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Alkynethiolate ligands in the syntheses of iron carbonyl derivatives. Crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SC{\equiv}CSiMe_3)]$

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Abstract

The complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SC{\equiv}CR)]$ (R = ^{t}Bu, SiMe$_3$) have been obtained by reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and the corresponding LiSC≡CR. These are the first examples of mononuclear iron compounds containing alkynethiolate ligands. The crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SC{\equiv}CSiMe_3)]$ has been determined by X-ray diffraction. The role of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SC{\equiv}CSiMe_3)]$ as a metalloligand in its reactions with metal carbonyls has been explored. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cyclopentadienyl iron complexes; Alkynethiolates derivatives; X-ray diffraction

1. Introduction

The use of organosulfur ligands in transition metal chemistry has been of interest due to the importance of the formation or cleavage of C–S bonds either from biological, industrial or environmental point of view [1].

Although thiolate or acetylide chemistry has been widely explored, just a few complexes containing alkynethiolate ligands are known [2]. To our knowledge, the only iron compounds with this type of ligands that have been reported are $[Fe_2(\mu\text{-}C{\equiv}CPh)(\mu\text{-}SC{\equiv}CPh)(CO)_6]$, prepared by reaction of $Fe_3(CO)_{12}$ and $S(C{\equiv}CPh)_2$ [3], and $[Fe_2(\mu\text{-}SMe)(\mu\text{-}SC{\equiv}CPh)(CO)_6]$ obtained from $[Fe_2(\mu\text{-}S_2)(CO)_6]$ by cleavage of the S–S bond using LiC≡CPh and further addition of MeI [4].

Keeping the above mentioned in mind, we have considered of interest to synthesize new mononuclear complexes such as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SC{\equiv}CR)]$ and to study their role as building blocks for the preparation of di- and polynuclear compounds.

2. Results and discussion

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SC{\equiv}CR)]$ [R = ^{t}Bu (**1**), SiMe$_3$ (**2**)] compounds have been prepared by reacting $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and LiSC≡CR. In the course of these reactions we have observed that a strict control of the temperature and reaction time is necessary in order to minimize the formation of Fp$_2$ as by-product. Although the above reactions are almost quantitative (based on spectroscopic data) only compound **2** is stable enough in solution to be isolated with a good yield as a crystalline compound.

The spectroscopic data of compounds **1** and **2** are in agreement with their formulation. Thus, the IR spectra show in both cases two strong C–O and a weak C–C stretching bands at the expected wavenumbers. The presence of acetylide ligand is clearly denoted by the observation of α-C and β-C resonances, respectively, (77.7 and 84.2 ppm for **1**; 80.1 and 108.8 ppm for **2**), in addition to the characteristic ^{t}Bu or SiMe$_3$ resonances. Although the chemical shift difference between α-C and β-C in **2** is large, it is still within the range observed for other complexes containing the trimetylsilylacetylide ligand [2b].

The structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SC{\equiv}CSiMe_3)]$ compound (**2**) (Fig. 1) was confirmed by X-ray diffrac-

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tion. Although the synthesis of a few mononuclear ruthenium complexes containing alkynethiolate ligands has been previously reported [2], compound **2** represents the first example of a Group 8 metal complex that has been characterized by X-ray diffraction. Compound **2** exhibits a typical three-legged piano-stool structure. A plane of symmetry passing through the alkynethiolate group (S, C(2), C(3), and Si atoms), the C(12) and the Fe atoms are observed in the molecule. The existence of the C≡C group is confirmed by the bond distance C(2)–C(3) [1.205(4) Å] (Table 1) which is analogous to those found for [(η^5-C_5H_5)Fe$(CO)_2$-(C≡CR)] [R = $SiMe_3$, 1.201(5) Å [5] and R = Ph, 1.201(9) Å [6]]. The Fe–S distance [2.3092(9) Å] and the Fe–S–C(2) angle [105.17(8)°] are similar to those measured for [(η^5-C_5H_5)Fe$(CO)_2$(SEt)] [2.296(2) Å and 107.0(2)°] [7]. Two CH_3 groups from the trimethylsilyl present a disorder around the mirror (m) parallel to the *bc* plane, which is a plane of symmetry for the molecule. The atoms C(51) and C(52) are statistically distributed on the each sides of this mirror with the ratio of occupancy equal to 60/40%.

The use of transition metal thiolate or acetylide derivatives as precursors in the syntheses of di- or polynuclear compounds has been widely developed [8], on the contrary, reports concerning the related alkynethiolate complexes are scarce. In this context, we have explored its potential as building block of [(η^5-C_5H_5)Fe$(CO)_2$(SC≡C$SiMe_3$)] by reaction with some metal carbonyls.

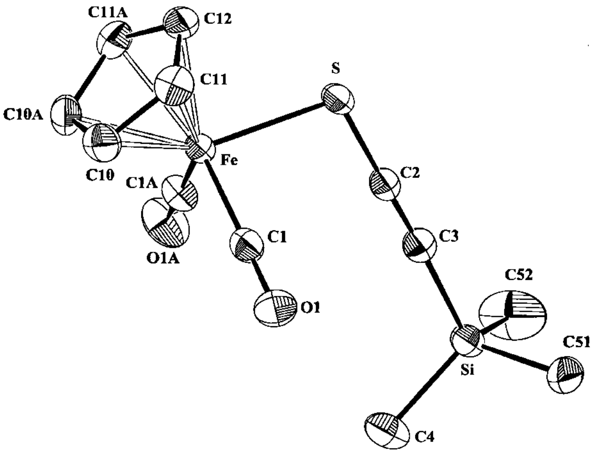

Fig. 1. View of [(η^5-C_5H_5)Fe$(CO)_2$(SC≡C$SiMe_3$)] (**2**).

Table 1
Selected bond distances (Å) and angles (°) of [(η^5-C_5H_5)Fe$(CO)_2$(SC≡C$SiMe_3$)] (**2**)

Bond lengths			
Fe–C(1)	1.7753(17)	C(2)–C(3)	1.205(4)
Fe–S	2.3092(9)	Si–C(3)	1.827(3)
S–C(2)	1.678(3)	Si–C(4)	1.844(3)
Bond angles			
C(1)–Fe–C(1A)	94.38(12)	C(4)–Si–C(51)	105.9(3)
C(1A)–Fe–S	91.28(7)	C(2)–C(3)–Si	177.5(2)
C(2)–S–Fe	105.17(9)	C(3)–C(2)–S	179.4(2)
C(3)–Si–C(4)	109.06(15)		

Unfortunately all reactions carried out between compound **2** and $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ at different temperatures and using either THF or toluene as solvents, in order to obtain higher nuclearity compounds failed probably due to the instability of the compound [(η^5-C_5H_5)$Fe_2(CO)_6$(μ-SC≡C$SiMe_3$)], which was probably formed at the first stage. Fp_2 and [$Fe_2(CO)_6$(μ-SC≡C$SiMe_3$)$_2$] compounds [IR (cm^{-1}, hexane): 2078 (m), 2038 (s), 2007 (s), 2002 (s), 1991 (w), 1979 (w). ^{1}H-NMR ($CDCl_3$): δ (ppm) 5.00 (s, 5H, C_5H_5), 0.12 (s, 9H, SiMe_3)] were the only products obtained in these reactions. This decomposition process is reminiscent of others observed in related mononuclear iron thiolate derivatives [9].

We have also studied the reaction between [(η^5-C_5H_5)Fe$(CO)_2$(SC≡CR$SiMe_3$)] (**2**) and the stoichiometric amount of $Co_2(CO)_8$ to produce [(η^5-C_5H_5)Fe-$(CO)_2$(μ_3, η^3-SC≡C$SiMe_3$)$Co_2(CO)_6$] (**3**) compound. The overall composition of this complex is confirmed through a FAB^+ mass spectrum, which exhibits peaks corresponding to the ($M^+ + 1$) ion, as well as fragments derived from loss of up to eight carbonyl ligands. On the other hand, the absence of the ν(C≡C) in the IR spectrum as well as the significant shift to lower field of the signals corresponding to acetylide groups (93.9 and 128.2 ppm) with the presence of two resonances at 200.7 and 212.4 ppm assigned to the carbonyl groups in the ^{13}C-NMR spectrum, are indicative of the coordination of the cobalt carbonyl fragment to the C≡CR group. Attempts to obtain a $FeCo_2$ cluster by forcing CO elimination from **3** have been unsuccessful.

3. Experimental

3.1. Synthesis of [(η^5-C_5H_5)Fe$(CO)_2$(SC≡CR)] (R = ^{t}Bu (**1**), $SiMe_3$ (**2**))

Details of the synthesis of **1** also apply to **2**. A solution of LiSC≡C^{t}Bu (1.1 mmol) in THF (10 ml) at − 45 °C was slowly added with stirring to a solution of [(η^5-C_5H_5)Fe$(CO)_2$I] (0.300 g, 0.99 mmol) in THF (15 ml) at the same temperature. The resulting mixture was allowed to reach 0 °C and then stirred for 30 min. The solvent was removed under vacuum and the residue extracted with *n*-hexane (3 × 10 ml) at 0 °C. Then the solution was concentrated to a volume of ca. 10 ml and cooled at − 76 °C. The crystals thus obtained were filtered off, washed with cold *n*-hexane and dried under vacuum, 0.04 g, 13.9% yield. For R = $SiMe_3$ (**2**), 0.187 g, 61.6% yield.

Compound **1**: IR (cm^{-1}, THF): 2141 (w; $C\equiv C$), 2032 (s), 1987 (s). IR (cm^{-1}, KBr): 2137 (w; $C\equiv C$), 2045 (s), 1994 (s). ^1H-NMR ($CDCl_3$): at 20 °C, δ (ppm) 4.97 (s, 5H, C_5H_5), 1.18 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): at 20 °C, δ (ppm) 28.7 [$\mathit{C}(CH_3)_3$], 31.4 [$C(\mathit{C}H_3)_3$], 77.7 ($SC\equiv\mathit{C}$), 84.2 ($S\mathit{C}\equiv C$), 85.7 (C_5H_5), 212.3 ($\mathit{C}O$). Anal. Calc. for $C_{13}H_{14}O_2SFe$ (Found): C, 53.81 (52.75); H, 4.86 (4.76)%.

Compound **2**: IR (cm^{-1}, THF): 2059 (m; $C\equiv C$), 2034 (s), 1991 (s). IR (cm^{-1}, KBr): 2062 (vw; $C\equiv C$), 2038 (m), 1996 (s), 1978 (sh). ^1H-NMR ($CDCl_3$): at 20 °C, δ (ppm) 0.12 [s, 9H, $Si(CH_3)_3$], 5.00 (s, 5H, C_5H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (ppm) at 20 °C, 0.5 ($Si(CH_3)_3$), 80.1 ($SC\equiv\mathit{C}$), 85.8 (C_5H_5), 108.8 ($S\mathit{C}\equiv C$), 211.8 (CO). Anal. Calc. for $C_{12}H_{14}O_2SSiFe$ (Found): C, 47.07 (47.22); H, 4.61 (4.75)%.

3.2. Reaction of [(η^5-C_5H_5)Fe(CO)$_2$(SC≡CSiMe$_3$)] with [Co$_2$(CO)$_8$]

[$Co_2(CO)_8$] (0.08 g, 0.23 mmol) dissolved in THF (15 ml) was added to a solution of **2** (0.07 g, 0.23 mmol) in the same solvent (15 ml). The mixture was stirred at 20 °C for 1 h. After evaporation of the solvent to dryness the solid residue was chromatographed on silica gel 100. Compound **3** was eluted from a mixture of *n*-hexane–THF (10:1) as a green band. Recrystallization from *n*-hexane at −76 °C afforded a green solid (0.107 g, 72.0% yield). IR (cm^{-1}, hexane): 2080 (m), 2046 (s), 2036 (m), 2018 (m), 2012 (m), 2005 (sh), 1995 (m), 1984 (w), 1962 (w).^1H-NMR ($CDCl_3$): at 20 °C, δ (ppm) 0.37 [s, 9H, $Si(CH_3)_3$], 5.10 [s, 9H, C_5H_5]. $^{13}C\{^1H\}$-NMR ($CDCl_3$): at 20 °C, δ (ppm) 0.5 [$Si(CH_3)_3$], 85.5 (C_5H_5), 93.9, 128.2 ($C\equiv C$), 200.7 (Co–CO), 212.4 (Fe–CO). FAB$^+$ (*m*/*z*): 593 ($M^+ + 1$), 564 ($M^+ - CO$), 536 ($M^+ - 2CO$), 508 ($M^+ - 3CO$), 480 ($M^+ - 4CO$), 452 ($M^+ - 5CO$), 424 ($M^+ - 6CO$), 396 ($M^+ - 7CO$), 368 ($M^+ - 8CO$). Anal. Calc. for $C_{18}H_{14}O_8SSiFeCo_2$ (Found): C, 36.51 (36.92); H, 2.38 (2.80)%.

4. Crystal data for 2

Light yellow crystals of **2** suitable for an X-ray study were obtained upon standing a solution overnight in *n*-hexane at −20 °C (0.40 × 0.40 × 0.20 mm). Compound **2** of formula $C_{12}H_{14}O_2SSiFe$ crystallizes in the orthorhombic cell of space group $Pmn2_1$, with $a = 9.756(2)$, $b = 9.271(2)$, $c = 8.156(2)$ Å, $V = 737.7(3)$ Å^3, $Z = 4$, $D_{calc} = 1.379$ mg m^{-3}, $\mu(Mo\text{–}K_\alpha) = 1.232$ mm^{-1}, 5398 reflections (1423 unique reflections) were measured ($3.3 < 2\theta < 52.1°$, ϕ scan, $T = 160(2)$ K) on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device diffractometer and using a monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å), overall completeness to 2θ: 95.9%. Data were corrected for absorption using numerical methods [10], theses corrections were optimized with the aid of the software [11], using a maximum and a minimum transmission of 0.837 and 0.492, respectively. Structure has been solved by Direct Methods using SIR92 [12] and refined by least-squares procedures on a F^2 with the aid of (SHELXL97) [13].

The model reached Final *R* indices: $R_1 = 0.0197$, $wR_2 = 0.0502$ for 1423 reflections with $I > 2\sigma(I)$, and $R_1 = 0.0201$, $wR_2 = 0.0503$ on all data, Goodness-of-fit $(S) = 1.069$.

Hydrogen atoms were introduced on calculated positions and refined riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters. A final Fourier map showed no residual density outside −0.244 and 0.200 e Å^{-3}. The absolute configuration of the compound **2** has been determined on the basis of refinement of Flack's parameter *X* [14], which is the fractional contribution of $F(-h)$ like it is showed in the following formula: $\mathrm{F}(h) = (1 - X)F(h) + XF(-h)$. The value of this parameter was found close to 0 [$-0.001(13)$], that proves the adequate choice of the enantiomer. The drawing of molecule has been performed with the program ZORTEP [15] with 50% probability displacement ellipsoids for non-hydrogen atoms.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 155925 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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