Preliminary communication

The cleavage of a coordinated SCNR group in [Fe(CO)$_2$L$_2$(η^2-SCNR)] by [Co(η-C$_5$H$_5$)(PPh$_3$)$_2$] to give complexes containing μ_3-CNR ligand. The preparation and structure of [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S){μ_3-CNC(O)C$_6$H$_5$}]

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Abstract

The reaction of [Fe(CO)$_2$(PPh$_3$)$_2${η^2-SCNC(O)Ph}] with [Co(η-C$_5$H$_5$)(PPh$_3$)$_2$] in benzene solution at room temperature results in the facile cleavage of the C–S bond of the SCNC(O)Ph ligand to give [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S){μ_3-CNC(O)Ph}], whereas [Fe(CO)$_2$(PPh$_3$)$_2$(η^2-SCNMe)] gives [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)(CNMe)(PPh$_3$)}(μ_3-S)(μ_3-CO)]. The structure of [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S){μ_3-CNC(O)Ph}] has been confirmed by X-ray diffraction.

Keywords: Cobalt; Iron; μ_3-Isocyanide; μ_3-Carbonyl; Crystal structure

We have shown that a CS bond in the η^2-bonded CS$_2$ ligand of [Fe(CO)$_2$(PPh$_3$)$_2$(η^2-CS$_2$)] can be cleaved by [Co(η-C$_5$H$_5$)(PPh$_3$)$_2$] to give [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S)(μ_3-CS)] [1]. The reaction has now been extended to [Fe(CO)$_2$(PPh$_3$)$_2$(η^2-SCNR)] complexes.

The addition of solid [Fe(CO)$_2$(PPh$_3$)$_2$(η^2-SCNR)] (R = Me [2] or C(O)Ph [3]) to a stirred solution of [Co(η-C$_5$H$_5$)(PPh$_3$)$_2$] [4] in benzene (reactant mole ratio 1 : 2) resulted in a colour change from red to green over a period of 5 h. Chromatography (dichloromethane-tetrahydrofuran on alumina) gave 70% yields of green crystals of [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)} (S)(CNR)] where R = Me or C(O)Ph.

These complexes have structures similar to that of [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S)(μ_3-CS)] [1]. They are based on a Co$_2$Fe triangle bridged on one face by a μ_3-S ligand and on the other by a triply-bridging two-electron donor coordinating through C. The infrared spectrum of that where R = C(O)Ph shows absorption bands at 1979, 1927 and 1562 cm^{-1} (KBr disc)

which are attributed respectively to the ν(CO$_t$), ν(CO)$_t$ and the ν(CN) vibrations of the μ_3-CNC(O)Ph isomer illustrated in Fig. 1(a) (ν(CO$_{acyl}$) is found at 1642 cm^{-1}). This is the sole species found in the solid state and in solution. In contrast, when R = Me the only species observed is that illustrated in Fig. 1(b). It contains a μ_3-CO ligand and a t-CNMe ligand and gives rise to absorption bands at 2143, 1919 and 1639 cm^{-1} (KBr disc) due respectively to ν(CN), ν(CO) and ν(μ_3-CO) vibrations. The ^{1}H NMR spectra of the two complexes also show significant differences. When R = Me the Fe(CO)(CNMe)(PPh$_3$) fragment is chiral and
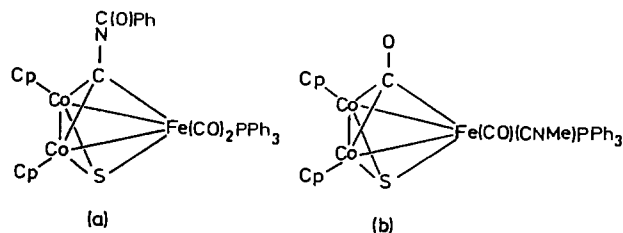

Fig. 1. Proposed structures of (a) [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)} (μ_3-S){μ_3-CNC(O)Ph}] and (b) [{Co(η-C$_5$H$_5$)}$_2${Fe(CO)(CNMe) (PPh$_3$)}(μ_3-S)(μ_3-CO)].

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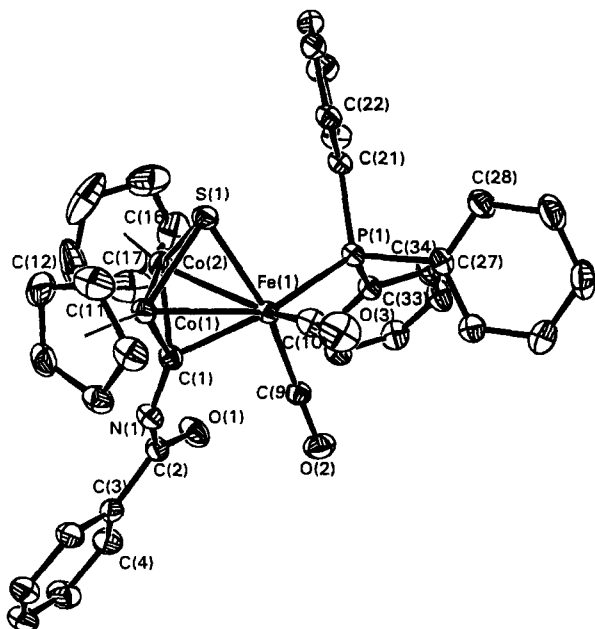
Fig. 2. The molecular structure and atom labelling for [{Co(η-C₅H₅)}₂{Fe(CO)₂(PPh₃)}(μ₃-S){ μ₃-CNC(O)Ph}]. Selected bond lengths (Å) and angles (°) are as follows: Co(1)–Co(2) 2.4266(5), Co(1)–Fe(1) 2.5224(4), Co(2)–Fe(1) 2.5483(4), Co(1)–S(1) 2.1244(6), Co(2)–S(1) 2.1333(6), Fe(1)–S(1) 2.1866(6), Co(1)–C(1) 1.917(2), Co(2)–C(1) 1.901(2), Fe(1)–C(1) 2.109(2), C(1)–N(1) 1.276(2), Co(1)–Co(2)–Fe(1) 60.87(2), Co(1)–Fe(1)–Co(2) 57.18(2), and Co(2)–Co(1)–Fe(1) 61.948(11).

the two Co(η-C₅H₅) moieties differ and give rise to two cyclopentadienyl resonances at δ 4.51 and 4.61 downfield from Me₄Si (CD₃CD₅ solution) with a single Me resonance at δ 2.21 which is a doublet ($J_{PH} = 1.8$ Hz). When R = C(O)Ph the Fe(CO)₂(PPh₃) fragment is not chiral, and there is a single C₅H₅ resonance at δ 4.69 with the PhC(O) resonances at δ 7.32, 7.43, and 9.13 (C₆D₆ solution). The spectra of both compounds also show the resonances due to the PPh₃ ligand at ca. δ 7–8.

Although crystals of [{Co(η-C₅H₅)}₂{Fe(CO)(CNMe)(PPh₃)}(μ₃-S)(μ₃-CO] could not be obtained, one of [{Co(η-C₅H₅)}₂{Fe(CO)₂(PPh₃)}(μ₃-S){ μ₃-CNC(O)Ph}] was subjected to an X-ray diffraction study [5], and the structure proposed on the basis of spectroscopic data confirmed (Fig. 2). It is very similar to that of [{Co(η-C₅H₅)}₂{Fe(CO)₂(PPh₃)}(μ₃-S)(μ₃-CS)], but with the μ₃-CS ligand replaced by μ₃-CNC(O)Ph which bonds through carbon more or less equally to the Co₂Fe triangle.

The RNCS ligand coordinates to iron through C and S rather than C and N [2]. Therefore the above results suggest strongly that it is the coordinated C=X of a η²-XCY ligand which is cleaved by [Co(η-C₅H₅)(PPh₃)₂], and not the uncoordinated C=Y bond.

References and notes

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[5] Crystal data: C₃₈H₃₀Co₂FeNO₃PS, M = 785.37, monoclinic, P2₁/C, a = 13.2350(10), b = 14.024(2), c = 17.928(2) Å, β = 91.41(2)°, Z = 4, U = 3326.6(7) Å³, Dc = 1.568 Mg m⁻³, F(000) = 1600. Diffraction data were collected with a CAD4F diffractometer. The structure was solved by direct methods [6] and refined by full matrix least squares analysis [7] using 12351 reflections of which 11524 were independent. For all data R₁ = 0.0584 and wR₂ = 0.1158, whilst for data where I > 2σI (4156 reflections) R₁ = 0.0323 and wR₂ = 0.1030. The drawing was obtained using the ORTEX program [8]. Tables of atom coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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