_4$, (Ie)	2062 (0.8)[d]	1965 (7.9)	1599 (3.2)	2071 (7.8)	1964 (6.7)	1658 (4.8)
		1896 (10)	1549 (6.9)		1908 (10)	
MeC(O), (If)[e]					1989 (10)	
					1939 (7.0)	
4-Me$_2$NC$_6$H$_4$C(O), (Ig)	1977 (10)	1479 (6.4)			1988 (10)	
		1917 (8.8)	1271 (6.2)		1937 (7.6)	
C$_6$H$_5$C(O), (Ih)		1979 (9.5)	1465 (m,10)		1991 (10)	
		1927 (10)	1266 (7.0)		1941 (7.8)	
[{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S) {μ_3-CN(Me)R}][SO$_3$CF$_3$]						
Me, [IIa]$^+$		1990 (10)	1495 (1.9)		1998 (9.8)	
		1944 (10)			1948 (10)	
4-Me$_2$NC$_6$H$_4$, [IIb]$^+$		2009 (10)			2015 (10)	
		1956 (9.6)			1965 (9.6)	
4-CH$_3$C$_6$H$_4$, [IIc]$^+$		1990(10)	1358 (3.1)		1999 (10)	
		1942 (9.7)			1949 (9.7)	
C$_6$H$_5$, [IId]$^+$		1988 (10)	1344 (3.0)		1998 (10)	
		1944 (9.8)			1948 (9.9)	
4-ClC$_6$H$_4$, [IIe]$^+$		2009 (10)	1307 (5.0)		2013 (10)	
		1952 (9.4)			1952 (9.6)	
4-Me$_2$NC$_6$H$_4$C(O), [IIg]$^+$		2009 (10)			2021 (10)	
		1961 (7.9)			1979 (7.6)	
C$_6$H$_5$C(O)[f], [IIh]$^+$		2005 (10)			2001 (10)	
		1952 (8.1)			1955 (7.7)	

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses. Spectra run in KBr discs unless it is stated otherwise.

[b] Absorption bands due to ν(μ_3-CO), ν(μ_3-CN), acyl ν(CO), and ν(μ_3-CN(Me)R). See text.

[c] Spectra run in CHCl$_3$ solution.

[d] Source uncertain. See text.

[e] Very unstable. See text.

[f] [BPh$_4$]$^-$ salt.

reduced pressure, and this chromatographed on an alumina column (Merck 1097). Dichloromethane–tetrahydrofuran mixtures (9:1) eluted a green band. This was evaporated to dryness and the residue recrystallized from ethanol–ether or tetrahydrofuran–hexane mixtures to give dark green crystals of [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)(S)(CNR)}] complexes, I, in 65–70% yields except where R = MeC(O) which decomposed during work-up.

2.2. Reactions of [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)(S)(CNR)}], I, with MeOSO$_2$CF$_3$

Solutions of [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)(S)(CNR)}] (0.36 mmol, ca. 0.25 g) in benzene (20 cm^3) were treated with MeOSO$_2$CF$_3$ (0.3 g, 1.8 mmol). Dark solids precipitated immediately. They were filtered off, washed with benzene and hexane, and dried. They required no further purification, and were identified as [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)(μ_3-S)(μ_3-CN(Me)R)}][SO$_3$CF$_3$] salts, [II][SO$_3$CF$_3$], except where R = 4-Me$_2$NC$_6$H$_4$C(O) when the product was found to be [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)(μ_3-S)(μ_3-CNC(O)C$_6$H$_4$NMe$_3$-4)}][SO$_3$CF$_3$]. In all cases the product yields were 70% or better. Similar products were obtained with EtOSO$_2$CF$_3$, but these are not described in detail.

Table 3
NMR spectral data[a,b] for the compounds described in the text

R	Resonances[c]					
	C_5H_5 (I^I)[a]	C_5H_5 (I^{II})[a]	R[a]	C_5H_5 (I^I)[b]	C_5H_5 (I^{II})[b]	Others[b]
[{Co(η-C_5H_5)}$_2${Fe$(CO)_2(PPh_3)$(CNR)}(μ_3-S)][d]						
Me, (Ia) (273 K)	4.51, 4.62		Me = 2.18	83.98, 84.33		
Me, (Ia) (323 K)	4.57		Me = 2.33			
4-$Me_2NC_6H_4$, (Ib) (293 K)	4.59, 4.75		Me_2N = 2.27			
4-$Me_2NC_6H_4$, (Ib) (293 K)	4.69		Me_2N = 2.31			
4-$CH_3C_6H_4$, (Ic) (293 K)	4.49, 4.68	4.61	4-Me = 1.91(I^I), 2.2 (I^{II})	84.53, 86.27	85.45	
4-$CH_3C_6H_4$, (Ic) (333 K)	4.60		4-Me = 1.96			
C_6H_5, (Id) (273 K)	4.46, 4.69	4.57		84.20, 85.08	84.7	
C_6H_5, (Id) (328 K)	4.6 (br)					
4-ClC_6H_4, (Ie) (273 K)	4.44, 4.69	4.52		84.66, 86.79	86.64	
4-ClC_6H_4, (Ie) (333 K)	4.56					
4-$Me_2NC_6H_4$C(O), (Ig)		4.70	4-Me_2N = 2.48		85.40	4-Me_2N = 39.8, acyl = 153.4, *C*O = 216.7[h]
C_6H_5C(O), (Ih)		4.69			85.55	
[{Co(η-C_5H_5)}$_2${Fe$(CO)_2(PPh_3)$}(μ_3-S){μ_3-CN(Me)R}][BPh_4][e]						
Me[f], [Ia]$^+$		4.43	Me = 4.43		87.4	Me = 53.9
4-$Me_2NC_6H_4$, [IIb]$^+$		4.79	Me = 4.58, 4-Me_2N = 2.81		87.2	
4-$CH_3C_6H_4$, [IIc]$^+$		4.64	Me = 4.59, 4-Me = 2.47		86.7	Me = 56.6, CO = 212.2[h]
C_6H_5, [IId]$^+$		4.84	Me = 4.64		86.7	Me = 56.9
4-ClC_6H_4, [IIe]$^+$		4.88	Me = 4.71		86.8	
4-$Me_2NC_6H_4$C(O)[g], [IIg]$^+$		5.21	4-Me_3N = 3.06		88.1	4-Me_3N = 57.6
C_6H_5C(O), [IIh]$^+$		4.89	Me = 4.55		86.9	

[a] All spectra were run at 293 K unless it is stated otherwise. They contain ^1H resonances due to the PPh_3 ligand and where appropriate, the aryl protons of the RNC ligand and $[BPh_4]^-$. These are not included.

[b] ^{13}C spectra were not of good quality. Only C_5H_5 resonances could be identified in all spectra apart from the aryl resonances.

[c] Chemical shifts in ppm downfield from $SiMe_4$ as an internal standard. Integrations are as required by the formulae. Isomer ratios are given in Table 6.

[d] Spectra run in $CD_3C_6D_5$ solution.

[e] Spectra run in $(CD_3)_2CO$ solution unless stated otherwise.

[f] $[SO_3CF_3]^-$ as anion.

[g] Spectrum run in CD_3CN solution.

[h] Doublet with $J = 16$ Hz in both cases.

Anion exchange was brought about when required by stirring [II][SO_3CF_3] with an excess of $NaBPh_4$ in the minimum volume of ethanol to effect their dissolution. Dark green [II][BPh_4] precipitated, and were worked-up as described above (yields > 90%).

The analyses and melting points of the various products are listed in Table 1, their IR spectra in Table 2, and their NMR spectra in Table 3.

2.3. The structure of [{Co(η-C_5H_5)}$_2${Fe(CO)(CNC$_6H_4$Me-4)(PPh_3)}(μ_3-S)(μ_3-CO)], Ic

The crystal was grown from a tetrahydrofuran–hexane mixture.

The structure was solved by direct methods, SHELXS-86 [7], and refined by full matrix least squares using SHELXL-97 [8]. SHELX operations were rendered paperless using ORTEX which was also used to obtain the drawings [9]. Data were corrected for Lorentz and polarization effects, but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The triply-bridging CO and S ligands were disordered over the two faces of the metal triangle in a 40:60 ratio. The cyclopentadienyl ligands were disordered over two sites with equal site occupancy and were refined as rigid pentagons. The non-hydrogen atoms were refined anisotropically. All calculations were carried out on a Pentium PC.

Crystal data are given in Table 4, and selected bond lengths and bond angles in Table 5. Heavy atom coordinates, complete lists of bond lengths and bond angles, anisotropic displacement parameters for heavy atoms, and hydrogen atom coordinates and isotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre together with a list of observed and calculated structure factors.

The structure and atom labeling for the two isomers of Ic are shown in Figs. 1 and 2. Views of both isomers along an axis from Fe to the center of the Co–Co bond are shown in Fig. 3.

Table 4
Crystal data and structure refinement for [{Co(η-C_5H_5)}$_2${Fe(CO)(CNC_6H_4Me)(PPh_3)}(μ_3-S)(μ_3-CO)], Ic, and [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$(PPh_3)}(μ_3-S){μ_3-CNC(O)C_6H_5}], Ih

	Ic	Ih
Empirical formula	$C_{38}H_{32}Co_2FeNO_2PS$	$C_{38}H_{30}Co_2FeNO_3PS$
Formula weight	771.39	785.37
Temperature	293(2) K	293(2) K
Wavelength	0.71069 Å	0.71069 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	15.878(3)	13.235(1)
b (Å)	11.489(2)	14.024(2)
c (Å)	19.335(6)	17.928(2)
α (°)	90	90
β (°)	107.27(2)	91.41(2)
γ (°)	90	90
V (Å^3)	3368.1(14)	3326.6(7)
Z	4	4
$D_{calc.}$ (mg m^{-3})	1.521	1.568
Absorption coefficient (mm^{-1})	1.543	1.566
F(000)	1576	1600
Crystal size (mm)	0.45 × 0.36 × 0.21	0.30 × 0.32 × 0.25
Theta range for data collection (°)	2.09–24.98	2.12–31.97
Index ranges	$0 \leq h \leq 16$, $-12 \leq k \leq 0$, $-20 \leq l \leq 20$	$0 \leq h \leq 19$, $0 \leq k \leq 20$, $-26 \leq l \leq 26$
Reflections collected	5913	12351
Independent reflections	5625 [$R_{int} = 0.0185$]	11524 [$R_{int} = 0.0166$]
Reflections observed (>2σ)	4156	7932
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5625/0/497	11524/0/424
Goodness-of-fit on F^2 [a]	1.063	0.808
Final R indices [$I > 2\sigma(I)$][b]	$R_1 = 0.0462$ $wR_2 = 0.1217$	$R_1 = 0.0323$ $wR_2 = 0.1030$
R indices (all data)	$R_1 = 0.0671$ $wR_2 = 0.1292$	$R_1 = 0.0584$ $wR_2 = 0.1158$
Largest diff. peak and hole (e Å^{-3})	0.738 and −0.472	0.595 and −0.335

[a] Goodness-of-fit = $[\Sigma_w(F_0^2-F_c^2)^2/(N_{obs}-N_{parameters})]^{\frac{1}{2}}$.
[b] R indices; $R_{1_1} = [\Sigma\|F_0|-|F_c\|]/\Sigma|F_0|$ (based on F). $wR_2 = [[\Sigma_w(|F_0^2-F_c^2|^2]/[\Sigma_w(F_0^2)^2]]^{\frac{1}{2}}$ (based on F^2). $w = 1/[(\sigma F_0)^2+(0.0804*P)^2+1.04*P]$.

2.4. The structure of [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$(PPh_3)}(μ_3-S)(μ_3-CNC(O)C_6H_5)}], Ih

The crystal was grown from a tetrahydrofuran–hexane mixture.

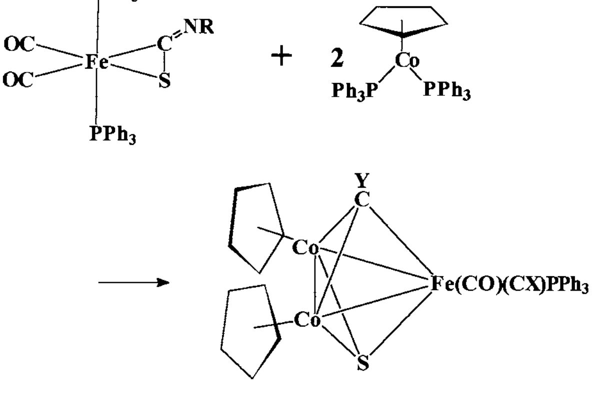
The structure was solved by direct methods, SHELXS-86 [7], and refined by full matrix least squares using SHELXL-93 [10]. Data were corrected for Lorentz and polarization effects, but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. The calculations were carried out on a VAX 6610 computer. The ORTEX program [9] was used to obtain the drawings.

Crystal data are given in Table 4, and selected bond lengths and bond angles in Table 5. Heavy atom coordinates, complete lists of bond lengths and bond angles, anisotropic displacement parameters for heavy atoms, and hydrogen atom coordinates and isotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre together with a list of observed and calculated structure factors.

The structure and atom labeling for Ih are shown in Fig. 4. A view of the molecule along an axis from Fe to the center of the Co–Co bond is shown in Fig. 3.

3. Results and discussion

The η^2-isothiocyanate ligand in [Fe(PPh_3)$_2$(CO)$_2$(η^2-SCNR)] complexes are cleaved by two moles of [Co(η-C_5H_5)(PPh_3)$_2$] to give [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$(PPh_3)(CNR)(μ_3-S)}] complexes I, (*ii*).



(*ii*)

I (CX, CY = CO, CNR)

Table 5
Selected bond lengths and bond angles for the two isomers of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)(CNC_6H_4Me)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CO)]$, Ic, and $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)\{\mu_3\text{-}CNC(O)C_6H_5\}]$, Ih

Ic[a]		Ic[b]		Ih	
Bond lengths (Å)					
Co(1)–Co(2)	2.4592(10)	Co(1)–Co(2)	2.4592(10)	Co(1)–Co(2)	2.4266(5)
Fe(1)–Co(1)	2.5232(9)	Fe(1)–Co(1)	2.5232(9)	Fe(1)–Co(1)	2.5224(10)
Fe(1)–Co(2)	2.25221(9)	Fe(1)–Co(2)	2.5221(9)	Fe(1)–Co(2)[c]	2.5483(40)
Co(1)–C(38)	1.82(2)	Co(1)–C(138)	1.86(2)	Co(1)–C(1)	1.917(2)
Co(2)–C(38)	1.89(2)	Co(2)–C(138)	1.83(2)	Co(2)–C(1)	1.901(2)
Fe(1)–C(38)	2.01(2)	Fe(1)–C(138)	1.89(2)	Fe(1)–C(1)	2.109(2)
Co(1)–S(1)	2.235(4)	Co(1)–S(2)	2.236(4)	Co(1)–S(1)	2.1244(6)
Co(1)–S(1)	2.195(4)	Co(1)–S(2)	2.241(7)	Co(2)–S(1)	2.1333(6)
Fe(1)–S(1)	2.296(3)	Fe(1)–S(2)	2.362(6)	Fe(1)–S(1)	2.1866(6)
C(38)–O(2)	1.181(12)	C(138)–O(102)	1.273(14)	C(1)–N(1)	1.276(2)
Fe(1)–P(1)	2.2227(12)	Fe(1)–P(1)	2.2227(12)	C(2)–N(2)	1.357(2)
Fe(1)–C(37)	1.757(4)	Fe(1)–C(37)	1.757(4)	C(2)–O(1)	1.228(2)
Fe(1)–C(29)	1.819(4)	Fe(1)–C(29)	1.819(4)	C(2)–C(3)	1.504(3)
C(29)–N(1)	1.172(5)	C(29)–N(1)	1.172(5)	Fe(1)–P(1)	2.2581(5)
C(37)–O(1)	1.147(5)	C(37)–O(1)	1.147(5)	Fe(1)–C(9)	1.775(2)
				Fe(1)–C(10)	1.768(2)
				C(9)–O(2)	1.143(2)
				C(10)–O(3)	1.142(3)
Bond angles (°)					
Fe(1)–Co(1)–Co(2)	60.81(3)	Fe(1)–Co(1)–Co(2)	60.81(3)	Fe(1)–Co(1)–Co(2)	61.948(11)
Fe(1)–Co(2)–Co(1)	60.85(3)	Fe(1)–Co(2)–Co(1)	60.85(3)	Fe(1)–Co(2)–Co(1)	60.87(2)
Co(1)–Fe(1)–Co(2)	58.34(3)	Co(1)–Fe(1)–Co(2)	58.34(3)	Co(1)–Fe(1)–Co(2)	57.18(2)
C(29)–Fe(1)–P(1)	91.09(13)	C(29)–Fe(1)–P(1)	91.09(13)	C(9)–Fe(1)–P(1)	91.41(9)
C(37)–Fe(1)–P(1)	92.82(15)	C(37)–Fe(1)–P(1)	92.82(15)	C(10)–Fe(1)–P(1)	99.10(7)
C(29)–Fe(1)–C(37)	104.32(19)	C(29)–Fe(1)–C(37)	104.32(19)	C(9)–Fe(1)–C(10)	91.45(9)
Fe(1)–C(29)–N(1)	177.6(4)	Fe(1)–C(29)–N(1)	177.6(4)	C(1)–N(1)–C(2)	132.4(2)
C(29)–N(1)–C(39)	171.2(5)	C(29)–N(1)–C(39)	171.2(5)	N(1)–C(2)–O(1)	126.0(2)
				C(3)–C(2)–O(1)	121.0(2)
				C(3)–C(2)–N(1)	113.0(2)

[a] Major isomer.
[b] Minor isomer.
[c] Fe(1)–Co(2) bond is eclipsed by the CNC(O)Ph ligand.

RNC = (a) MeNC, (b) $4\text{-}Me_2NC_6H_4NC$, (c) $4\text{-}MeC_6H_4NC$, (d) C_6H_5NC, (e) $4\text{-}ClC_6H_4NC$, (f) MeC(O)NC, (g) $4\text{-}Me_2NC_6H_4C(O)NC$, (h) $C_6H_5C(O)NC$.

The reaction is similar to that of $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}SCS)]$ complexes with $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ which gives $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ [1], and of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ with RNCS which gives $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ complexes [11,12]. These green–brown crystalline solids are soluble in the usual organic solvents. They are less stable in solution than in the solid state especially in the presence of chloroalkanes. Their thermal and oxidative stabilities are lower than those of their thiocarbonyl counterpart, and If is very unstable. Comparable relative stabilities have been observed for $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ and the $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ derivatives.

Spectroscopic data discussed below show that there are two isomers of I, I^I with a μ_3-CO ligand and I^{II} with a μ_3-CNR ligand (Fig. 5).

The structure adopted is a function of RNC but some compounds exist as an equilibrium mixture of the two forms in solution. In general I^I is favored by electron donating R such as Me, $4\text{-}Me_2NC_6H_4$ and $4\text{-}MeC_6H_4$, and I^{II} by electron withdrawing groups such as $4\text{-}ClC_6H_4NC$, MeC(O)NC, $4\text{-}Me_2NC_6H_4C(O)NC$, $C_6H_5C(O)NC$ and $4\text{-}Me_3NC_6H_4^+$. In the solid state the matter is not simple. IR spectroscopy in the 1600–2150 cm^{-1} shows that Ia, Ib and Ic exist solely as the I^I isomer, whilst If, Ig and Ih exist solely as I^{II}. However for Id and Ie there is a weak absorption band which may be due to the presence of small amounts of I^I in the presence of the predominant I^{II} isomer or it may be due to an impurity.

3.1. Reactions of II with electrophiles

The μ_3-CX ligands (X = O, S and NR) are, in general, good nucleophiles and react with electrophiles such as sources of Me^+ to give μ_3-$CXMe^+$adducts [1,12,13]. I are no exception. Irrespective of their structure in solution, $MeOSO_2CF_3$ alkylates the μ_3-CNR ligand, normally at the isocyanide N atom, to give $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)\{\mu_3\text{-}CN(M\text{-}e)R\}]$-$[SO_3CF_3]$ salts, $[II][SO_3CF_3]$. However, in the case of Ig methylation with $MeOSO_2CF_3$ gives a product which has υ(CO) frequencies which are comparable with those of $[IIh]^+$, but the NMR spectra (see below) suggest that the 4-Me_2N group of the 4-$Me_2NC_6H_4C(O)NC$ ligand has been methylated rather than its μ_3-CN N atom. Consequently it appears to be a I^{II} species. In no case was the μ_3-CO ligand alkylated.

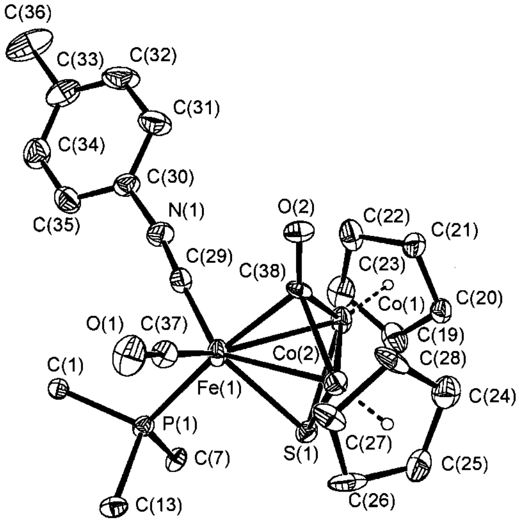


Fig. 1. The structure and atom labeling for the major isomer of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)(CNC_6H_4Me\text{-}4)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CO)]$.

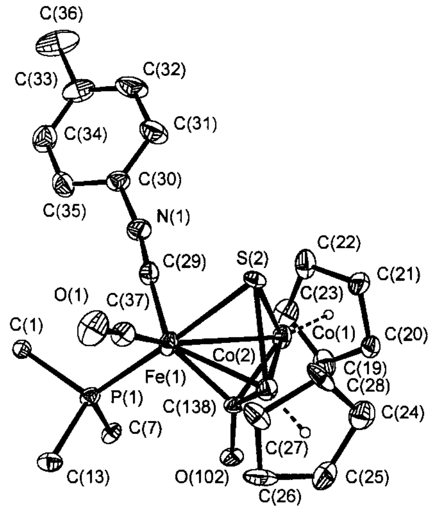


Fig. 2. The structure and atom labeling for the minor isomer of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)(CNC_6H_4Me\text{-}4)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CO)]$.

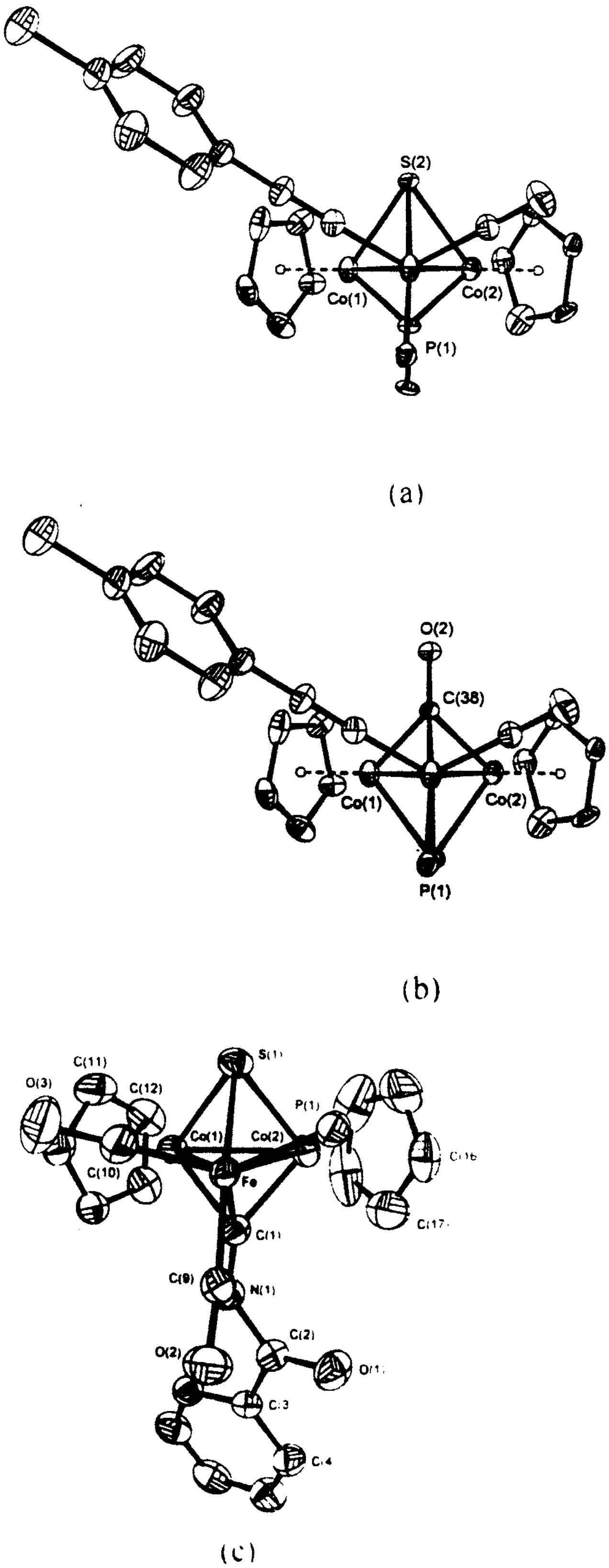


Fig. 3. Views of (a) the major isomer of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)(CNC_6H_4Me\text{-}4)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CO)]$, (b) the minor isomer of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)(CNC_6H_4Me\text{-}4)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CO)]$, and (c) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)\{\mu_3\text{-}CNC(O)C_6H_5\}]$.

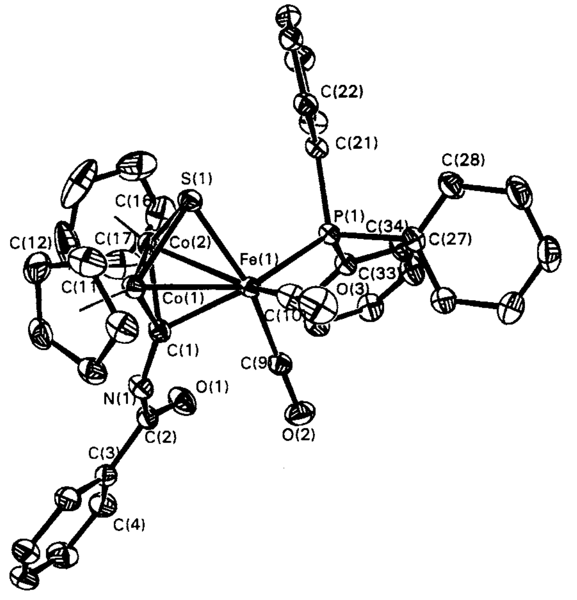


Fig. 4. The structure and atom labeling for $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)\{\mu_3\text{-}CNC(O)C_6H_5\}]$.

Table 6
Ratio of I^I:I^{II} isomers of the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\text{-}(CNR)(\mu_3\text{-}S)]$ complexes in $CD_3C_6D_5$ solutions and the energies of activation (kJ mol^{-1}) for their fluxional processes

RNC	I^I:I^{II} ratio (273 K)	ΔG^{*a}	$\Delta G^{*b}/\Delta G^{*c}$
MeNC, (Ia)	100:0	64.8	
4-MeC_6H_4NC, (Ib)	74:26	65.2	87.4/84.4
C_6H_5NC,	57:43	64.8	81.5/80.7
4-ClC_6H_4NC	22:78	65.6	77.7/81.1

[a] The process which inverts the configuration at Fe and equivalences the two η-C_5H_5 resonances.

[b] For the $I^I \rightarrow I^{II}$ process.

[c] For the $I^{II} \rightarrow I^I$ process.

3.2. IR spectra

The IR spectra of the complexes I and $[II]^+X^-$ contain numerous absorption bands due to the vibrations of the various ligands and X^- which give no structural information and are not included in Table 2. However they can make it difficult to identify the weaker, structurally-important bands which have frequencies < 1600 cm^{-1}. Furthermore, the presence of solvent absorption bands and of isomers make solution spectra even more difficult to interpret, so the IR spectra that will be discussed here are those of solids (KBr discs) unless it is stated otherwise.

I^I isomers would be expected to give rise to single absorption bands due to $\nu(t\text{-CNR})$, $\nu(t\text{-CO})$ and $\nu(\mu_3\text{-CO})$ with their frequencies decreasing along this series. This pattern is observed for Ia and Ib where the $\nu(t\text{-CO})$ and $\nu(\mu_3\text{-CO})$ vary little with t-CNR ligand. However, as anticipated, the $\nu(t\text{-CNMe})$ band has a much higher frequency than the $\nu(t\text{-}CNC_6H_4NMe_2\text{-}4)$, cf. Ref. [14].

The spectrum of Ic in the solid state is broadly similar to those of Ia and Ib, but there are two absorption bands each due to $\nu(t\text{-}CNC_6H_4Me\text{-}4)$ and $\nu(\mu_3\text{-CO})$ vibrations. This a consequence of the presence of two forms of the I^I isomer which differ in the rotational conformation adopted by the $Fe(CO)(CNC_6H_4Me\text{-}4)(PPh_3)$ moiety (see below).

I^{II} is the sole isomer observed for If, Ig and Ih in the solid state (and in solution). It gives rise to two ν(CO) absorption bands of comparable intensities, consistent with the OC–Fe–CO angle of 91.4° found in Ih (see below) [15].

In the solid state, Id and Ie are I^{II} isomers, but the spectra also show weak absorption bands which may be due to the presence of small amounts of I^I isomers or to impurities. It is not clear which. In solution both Id and Ie, like Ic, are mixtures of I^I and I^{II} isomers, but this is best investigated by ^{1}H-NMR spectroscopy (see below).

Alkylation of Ia–If and Ih leads, respectively, to $[II]^+$–$[IIf]^+$and $[Ih]^+$cations isolated as their $[SO_3CF_3]^-$ or $[BPh_4]^-$ salts. All have the structure shown

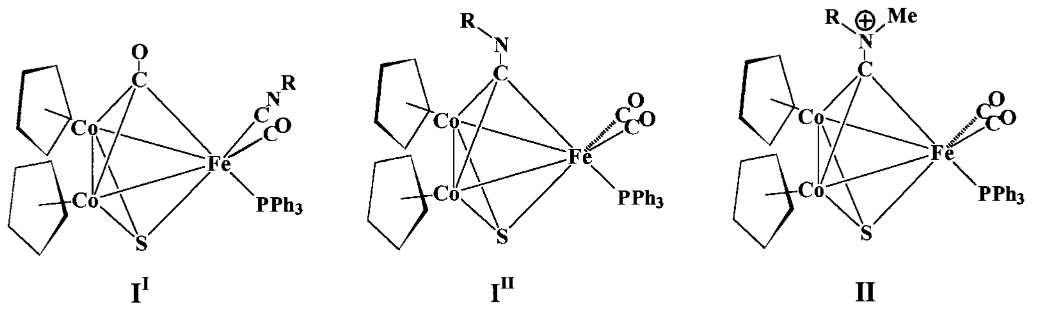
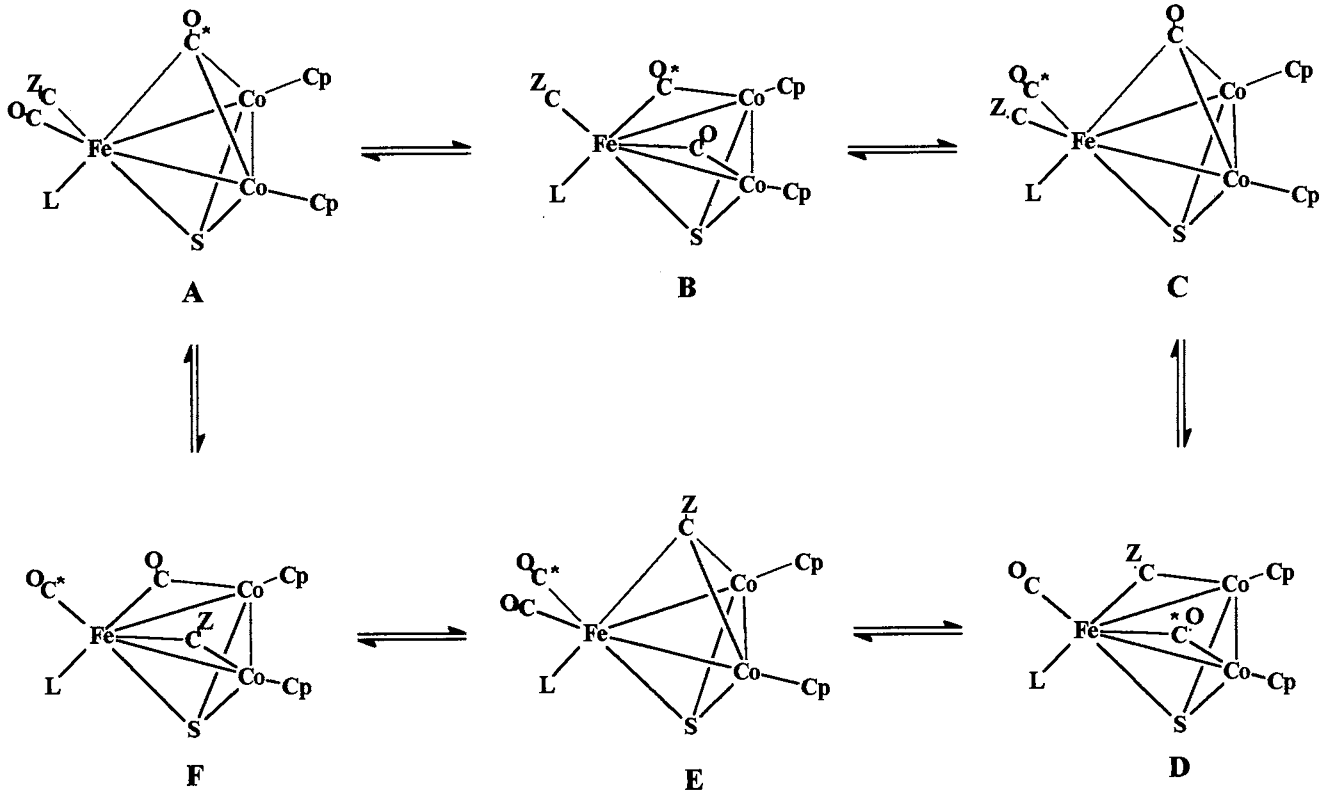


Fig. 5. The structures of the two isomers of I and of the $[II]^+$ cations.



Scheme 1.

in Fig. 5 with a μ_3-CN(Me)R$^+$ ligand, and a Fe $(CO)_2PPh_3$ moiety except for that from Ig (see above). Consequently all give rise to two υ(CO) absorption bands of comparable intensities which indicates OC–Fe–CO angles of ca. 90° [15].

The ν(CO) absorption bands of the $Fe(CO)_2(PPh_3)$ moiety in a series of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CY)]$ complexes enables the overall electron-withdrawing abilities of various μ_3-CX ligands to be assessed. The ν(CO) frequencies (chloroform solution in parentheses) and theCX acceptor abilities increase along the series $CX = CNC_6H_4Cl$-4 (1904, 1963) $\ll$ CS (1934, 1986 [17]) $<$ CNC(O)Ph (1940, 1990) $<$ $CNMe_2^+$ (1948, 1998) $\sim$ CN(Me)Ph$^+$ (1948, 1998) $<$ CN(Me)C(O)Ph$^+$ (1955, 2001) $<$ CSMe$^+$ (1959, 2011 [17]) $<$ $CN(Me)C_6H_4NMe_2$-4$^+$ (1965, 2015) $<$ $CNC(O)C_6H_4NMe_3$-4$^+$ (1979, 2021). This series is much as would be expected, except for the positions of the $CN(Me)C_6H_4NMe_2$-4$^+$ and $CNC(O)C_6H_4NMe_3$-4$^+$ ligands. The high acceptor ability of the former may be due to delocalization of the positive charge onto the *para* Me_2N group, and of the former to the lowering of the energies of $XC_6H_4C(O)$ orbitals by the powerful electron-withdrawing effect of the NMe_3^+ group.

Identification and assignment of absorption bands due to $\nu(\mu_3\text{-}CNR)$, $\nu(\mu_3\text{-}CNR_2)^+$ and acyl ν(CO) vibrations is not straight-forward. The conversion of the μ_3-CNAr ligands in Id and Ie to the μ_3-CN(Me)Ar$^+$ would be expected to result in a decrease in the frequency of the $\nu(\mu_3\text{-}CN)$ frequency from ca. 1550 to ca. 1320 cm^{-1} as has been found in the related $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNAr)]/[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)Ar\}]^+$ derivatives [12]. However, careful inspection of the spectra of (Id), (Ie) and $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNAr)]$ (ArNC = PhNC and 4-MeC_6H_4NC[2]) shows that there are two absorption bands which disappear on methylation, a weaker one at ca. 1600 cm^{-1} and a more intense one at ca. 1550 cm^{-1}. Counterparts of neither of these bands are present in the spectrum of Ic with its terminal 4-MeC_6H_4NC and μ_3-CO ligands, and there is only one at 1646 cm^{-1} in the spectrum of $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$ [12]. This implies that both bands are due to vibrations of the μ_3-CNAr ligands. Perhaps its $\nu(\mu_3\text{-}CN)$ mode couples with a N–Ar mode which has a relatively high frequency in ArNC due to the multiple bond character of the N–Ar bond [16]. This could not occur in *t*-CNAr or μ_3-CNEt complexes.

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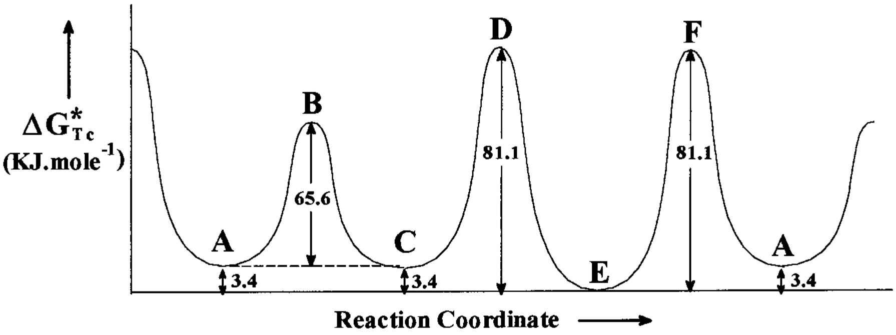
[2] The two relevant absorption bands for the $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNAr)]$ complexes are found at 1606 (w) and 1556 (s) cm^{-1} (ArNC = PhNC; Kbr disc) and 1608 (w) and 1544 (s) cm^{-1} (ArNC = 4-MeC_6H_4NC; KBr disc).



Scheme 2.

The $\nu(\mu_3\text{-CN})$ and acyl $\nu(CO)$ bands in μ_3-CNC(O)Ar complexes must have frequencies below ca. 1500 cm^{-1}. A comparison of the spectra of [{Co(η-C_5H_5)}$_3$(μ_3-S)(μ_3-CNPh)] and [{Co(η-C_5H_5)}$_3$(μ_3-S){μ_3-CNC(O)Ph}] [17] shows that the two absorption bands at 1606 and 1556 cm^{-1} in the former have been replaced by bands at 1422(s) and 1271(m) cm^{-1} in the latter. A similar comparison of the spectra of Id and Ih allows the identification of a group of three bands with the most intense at 1479 cm^{-1} and a sharp weaker band at 1265 cm^{-1}. On methylation of Ih to [IIh][SO_3CF_3] these disappear.

Although we have been able to identify the $\nu(\mu_3\text{-CN})$ absorption band in the spectra of $[IIa]^+$–$[IIe]^+$, we have not been able to identify those due to $\nu(\mu_3\text{-CN})$ or acyl $\nu(CO)$ in the spectrum of [IIh][SO_3CF_3].

3.3. NMR spectra

The NMR spectra I and $[II]^+$ salts are summarized in Table 3 which does not include the prominent but overlapping resonances due to the aryl groups of the isocyanide and PPh_3 ligands. As a consequence of the poor stability of I in halocarbon solution, we were unable to obtain good quality spectra in $CDCl_3$ or CD_2Cl_2 solutions and were limited to C_6D_6 or $CD_3C_6D_5$ as solvents. Even in these I decompose slowly and the ^{13}C spectroscopic resonances of *C*O and *C*NR ligands could not be observed in most instances.

The ^1H-NMR spectra are the most informative. They confirm that Ia and Ib exist as I^I isomers only in solution, that If, Ig and Ih exist as I^{II} isomers, and Ic, Id and Ie are an equilibrium mixture of the two which do not interconvert rapidly on the NMR timescale at room temperature. The most important resonances are those due to the cyclopentadienyl protons. There are two of these for the I^I isomers at room temperature, but only one for the I^{II}. This is because the chiral iron atom in the former renders the two Co(η-C_5H_5) moieties inequivalent. Where both species are present in equilibrium, their relative concentrations can be estimated (Table 6).

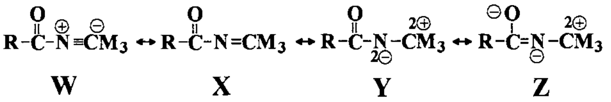
All $[II]^+$ cations except $[IIg]^+$ have structures based on the I^{II} isomer but with the μ_3-CNR ligand replaced by μ_3-CN(Me)R^+. The spectra show a single resonance due to the C_5H_5 ligand and the anticipated resonances due to R, Ph_3P and NMe_2 moieties with the expected chemical shifts and integrations. However, the spectrum of $[If]^+$ does not conform to this pattern as the NMe_2 protons of R and the Me protons give a single resonance attributable to an NMe_3^+ group. The same is observed in the ^{13}C-NMR spectrum. Consequently this salt is best formulated as a I^{II} complex, [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S){μ_3-CNC(O)$C_6H_4NMe_3$-4}]$^+$.

The ^{13}C-NMR spectra have proved difficult to obtain as a consequence of compound fragility and insolubility. In particular, resonances due to μ_3-*C*O, μ_3-*C*NR, μ_3-*C*N(Me)R^+ or *C*NR have not been observed, and *C*O only occasionally. When they are observed, the latter are doublets due to ^{31}P–^{13}C coupling. The most useful resonances are those due to the cyclopentadienyl groups which are a doublet for the I^I isomers and a singlet for the I^{II}. Both are observed in the spectra of Ic–Ie, proving that isomer interchange does not take place at room temperature on the ^{13}C-NMR timescale.

For the $[II]^+$ salts, resonances are observed for the N*C*H_3 except in the case of $[IIg]^+$ (see above).

3.4. Isomerism and fluxionality

NMR spectroscopy shows that in C_6D_6 or $CD_3C_6D_5$ solutions, the I^I:I^{II} ratio decreases along the series RNC = MeNC, 4-$Me_2NC_6H_4NC$ > 4-MeC_6H_4NC > C_6H_5NC > 4-ClC_6H_4NC > MeC(O)NC, 4-$Me_2NC_6H_4C$(O)NC, C_6H_5C(O)NC, 4-$Me_3N^+C_6H_4C$(O)NC (Table



Scheme 3.

6). This parallels the increasing electron-withdrawing ability of R and the increasing acceptor ability of the RNC ligand. As the back-bonding from the Co_2Fe cluster into the π^* orbitals of the RNC ligand would be expected to be greater for a μ_3 as opposed to a *t*-CNR ligand, better π-acceptor isocyanide ligands would be expected to prefer the μ_3-sites.

At room temperature and below, I are stereochemically rigid on the NMR timescale, but on warming they become fluxional. Two processes are observed. The first interconverts the two η-C_5H_5 ligands in isomer I^I and is equivalent to an inversion of configuration at the chiral Fe atom in Ia–If. The second interconverts the two isomers I^I and I^{II} in Ic–If. The coalescence temperatures, T_c may be determined by variable temperature ^{1}H-NMR spectroscopy, and used to calculate the energies of activation, $\Delta G^{\ddagger}_{Tc}$ [18]. These are given in Table 6. As can be seen, the energy barrier to inversion at Fe is ca. 65 kJ mol^{-1}, whilst that to interconversion of I^I and I^{II} is ca. 77–88 kJ mol^{-1}.

Site exchange processes of μ_3-CO and *t*-CO ligands have been observed in $[Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-CO})]$ which are 48e clusters related to I [19]. It was proposed that they proceeded via intermediates containing two μ_2-CO ligands. A modification of this mechanism as applied to I is shown in Scheme 1.

E is the I^{II} isomer; both **A** and **C** are the I^I isomers which differ in their chirality at Fe. Consequently the **A**⇌**B**⇌**C** process is that which brings about the equivalencing of the two cyclopentadienyl ligands.

A schematic energy diagram for this process is shown in Scheme 2 using the energy values for Ie. The lower activation energy for the inversion at Fe (**A**⇌**C**) implies that the intermediate **B** with its $(\mu_2\text{-CO})_2(t\text{-CNR})$ configuration has a lower energy than **D** or **F** with their $(\mu_2\text{-CNR})(\mu_2\text{-CO})(t\text{-CO})$ configurations. The $\Delta G^{\ddagger}_{Tc}$ values for μ_3-CO/*t*-CO exchange are comparable with those found for $[Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-CO})]$ (58.1 kJ mol^{-1}) [19].

3.5. Structures of Ic and Ih

The structures of the two isomers of Ic and Ih along with the atom labeling are illustrated in Figs. 1, 2 and 4. All are based on a $FeCo_2$ triangle capped on one face by a μ_3-S atom and on the other face by a μ_3-CO ligand, Ic, or a μ_3-CNR ligand bent at N, Ih. The coordination about each Co atom is completed by a η-C_5H_5 ligand which has its centroid lying in the $FeCo_2$ plane, and about Fe by *cis*-$(CNC_6H_4Me)(CO)PPh_3$ or $(CO)_2PPh_3$ ligand arrays with L–Fe–L angles of ca. 90–102°. These are 48 electron *closo* clusters in which the μ_3-CO or CNR ligand acts as a 2e donor through C and the μ_3-S ligand as a 4e donor. They are closely related to the homo-nuclear clusters $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-Y})(\mu_3\text{-CX})]$ (Y/CX = S/CS [13], S/CNR [11,12,16], S/CO [20], O/CO [21], or NR/CO [22].

The unit cell of Ih contains a single isomer, but that of Ic is disordered as a consequence of the presence of two isomers in the ratio of 60:40. In this disorder the $FeCo_2$ triangles and all terminal ligands of the two isomers are in identical positions, but the μ_3-CO and μ_3-S ligands are disordered over their two sites. This means that the orientation of the Fe(CO)$(CNC_6H_4Me)(PPh_3)$ moiety differs in the two isomers as is shown in Fig. 3 where the two isomers and Ih are viewed along an axis through Fe to the midpoint of the Co–Co bond. The cyclopentadienyl ligands are disordered over two sites in both isomers. A similar disorder of the two μ_3 ligands has been observed in $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-S})(\mu_3\text{-CO})]$ [20] and $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-O})(\mu_3\text{-CO})]$ [21].

The three metal atoms in Ic constitute an isosceles triangle with Fe–Co distances of 2.5232/2.5221(6) Å and Co(1)–Co(2) of 2.4592(10) Å. These are similar to but longer than the comparable bond lengths of 2.5099/2.5061(6) Å and 2.4378 Å found in $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-S})(\mu_3\text{-CS})]$ [1]. The differences are small but appear to be real. As a consequence of the μ_3-CO/μ_3-S disorder the M–S distances in (Ic) are not as well-defined as they might be, but at Fe–S = 2.296(3)/2.362(6) Å and Co–S = 2.235(4), 2.236(7)/2.195(4), 2.241(7) Å they appear to be longer than the 2.1925(7) Å and 2.1370/2.236(7) Å found in $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-S})(\mu_3\text{-CS})]$ [1]. Unfortunately, the disorder means that the M–(μ_3-C) and μ_3-C–O bond lengths are only poorly defined. However they are comparable with those in related complexes such as $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-S})(\mu_3\text{-CO})]$ [20] and $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-O})(\mu_3\text{-CO})]$ [21].

In contrast to Ic the two Fe–Co bonds in Ih are not of equal length, 2.5524(4) and 2.5483(4) Å. That eclipsed by the PhC(O) group of the bent μ_3-CNC(O)Ph ligand is the longer. A similar but much larger difference in $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-S})(\mu_3\text{-CNC}_6H_4Me\text{-}4)]$ (0.08 Å) has been attributed to the differential back-bonding from the cluster into the two non-equivalent π^* orbitals of the non-linear CNR ligand [16]. There are also small differences in the Co–C and Co–S distances in Ih.

The various metal–metal distances in the 48 electron $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-Y})(\mu_3\text{-CX})]$ clusters is a function of the size of Y and CX [20]. In Ic, Ih and their counterparts where Y is S, any variation in metal–metal bond lengths with μ_3-CX is very small and other factors have their effects (see above). However it is noticeable that the bond distances to Fe are all much longer than those to Co, but inspection shows that this lengthening is not constant for all bonds. Thus in Ih the two bond length differences (Fe–C)–(Co–C) are 0.192/0.20 Å and the two Fe:Co–C ratios are 1.10/1.11:1. Comparable figures for bonds to S are 0.0622/0.0533 Å and 1.02/1.02:1, and for those to Co are 0.1117/0.0958 Å and 1.03/1.05:1. A similar pattern is found for $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ [1] and perhaps in Ic but here the errors are very large and the conclusion not clear-cut. This excessive shortening of the Co–C bonds suggests that the M–C bonding to the μ_3-CX ligand is much stronger for M=Co than Fe in these clusters.

The M–C_μ distances in Ih are comparable with those in $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ [1], but longer than those in $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$ [1].

Within the $Fe(CO)(CNC_6H_4Me\text{-}4)(PPh_3)$ moiety of Ic, the Fe–CO bond length of 1.757(4) Å is comparable with that found in Ih {1.775, 1.768(2) Å}, but it is much shorter than the $Fe\text{–}CNC_6H_4Me\text{-}4$ distance of 1.819(4) Å. This may be a reflection of the stronger π-bonding in the Fe–CO bond. If the dimensions of the $t\text{-}CNC_6H_4Me\text{-}4$ ligand in Ic {C–N = 1.172(5) Å, N–Ar = 1.402(5) Å} are compared with those of the $\mu_3\text{-}CNC_6H_4Me\text{-}4$ ligand in $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNC_6H_4Me\text{-}4)]$ {C–N = 1.243(6), N–Ar = 1.401(6) Å}, this reflects the higher C–N bond order in the $t\text{-}CNC_6H_4Me\text{-}4$ as opposed to the $\mu_3\text{-}CNC_6H_4Me\text{-}4$ as a consequence of the back-bonding into the CN π^* orbitals of the latter which does not affect the N–Ar bond.

The orientation of the $Fe(L)(CO)PPh_3$ moiety differs in all three molecules (Fig. 3). This suggests that its rotation is a facile process, cf. [1].

The μ_3-C–N bond length within the μ_3-CNC(O)Ph ligand of (Ih) is longer than the comparable distance {1.243(6) Å} in $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNC_6H_4Me\text{-}4)]$, whilst N(1)–C(2) is longer than that generally found in amides and C(2)=O is similar to that found in amides but longer than in ketones. This pattern of bond lengths and angles, and the near planarity of the CN(CO)Ph ligand is consistent with delocalization of the backbonding from the $FeCo_2$ cluster into π orbitals which extend over the whole C–N–(C–O)- system. The overall bonding may be described as a resonance hybrid of the four forms shown in Scheme 3 ($M_3 = Co_2Fe$).

It accounts for the fact that the μ_3-CNC(O)Ph ligand is a better π-acceptor than e.g. μ_3-CNPh. Furthermore, the delocalisation of negative charge from N to O in **Z** means that this N atom becomes a poorer nucleophile. Consequently Ib, where there can be no resonance form **Z**, is alkylated by $MeOSO_2CF_3$ at the isocyanide N atom and Ig at the NMe_2.

The μ_3-CNC(O)Ph ligand in Ih is bent at N with an angle of 132.4°. This is comparable with the angles found in $[\{Co(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ (130.8(5)° when $R = C_6H_4Me\text{-}4$ [16] and 130.6(6) when R = Et [12]. At this C–N–R angle, the isocyanide ligand is a strong π-acceptor [23] and resonance forms **X**, **Y** and perhaps **Z** are more important than **W**. In contrast the μ_3-CNMe ligand in $[Ni_3(Ph_2PCH_2PPh_2)_2(CNMe)_2(\mu_3\text{-}I)(\mu_3\text{-}CNMe)]^+$ is almost linear with $\angle$C–N–Me = 170(1)° and gives rise to a (μ_3-C–N) stretching frequency of 1943 cm^{-1} [24]. This implies strongly that it acts largely as a donor ligand, i.e. resonance form **W** is very important (Scheme 3, $M_3 = Ni_3$) and that back-bonding is less important than for I.

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