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Substitution reactions of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$

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Abstract

On heating, the cluster $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1a**, reacts with PR_3 ligands (R = (b) MeO, (c) PhO and (d) Bu^n) by replacement of PPh_3 to give $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PR_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1b**–**d**, and with CNR (R = (e) Me, (f) 2,4,6-$Me_3C_6H_2$ and (g) 2,6-$Cl_2C_6H_3$) by replacement of PPh_3 and then CO to give $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(CNR)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1e**–**g**, and $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(CNR)_2\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **2e**–**g**. These reactions are successful only under a very limited range of conditions, i.e. with a large excess of the incoming ligand and very short reaction times and/or moderate temperatures. The CO ligands in $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(CNR)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ are labile and may be replaced by more CNR in a reversible reaction or by PPh_3 to give, respectively, $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(CNR)_2\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **2e**–**g**, and $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(CNR)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **2h** (R = 2,6-$Cl_2C_6H_3$). The IR spectra of the clusters have been studied and for the first time the absorption band in each due to the ν(CS) vibration of the μ_3-CS ligand has been identified unambiguously. Its frequency depends on the FeL_3 ligand set in a predictable way and lies in the range 1022–1041 cm^{-1}. In the ^{13}C-NMR spectra the μ_3-C atom gives rise to resonances between δ 354 and 359. The clusters do not undergo bridge–terminal ligand site exchange. In particular, there is no evidence for the formation of isomers, which contain terminal CS and μ_3-CNR ligands. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Cobalt; Thiocarbonyl; Cluster; Ligand substitution

1. Introduction

It has been reported from these laboratories that the mixed-metal cluster $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1a**, undergoes replacement of PPh_3 by other P(III) ligands [1]. The reactions were brought about photochemically as thermal reactions resulted in decomposition. They were limited to L = $P(OMe)_3$ and $P(OPh)_3$ and failed with L = trialkylphosphines and organoisocyanides.

Subsequently we found that **1a** reacts with CS_2 to give $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PR_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSCS_2)]$ [2]. Whilst studying the reactions of this adduct with L = PR_3 and CNR [3], we found that organoisocyanide complexes derived from **1a** were sufficiently stable to be isolated and decided to reinvestigate its substitution reactions.

We also report a very convenient synthesis for $[Co(\eta^5\text{-}C_5H_5)(PPh_3)_2]$.

2. Experimental

Literature methods were used to prepare $[Co(\eta^5\text{-}C_5H_5)(PPh_3)I_2]$ [4] and $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}CS_2)]$ [5]. Other chemicals were purchased.

Unless it is stated otherwise, all reactions were carried out under an atmosphere of nitrogen in dried and deoxygenated solvents at room temperature (r.t.). Where necessary, reactions were monitored by infrared spectroscopy.

IR spectra were recorded on a Perkin–Elmer Paragon 2000 FT IR spectrometer. NMR spectra were run on a JEOL JNM-GX-270 MHz spectrometer. Elemental

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analyses were carried out in the Microanalytical Laboratory of University College Dublin.

2.1. Preparation of [Co(η^5-C_5H_5)(PPh_3)$_2$]

A solution of [Co(η^5-C_5H_5)(PPh_3)I_2] (10 g, 15 mmol) and PPh_3 (4 g, 15 mmol) in tetrahydrofuran (250 cm^3) was shaken with an amalgam of sodium (2 g) in mercury (60 cm^3) for 15 min. The color of the mixture changed from green to red. The mixture was allowed to stand for 20 min, the amalgam run off and the tetrahydrofuran solution filtered. [Co(η^5-C_5H_5)(PPh_3)$_2$] could be isolated in 85% yield, but was normally used directly in Section 2.2 below.

2.2. Preparation of [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(PPh_3)}(μ_3-S)(μ_3-CS)], **1a**

[Fe(PPh_3)$_2$(CO)$_2$(η^2-CS_2)] (5 g, 7.0 mmol) was added to the solution of [Co(η^5-C_5H_5)(PPh_3)$_2$] prepared above. The color of the mixture changed from red to dark green. After 15 min, the reaction mixture was filtered and evaporated to dryness at reduced pressure. The residue was chromatographed on alumina and eluted with CH_2Cl_2–hexane–tetrahydrofuran (45:45:10). The product was recrystallized from tetrahydrofuran–hexane mixtures to give green crystals of [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(PPh_3)}(μ_3-S)(μ_3-CS)] (yield 3.4 g, 70%).

2.3. Substitution reactions of [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(PPh_3)}(μ_3-S)(μ_3-CS)], **1a**

Solutions of **1a** (0.7 g, 1.0 mmol) and a large excess of PR_3 (2–3 cm^3; R = (b) OMe, (c) OPh, or (d) Bu^n) in benzene (30 cm^3) were refluxed for not longer than 1 min, and then allowed to cool. The solvents were removed at reduced pressure. The residues were chromatographed on alumina and the green products eluted as for **1a** above. They were recrystallized from tetrahydrofuran–hexane (R = OMe and OPh) or toluene–hexane (R = Bu^n) to give green crystals of [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(P(OMe)$_3$)}(μ_3-S)(μ_3-CS)], **1b** (yield 0.50 g, 90%), [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(P(OPh)$_3$)}(μ_3-S)(μ_3-CS)], **1c** (yield 0.62 g, 90%), and [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(PBu^n_3)}(μ_3-S)(μ_3-CS)], **1d** (yield 0.49 g, 80%).

Solutions of **1a** (0.5 g, 0.71 mmol) and CNR (1.5 cm^3) (R = (e) Me, (f) 2,4,6-$C_6H_2Me_3$ and (g) 2,6-$C_6H_3Cl_2$) in dichloromethane (30 cm^3) were refluxed for 80 min. The reaction mixtures were cooled, their volume reduced to ca. 3 cm^3 and this residue chromatographed on alumina. Elution with dichloromethane–hexane mixtures gave two green bands. The compounds were isolated from the latter by removal of eluent at reduced pressure and recrystallization of the residues from tetrahydrofuran–hexane mixtures. The first of the green bands was identified as [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(CNR)}(μ_3-S)(μ_3-CS)], **1e**–**g** (**1e**, R = Me, yield = 0.28 g, 55%; **1f**, R = 2,4,6-$C_6H_2Me_3$, yield = 0.40 g, 70%; **1g**, R = 2,6-$C_6H_3Cl_2$, yield 0.36 g, 60%), and the second as [{Co(η^5-C_5H_5)}$_2${Fe(CO)(CNR)$_2$}(μ_3-S)(μ_3-CS)], **2e**–**g** (**2e**, R = Me, yield = 0.2 g, 40%; **2f**, R = 2,4,6-$C_6H_2Me_3$, yield = 0.17 g, 25%; **2g**, R = 2,6-$C_6H_3Cl_2$, yield 5%). Longer reaction times resulted in a decrease in the yields of **1e**–**g** and a small increase in the yields of **2e** and **2f** but not of **2g**, as this is unstable.

2.4. Reaction of [{Co(η^5-C_5H_5)}$_2${Fe(CO)-(CN$C_6H_2Me_3$-2,4,6)$_2$}(μ_3-S)(μ_3-CS)], **2f**, with CO

When a solution of **2f** in dichloromethane (15 cm^3) under an atmosphere of CO is refluxed for ca. 5 min, it undergoes a ca. 30% conversion to [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(CN$C_6H_2Me_3$-2,4,6)}(μ_3-S)(μ_3-CS)], **1f**. If anhydrous $CoCl_2$ (0.1 g) is added to the reaction mixture, the reaction proceeds to completion within 2 h at r.t. Isolation and purification as above gave **1f** in 50% yield.

2.5. Reaction of [{Co(η^5-C_5H_5)}$_2${Fe(CO)-(CN$C_6H_3Cl_2$-2,6)$_2$}(μ_3-S)(μ_3-CS)], **2g**, with PPh_3

A solution of [{Co(η^5-C_5H_5)}$_2${Fe(CO)(CN$C_6H_3Cl_2$-2,6)$_2$}(μ_3-S)(μ_3-CS)], **2g**, (0.082 g, 0.13 mmol) and PPh_3 (0.3 g, 1.14 mmol) in benzene (5 cm^3) was refluxed for 5 min. Isolation and purification as above gave dark green crystals of [{Co(η^5-C_5H_5)}$_2${Fe(CO)(CN$C_6H_3Cl_2$-2,6)(PPh_3)}(μ_3-S)(μ_3-CS)], **2h** (yield 0.13 g, 95%).

The compounds prepared in the course of this work are listed in Table 1 together with their analytical data and IR spectra in the ν(CN/ν(CO) region (1900–2200 cm^{-1}). Table 2 contains the frequencies of the IR absorption bands of **1** found in the 1000–1100 cm^{-1} region together with their ν(CO) frequencies. In Table 3 are listed ^1H and ^{13}C-NMR spectra.

3. Results and discussion

The work reported herein describes the thermal substitution of Ph_3P in [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$-(PPh_3)}(μ_3-S)(μ_3-CS)], **1a**, by other R_3P ligands, and of Ph_3P and then CO by organoisocyanides. With both types of ligands we were able to prepare successfully compounds that were not accessible photochemically [1]. The reactions carried out in the course of this work are illustrated in Scheme 1. **1** and **2** are neutral [{Co(η^5-C_5H_5)}$_2${Fe(ligand)$_3$}(μ_3-S)(μ_3-CS)] derivatives containing the Fe(CO)$_2$L and Fe(CO)L_2 moieties, respectively.

Analytical and spectroscopic data for all of the clusters described herein are consistent with the struc-

Table 1
Analyses and IR spectra (1900–2200 cm^{-1} region) of the compounds described in the text

Compound		Analyses [a]			IR spectra [b]		
L	Number	%C	%H	%P/N/others	ν(CN)/ν(CO)		
[{$Co(\eta^5$-$C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3$-$S)(\mu_3$-$CS)$] (**1**)							
Ph$_3$P [c]	**1a**	53.7 (53.4)	3.7 (3.5)	S = 8.7 (9.1)	1982 (10)	1927 (7)	
(MeO)$_3$P [c]	**1b**				1993 (10)	1944 (5)	
(PhO)$_3$P [c]	**1c**				1995 (10)	1947 (8)	
Bu$^n_3$P	**1d**	46.9 (47.0)	5.9 (5.8)	5.1 (4.9)	1978 (10)	1924 (8)	
MeNC	**1e**	37.9 (37.8)	2.7 (2.7)	2.8 (2.9)	2180 (6)	2000 (10)	1954 (5)
MesNC [d]	**1f**	47.5 (47.5)	3.6 (3.6)	2.4 (2.4)	2123 (10)	2000 (10)	1958 (6)
DcNC [d]	**1g**	36.9 (36.8)	2.2 (2.3)	2.1 (2.3)	2103 (10)	2000 (10)	1966 (7)
[{$Co(\eta^5$-$C_5H_5)\}_2\{Fe(CO)(L)_2\}(\mu_3$-$S)(\mu_3$-$CS)$] (**2**)							
MeNC	**2e**	38.7 (39.1)	2.9 (3.3)	5.6 (5.7)	2173 (10)	2153 (6)	1948 (6)
MesNC	**2f**	55.1 (55.0)	4.8 (4.6)	3.8 (4.0)	2119 (10)	2083 (7)	1959 (4)
DcNC [e]	**2g**				2119 (10)	2078 (5)	1964 (3)
(DcNC)(PPh$_3$)	**2h**	52.9 (53.2)	3.5 (3.4)	1.6 (1.6)	2075 (8)	2041 (10)	1944 (7)

[a] Found (calculated).

[b] Peak positions (cm^{-1}) with relative peak heights in parentheses. Spectra run in CH$_2$Cl$_2$ solution unless it is stated otherwise. ν(CN) = 2041–2180 cm^{-1}; ν(CO) = 1920–2000 cm^{-1}.

[c] Taken from ref. [1] for comparison. IR spectra run in KBr discs.

[d] MesNC = 2,4,6-Me$_3$C$_6$H$_2$NC. DcNC = 2,6-Cl$_2$C$_6$H$_3$NC.

[e] Unstable; consistent analyses could not be obtained.

tures shown in the Scheme. They are similar to that found in the solid state for [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$-(PPh$_3$)}(μ_3-S)(μ_3-CS)] [1] with a μ_3-CS group capping one face of a Co$_2$Fe triangle and a μ_3-S ligand the other. There is no evidence for isomers of **1e**–**g** and **2e**–**h** which contain a μ_3-CNR ligand. The CS ligand strongly prefers the μ_3 position and inhibits any μ_3-terminal ligand exchange processes. This contrasts with the situation in [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(CNR)(PPh$_3$)}-(μ_3-S)(μ_3-CO)] where CO and CNR exchange between terminal and bridging positions is usually facile [6].

The compounds described herein, **1a**–**g** and **2e**–**h**, are dark green or green-brown solids soluble in the normal organic solvents. Most are reasonably stable both in the solid state and in solution. They may be isolated, and characterized fully, but **2g** is unstable and was identified by its IR spectrum only.

3.1. Ligand substitution

Contrary to our previous report [1], **1a** undergoes a thermal reaction with the three P(III) ligands investigated, L = (b) (MeO)$_3$P, (c) (PhO)$_3$P, and (d) Bu$^n_3$P, with replacement of Ph$_3$P and retention of the cluster framework to give, respectively, **1b**–**d** in good yields. However, the reactions must be carried out under very specific conditions. It is necessary to use a three to fourfold excess of the free ligand and a 1 min reflux in benzene solution. At lower temperatures or lower concentrations of the free ligand, the reaction is too

Table 2
The frequencies of the absorption bands due to the ν(CO) and ν(CS) modes of [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$(L)}(μ_3-S)(μ_3-CS)] (**1**) and [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(CNMe)$_2$}(μ_3-S)(μ_3-CS)] (**2e**)

L		ν(CO) [b]	ν(CO) [c]	ν(CO)$_{\mathrm{mean}}$ [d]	Absorption bands in the 1000–1000 region		
Bu$^n_3$P	**1d**	1978 (10)	1924 (8)	1951	1061 (2.7)	1026 (3.3)	1022 (3.2, sh)
Ph$_3$P	**1a**	1982 (10)	1927 (7)	1955	1062 (1.9)	1034 (3.2, sh)	1030 (3.3)
(MeO)$_3$P	**1b**	1993 (10)	1944 (5)	1969	1062 (2.8)	1036 (3.3)	1018 (3.2)
MeNC	**1e**	2000 (10)	1954 (5)	1977	1062 (2.8)	1037 (3.3)	
MesNC	**1f**	2000 (10)	1958 (6)	1979	1063 (2.8)	1038 (3.3)	
DcNC	**1g**	2000 (10)	1966 (7)	1983	1064 (2.4)	1041 (3.3)	
CNMe [e]	**2e**		1948 (10)	1948	1060 (2.0)	1022 (5.0)	

Spectra measured in CH$_2$Cl$_2$ solution. Peak positions in cm^{-1} with relative peak heights in parentheses.

[b] Due to the symmetric vibration of the Fe(CO)$_2$ moiety of **1**.

[c] Due to the antisymmetric vibration of the Fe(CO)$_2$ moiety of **1**.

[d] $\nu(\mathrm{CO})_{\mathrm{mean}} = \frac{1}{2}[\nu(\mathrm{CO})_{\mathrm{sym}} + \nu(\mathrm{CO})_{\mathrm{antisym}}]$ for **1**.

[e] [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(CNMe)$_2$}(μ_3-S)(μ_3-CS)].

Table 3
NMR spectroscopic data for some of the compounds described in the text [a]

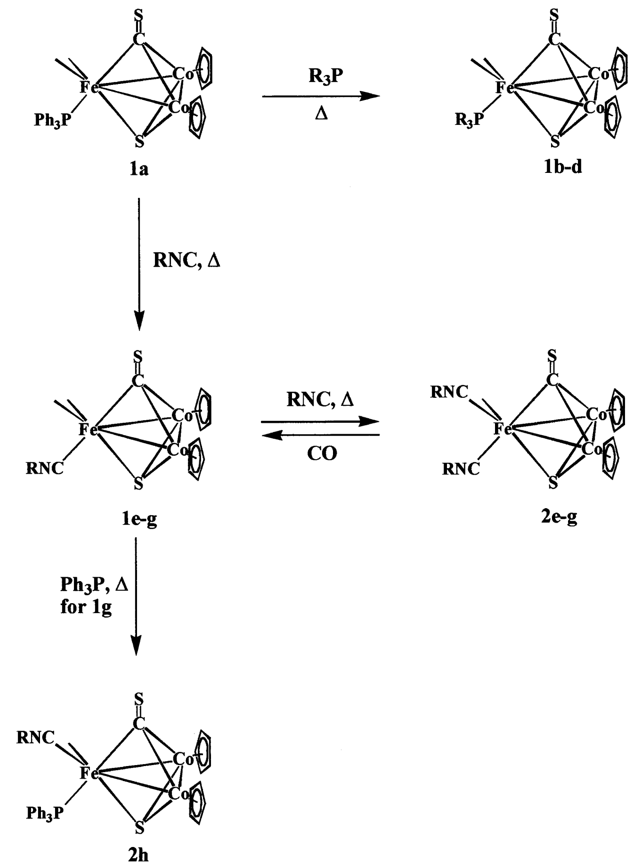
Compound [b]	^{1}H		^{13}C				
L	C_5H_5	L	μ^3-CS	CO	CNR	C_5H_5	L
$[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ (**1**)							
Ph_3P, **1a**	4.52 [c] (10H)	7.1–7.8 (15H, m) [c]	355.5	216.7 (d, $J = 17.0$)		87.7	136.3 (d, $J = 42.6$), 133.1 (d, $J = 11.9$), 130.0, 128.1 (d, $J = 10.2$)
Bu^n_3P, **1d**	4.65 (10H)	1.69 (6H, dd, $J = 8.9$ and 16.5), 1.35 (12H, br, m), 0.94 (9H, t, $J = 6.9$)	357.4 (d, $J = 3.4$)	216.4 (d, $J = 18.7$)		88.6	30.4 (d, $J = 25.6$), 25.8, 24.3 (d, $J = 13.7$), 13.8
MeNC, **1e**	4.68 (10H)	3.43 (3H)	358.0	212.9	157.9	87.8	30.8
MesNC, **1f**	4.71 (10H)	6.88 (2H), 2.35 (6H), 2.28 (3H)	355.7	212.8	167.5	87.8	138.2, 134.2, 128.5, 128.4, 21.2, 18.7
DcNC, **1g**	4.79 (10H)	7.37 (2H, d, $J = 8.5$), 7.18 (1H, t, $J = 8.5$)	354.5	212.1	179.1	88.1	131.8, 128.6, 128.3, 128.2
$[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)_2\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ (**2**)							
MeNC [d], **2e**	4.68 (10H)	3.45 (6H)				87.0	
MesNC, **2f**	4.68 (10H)	6.47 (4H), 2.29 (12H), 1.95 (6H)	356.9	216.6	176.8	87.6	137.1, 134.2, 128.7, 127.5, 20.9, 18.73
(DcNC)(PPh_3), **2h**	4.39 (5H) 4.51 (5H)	DcNC at 7.37 (2H, d, $J = 8.5$), 7.18 (1H, d, $J = 8.5$); Ph_3P at 7.48 (6H, m), 7.33 (9H, m)	359.0 (d, $J = 3.4$)	219.8 (d, $J = 17.1$)	191.8 (d, $J = 17.0$)	87.8, 87.9	DcNC at 132.3, 131.3, 128.4,127.4; Ph_3P at 137.2 (d, $J = 40.9$), 133.8 (d, $J = 10.2$), 130.1, 128.2 (d, $J = 10.2$)

[a] Spectra measured in $CDCl_3$ solution unless it is stated otherwise. Chemical shifts in ppm downfield from Me_4Si as an internal standard. All resonances are singlets unless it is stated otherwise. In parentheses are integration where appropriate, multiplicity (d = doublet, t = triplet, m = multiplet) and coupling constant J in Hz.

[b] MesNC = 2,4,6-$Me_3C_6H_2NC$. DcNC = 2,6-$Cl_2C_6H_3NC$.

[c] Taken from ref. [1]. Spectrum run in C_6D_6 solution.

[d] Low sample solubility prevents the observation of all resonances.



Scheme 1. CO ligands have been omitted for clarity. R_3P = (a) Ph_3P, (b) $(MeO)_3P$, (c) $(PhO)_3P$, (d) $^nBu_3P$; RNC = (e) MeNC, (f) 2,4,6-$Me_3C_6H_2NC$, (g) 2,6-$Cl_2C_6H_3NC$.

slow; at higher temperatures, decomposition is too fast. There is no evidence for the substitution of CO by R_3P. Clusters containing the $Fe(CO)(PR_3)_2$ moiety are not formed even with $Ph_2PCH_2CH_2PPh_2$.

Similar constraints were observed in the substitution reactions of **1a** with organoisocyanides CNR {R = (e) Me, (f) 2,4,6-$Me_3C_6H_2$ (Mes) or (g) 2,6-$Cl_2C_6H_3$ (Dc)} where very large excesses of CNR were used (10 to 40-fold) together with low temperatures. The reactions could be carried out at room temperature when they required 50–70 h for completion, but the best results were obtained on refluxing in dichloromethane solution for 80 min. This substitution proceeds in two stages (i) by Ph_3P replacement to give **1e**–**g** and then (ii) by CO replacement to give **2e**–**g**. Increasing the reaction times to 110 min resulted in a marked decrease in the yields of **1e** and **1f**, but only a small increase in the yields of **2e** and **2f**. There is no evidence for the formation of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CNR)_3\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ derivatives. The reaction of **1e**–**g** with excess CNR suggests that their CO ligands are labile. This is further demonstrated by refluxing **1g** with a large excess of Ph_3P in benzene solution which converts it to $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(CNDc)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **2h**. That stage (ii) is a reversible equilibrium is demonstrated by allowing a solution of **2f** to stand under an atmosphere of CO, when ca. 30% of it is converted to **1f**. The reaction goes to completion if $CoCl_2$ is added to the reaction mixture to sequester the free CNMes. It may also catalyse the ligand substitution (cf. ref. [7]). CO does not replace the remaining CNMes ligand in **1f** under these conditions.

3.2. Spectroscopy

3.2.1. IR spectra

These show numerous absorption bands but the only ones which can be identified with confidence are those due to ν(CN), ν(CO) and, in most cases, ν(CS) vibrations of the CNR, CO and CS ligands. The ν(CN) and ν(CO) bands are listed in Table 1, and the ν(CS) bands in Table 2 together with ν(CO) data for comparison.

The variation of the ν(CO) frequencies of **1** suggests that the overall electron-withdrawing ability of the phosphine, phosphite and isocyanide ligands L increases along the series $L = PBu^n_3 < PPh_3 < P(OMe)_3 < P(OPh)_3 <$ CNMe < CNXy < CNDc. It also suggests that the CNDc ($CNC_6H_3Cl_2$-2,6) ligand is, in many respects, comparable to CO itself as the ν(CO) frequency of **2h** with its $Fe(CO)(CNDc)(PPh_3)$ ligand set (1944 cm^{-1}) is lower than the mean ν(CO) frequency for **1a** with its $Fe(CO)_2(PPh_3)$ set (1954 cm^{-1}).

The unambiguous identification of the absorption band due to the ν(CS) vibration of clusters containing the μ_3-CS ligand has proved difficult. The IR spectra of complexes containing this ligand, **1a**–**c** and $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, all have two or three absorption bands in the appropriate region (1000–1100 cm^{-1}) where only one would be anticipated [1,8,9], and the same is true for the new compounds reported here. However, the $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ compounds **1a**–**g** represent the most extensive series of isostructural clusters containing the μ_3-CS ligand which has been reported to date. Furthermore, we were able to obtain good quality spectra of these compounds in the appropriate region using CH_2Cl_2 solutions. This removes the consequences of solid state effects so that absorption band frequencies can be compared. It would be expected that changes of the σ-donor/π-acceptor abilities of L should affect the ν(CS) frequencies of **1** in the same way as they affect their ν(CO) frequencies. Consequently we are able to say that the band at ca. 1061–1064 cm^{-1} found in all spectra, which has a frequency that is virtually independent of L, is unlikely to be due to the ν(CS) vibration. The bands which follow the required pattern lie between 1020 and 1041 cm^{-1} and their frequencies increase along the same series as above, i.e. $L = PBu^n_3$ (1026) < PPh_3(1030) < $P(OMe)_3$ (1036) < CNMe (1037) < CNMes (1038) < CNDc (1041 cm^{-1}). The appropriate band in the spectrum of **2e** lies at 1022 cm^{-1}, again following the pattern set by the ν(CO) frequencies.

3.2.2. ^{1}H-NMR spectra

These are generally unremarkable except to confirm the formulae. They all show the expected resonances due to the η^5-C_5H_5 and L ligands (Table 3). There are two C_5H_5 resonances in the spectrum of **2h** due to its chiral Fe(CO)(CNDc)(PPh_3) moiety which renders the two Co(η-C_5H_5) inequivalent. This has been observed previously in the ^{1}H-NMR spectrum of [{Co(η^5-C_5H_5)}$_2${Fe(CO)(CNMe)(PPh_3)}(μ_3-S)(μ_3-CO)] [6].

3.2.3. ^{13}C-NMR spectra

Where obtained, these are more informative than the ^{1}H spectra. They show resonances due to the ligating C atoms of CO, CNR and CS ligands. Their chemical shifts are listed in Table 3 together with those for the C_5H_5 and L ligands. Resonances due to μ_3-*C*S ligands are very weak and have not been observed previously. They are strongly deshielded at ca. δ 355–359. They may appear as doublets due to coupling to ^{31}P (J = ca. 3 Hz). These coupling constants are quite small when compared with those to the CO or CNR groups of the $FeL_2(PR_3)$ moiety (J = 17-21 Hz).

4. Conclusions

The PPh_3 ligand in the trigonal bipyramidal [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(PPh_3)}(μ_3-S)(μ_3-CS)] cluster may be replaced successfully by other PR_3 and by CNR ligands in thermal reactions but only under very specific conditions. The CO ligands in the [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(CNR)}(μ_3-S)(μ_3-CS)] complexes are labile and may be replaced by another CNR ligand in a reaction which is shown to be reversible, and by PPh_3. In the IR spectra of these complexes, the ν(CS) band of the μ_3-CS ligands has been identified. Its frequency is a function of L and lies in the range 1022–1041 cm^{-1} whilst in their ^{13}C-NMR spectra the resonance due to these μ_3-C atoms has been detected for the first time at δ 354–359.

There is no evidence for the formation of isomers of [{Co(η^5-C_5H_5)}$_2${Fe(CO)$_2$(CNR)}(μ_3-S)(μ_3-CS)] and [{Co(η^5-C_5H_5)}$_2${Fe(CO)(CNR)$_2$}(μ_3-S)(μ_3-CS)] which contain *t*-CS and μ_3-CNR ligands. This is a reflection of the very strong preference of the thiocarbonyl ligand for a bridging situation which prevents μ–t site exchange.

References

[1] A.R. Manning, L. O'Dwyer, P.A. McArdle, D. Cunningham, J. Organomet. Chem. 551 (1998) 139.

[2] A.R. Manning, A.J. Palmer, C.J. McAdam, B.H. Robinson, J. Simpson, J. Chem. Soc. Chem. Commun. (1998) 1577.

[3] A.R. Manning, A.J. Palmer, C.J. McAdam, B.H. Robinson, J. Simpson, Unpublished work.

[4] R.B. King, Inorg. Chem. 5 (1966) 82.

[5] (a) M.C. Baird, G. Hartwell Jr., G. Wilkinson, J. Chem. Soc. (A) (1967) 2037;
(b) P. Conway, S.M. Grant, A.R. Manning, J. Chem. Soc. Dalton Trans. (1979) 1920.

[6] A.R. Manning, L. O'Dwyer, P.A. McArdle, D. Cunningham, J. Organomet. Chem. 573 (1999) 109.

[7] M.O. Albers, N.J. Colville, T.V. Ashworth, E. Singleton, H.E. Swanpoel, J. Organomet. Chem. 199 (1980) 55.

[8] H. Werner, K. Leonhard, O. Kolb, E. Röttinger, H. Vahrenkamp, Chem. Ber. 113 (1980) 1654.

[9] J. Fortune, A.R. Manning, Organometallics 2 (1983) 1719.