Reaction of η^4-ketene complexes of iron with a phosphorus–sulfur ylide (Davy reagent): Insertion of sulfur into a carbon–iron bond with formation of ferrathiolactones

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Abstract

Complexes $Fe(CO)_3(\eta^4\text{-PhCH}=CH=C(Ph)=C=O)$ (1) and $Fe(CO)_3(\eta^4\text{-PhCH}=CH-(CH=CHPh)C=C=O)$ (2) react with Davy's reagent (2,4-bis(methylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide) to give complexes $(Fe(CO)_3(SC(O)-C(Ph)=CH-CHPh)$ (3) and $[Fe(CO)_3(SC(O)-C(CH=CHPh)=CH-CH(Ph))]$ (4) upon insertion of sulfur into an Fe–C bond. Complex 4 could be fully characterized by X-ray crystallography: $C_{21}H_{14}FeO_4S$; triclinic; space group, $P\bar{1}$; $a = 6.825(2)$, $b = 10.770(2)$ and c 13.375(2) Å; $\alpha = 103.55(2)$, $\beta = 91.60(2)$ and $\gamma = 91.10(2)°$; $U = 955.0(2)$ Å^3; $D_c = 1.454$ g cm^{-3}; $Z = 2$.

Keywords: Iron; Ketene complexes; Davy reagent; Ylides; Ferrathiolactones

1. Introduction

Both Davy's reagent and Lawesson's reagent have been used for the thiation of carbonyl-containing molecules [1,2]. Especially worth noting is the transformation of lactones into thiolactones induced by these reagents [3]. In connection with our investigations on the reactivity of ketene complexes of transition metals toward nucleophiles [4] we examined their behavior towards two ketene complexes of iron tricarbonyl; indeed iron tricarbonyl is known [5,6] to stabilize sulfur-containing ligands and especially thioesters and thioketones. Moreover, the ketene complexes are readily available [7] and might hopefully lead to the related thioketene complexes. Surprisingly this was, however, not the case.

2. Results and discussion

When a solution of 1 in benzene was reacted with an excess of Davy's reagent (2,4-bis(methylthio)-1,3-di-thia-2,4-diphosphetane-2,4-disulfide) at room temperature for 5 h, the formation of a new complex was observed by thin layer chromatography. After filtration of the solution over alumina followed by evaporation of the solvent, the residue was chromatographed on silica gel to give apart from the starting complex 1 (12.2%), a new greenish-yellow complex 3 which was isolated with a 20.7% yield. The elemental analysis was in agreement with the incorporation of sulfur into the starting material without removal of oxygen; thus the formation of the expected thioketene 6 did not take place (Scheme 1). IR showed three bands in the $v(CO)$ region, at 2040, 2015 and 2005 cm^{-1}, a fact which indicated a greater electronic density at the metal for this new complex; this was a first indication of the coordination of the sulfur atom to the iron. Moreover, the absorption at 1790 cm^{-1} for the carbonyl of the coordinated ketene appeared in the new complex at 1650 cm^{-1}. The ^1H NMR spectrum confirmed the presence of a coordinated double bond as in the ketene complex, with signals at $\delta = 6.02$ (d, 1H, $J = 12.4$ Hz) ppm and at 4.81 (d, 1H, $J = 12.4$ Hz) ppm. This appeared also in the ^{13}C NMR spectrum with signals at $\delta = 94.9$, 89.7 and 82.5 ppm for the three sp^2 carbon
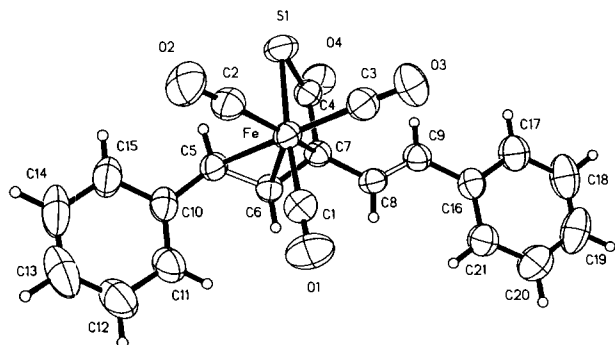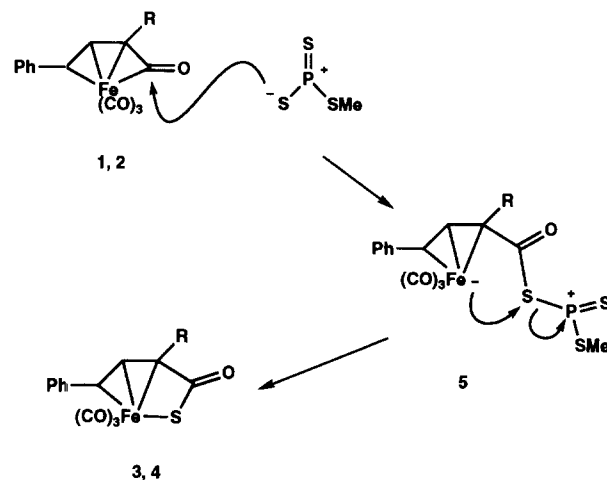
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1: R = Ph

2: R = (CH=CHPh)

3: R = Ph

4: R = (CH=CHPh)

6

Scheme 2.

Davy's Reagent=
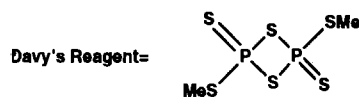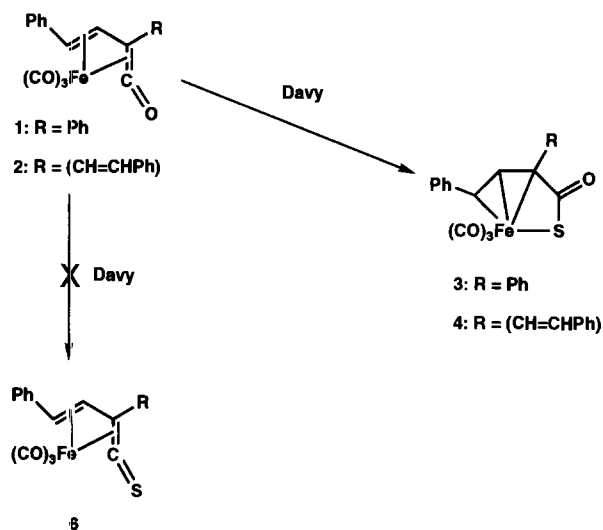
Scheme 1.

atom (at $\delta = 49.7$, 60.8 and 91.4 ppm in the starting complex 1). Nevertheless this spectrum confirmed the disappearance of the signal at 233 ppm typical of the carbonyl of the ketene. Signals at $\delta = 207.4$, 205.0, 204.2 and 196.2 ppm indicated, however, the presence of four different CO groups. Among these, three must be M–CO group and one a non-metallic CO group. The position of this signal at around 200 ppm, together with the IR absorption at 1650 cm^{-1} indicated that cleavage of the bond between Fe and the central carbon atom of the ketene function in 1 probably took place.

When the same reaction was carried out on 2, 4 could be isolated as a yellow solid with a low 6% yield (Scheme 1). The high resolution mass spectrum indicated the presence of three metallic CO groups (M$^+$– 3CO, 334.0114) and again the insertion of one sulfur atom. The NMR data of this new complex agreed with those of 3; the ^{1}H NMR spectrum indicated signals for a free carbon–carbon double bond, the signal of one

proton appearing among the signals of the aromatic protons and the second at $\delta = 6.62$ ppm as a doublet ($J = 16.1$ Hz), and of a coordinated double bond, with signals at $\delta = 6.03$ and 4.81 ppm as two doublets ($J = 12.7$ Hz). The ^{13}C NMR spectrum disclosed the same pattern of signals as for 3; four signals for the CO groups at $\delta = 195.2$, 203.6, 205.5 and 207.3 ppm and, besides the signals of the free double bond and the aromatic groups, three additional signals at $\delta = 81.5$, 91.6 and 95.7 ppm.

Crystals of 4 suitable for X-ray determination could be grown from chloroform. The ORTEP projection appears in Fig. 1 whereas the bond distances and bond angles are listed later in Table 2. This confirms that the interaction between 2 and the phosphorus–sulfur ylide resulted in the insertion of sulfur into the Fe–C(4) bond with formation of a ferrathiolactone. The overall structure of this complex is best described as a deformed octahedron in which two CO groups and the π-allyl system C(5)–C(6)–C(7) occupy the equatorial plane, whereas the last CO and the Fe–S bond are in the axial positions. The length of this latter Fe–S(1) bond, 2.322(1) Å, is consistent with a σ Fe–S bond, whereas the C(4)–S(1) bond, 1.738(4) Å, shorter than a classical C–S single bond shows some partial double-bond character.

It is interesting to note that the Fe–S(1)–C(4)–C(7)–C(6) framework presents many analogies with the framework observed in the complexes resulting from the interaction of Fe(CO)$_3$ with thioamides (O(4) being replaced by NR$_2$) especially as far as the Fe–S and the C–S bond lengths are concerned [7].

3. Conclusion

A mechanism which would account for the formation of 3 and 4 is given in the Scheme 2; like other nucle-

Fig. 1. The molecular structure and atom numbering scheme for 4.

ophiles [8], the negatively charged sulfur of the monomeric ylide might attack the central carbon atom of the coordinated ketene and lead to **5**, which upon intramolecular nucleophilic displacement with cleavage of the S–P bond might give the observed complexes **3** and **4**. Surprisingly, no insertion of sulfur could be detected when **1** and **2** were treated under the same conditions with Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide); only decomposition of the starting complexes was observed.

4. Experimental details

4.1. General methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR-300S spectrometer. IR spectra were recorded on a Perkin–Elmer 283B spectrometer and mass spectra on a ZAB HSQ (Fisons) instrument. Microanalyses were performed by the Service Central d'Analyses du CNRS, Solaize. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. Column chromatography was performed with Merck silica gel (70-230 mesh) using various ratios of ethyl acetate:hexane or dichloromethane:hexane as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under a nitrogen atmosphere in carefully dried glassware. Benzene was distilled from sodium–benzophenone ketyl under an argon atmosphere. Complexes **1** and **2** were prepared by known procedures [9,10].

4.2. Reaction of $Fe(CO)_3(\eta^4$-$(PhCH = CH–C(Ph) = C = O)$ (1) with Davy's reagent: formation of 3

A solution of **1** (1.4 g, 3.88 mmol) in benzene (50 ml) was treated at room temperature with Davy's reagent (2.0 g, 7.04 mmol) for 5 h. The solution was then filtered through a short column of neutral alumina to remove decomposition products, the solvent evaporated under vacuum, and the residue chromatographed on silica gel. Elution with 90 : 10 hexane; ethyl acetate first gave **1** (0.176 g, (12.6%)) and then **3** (0.302 g, (19.8%)) as a greenish-yellow solid (melting point (m.p.), 146 °C (decomposition)). IR (KBr): ν 2040, 2015 2005, 1650 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.76–7.31 (m, 10H, Ar), 6.02 (d, 1H, $J = 12.4$ Hz), 4.81 (d, 1H, $J = 12.4$ Hz) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 207.4, 205.0, 204.2, 196.2 (4CO), 137.0, 135.5, 129.6, 129.4, 128.9, 126.9 (Ar), 94.9, 89.7, 82.5 (FeCH=CH, FeC=). ppm. Anal. Found: C, 58.98; H, 3.06; Fe, 14.93; S, 8.31. C$_{19}$H$_{12}$FeO$_4$S: Calc.: C, 58.14; H, 3.06; Fe, 14.28; S, 8.16% HRMS. Found, 335.9905. C$_{17}$H$_{12}$FeO$_2$S (M$^+$ – 2CO) Calc.: 335.9907.

4.3. Reaction of $Fe(CO)_3(\eta^4$-$PhCH = CH–(CH = CHPh)C = C = O)$ (2) with Davy's reagent: formation of 4

A solution of **2** (0.954 g, 2.47 mmol) in benzene (50 ml) was treated at room temperature with Davy's reagent (1.053 g, 3.71 mmol) for 5 h. Treatment as above first gave, upon silica gel chromatography with 98 : 2 hexane : ethyl acetate as eluent, **2** (0.225 g (23.6%)) and then **4** (0.060 g (6%)) as a yellow solid (m.p. 173 °C). IR (KBr): 2070, 2015, 2000, 1653 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.33–7.52 (m, 11H, Ar CH=), 6.62 (d, 1H, $J = 16.1$ Hz), 6.03 (d, 1H, $J = 12.7$ Hz), 4.81 (d, 1H, $J = 12.7$ Hz). ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ 207.3, 205.5, 203.6, 195.2 (4CO), 136.9, 136.1, 134.0, 129.5, 128.8, 126.9, 126.2, 124.7 (Ar, C=C), 95.7, 91.6, 81.5 (FeCH=CH, Fe–C) ppm. HRMS. Found, 334.0113. C$_{18}$H$_{14}$FeOS (M$^+$ – 3CO) Calc.: 334.0114.

4.4. X-ray data collection and structure solution for 4

Crystals of **4** suitable for X-ray examination were grown from CHCl$_3$ at room temperature.

Table 1
Atomic coordinates and equivalent isotropic displacement coefficients for C$_{21}$H$_{14}$FeO$_4$S (**4**)

Atom	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	U_{eq} [a] ($\times 10^3$ Å^2)
Fe	2044(1)	7686(1)	1424(1)	39(1)
S(1)	4895(1)	8052(1)	618(1)	55(1)
O(1)	−1598(4)	6982(3)	2284(3)	81(1)
O(2)	4356(5)	8016(3)	3361(2)	83(1)
O(3)	2391(5)	5066(3)	158(3)	81(1)
O(4)	3737(4)	8865(3)	−1027(2)	62(1)
C(1)	−210(6)	7277(4)	1946(3)	51(1)
C(2)	3459(5)	7832(3)	2614(3)	52(1)
C(3)	2267(6)	6050(4)	672(3)	53(1)
C(4)	3309(5)	8520(3)	−256(3)	46(1)
C(5)	1818(5)	9789(3)	1824(3)	45(1)
C(6)	587(5)	9179(3)	994(3)	40(1)
C(7)	1223(5)	8387(3)	60(3)	39(1)
C(8)	−224(5)	7682(3)	−699(3)	43(1)
C(9)	99(5)	7050(3)	−1650(3)	47(1)
C(10)	1103(6)	10452(3)	2840(3)	50(1)
C(11)	−832(7)	10460(4)	3107(3)	68(2)
C(12)	−1367(8)	11063(5)	4089(3)	87(2)
C(13)	−16(11)	11664(5)	4801(4)	99(3)
C(14)	1896(10)	11701(5)	4557(4)	92(2)
C(15)	2481(7)	11097(4)	3569(3)	71(2)
C(16)	−1350(5)	6294(3)	−2382(3)	48(1)
C(17)	−783(7)	5593(4)	−3324(3)	70(2)
C(18)	−2120(9)	4860(5)	−4020(3)	83(2)
C(19)	−4030(9)	4811(5)	−3794(4)	85(2)
C(20)	−4643(8)	5481(5)	−2868(4)	90(2)
C(21)	−3320(6)	6224(5)	−2166(3)	73(2)

[a] $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

4.4.1. Crystal data

$C_{21}H_{14}FeO_4S$; $M_7 = 418.2$; triclinic; $a = 6.825(2)$, $b = 10.770(2)$ and $c = 13.375(2)$ Å; $\alpha = 103.55(2)$, $\beta = 91.60(2)$ and $\gamma = 91.10(2)°$; $U = 955.0(2)$ Å^3; space group, $P\bar{1}$; $Z = 2$; $D_c = 1.454$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 0.922$ mm^{-1}; $F(000) = 428$.

4.4.2. Data collection

Intensity for an orange prismatic crystal ($0.30 \times 0.28 \times 0.22$ mm) was measured at room temperature on a Siemens P4/PC diffractometer fitted with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). 3643 reflections were collected in the ω scan mode in the range $3.0° \leqslant \Theta \leqslant 50°$, of which 3337 were unique and 2601 had $F \geqslant 3\sigma(F)$. Data were corrected for Lorentz and polarization factors but no absorption correction was applied.

4.4.3. Structure solution and refinement

The structure was solved by direct methods, followed by different Fourier syntheses. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method and the hydrogen atoms of phenyl rings were included using a riding model and refined with an isotropic U temperature factor of 0.06 Å^2. The weighting scheme $w^{-1} = \sigma^2(F) + 0.0008F^2$ gave final conventional R and R_w values of 4.38 and 5.12% and a goodness of fit of 1.06 with a data-to-parameter ratio of 10.1 to 1. All atomic scattering factors were taken from [11]. Computation used the SHELXTL PLUS (PC version) program [12]. The final atomic coordinates and U_{eq} for non-hydrogen atoms are listed in Table 1. Interatomic distances and bond angles for non hydrogen atoms are given in Table 2.

Supplementary data including anisotropic displacement coefficients (Table S1), hydrogen atom coordinates (Table S2) and structure factors (Table S3) are available from the authors (10 pages).

Table 2
Bond lengths (Å) and bond angles (°) for $C_{21}H_{14}FeO_4S$ (**4**) where the estimated standard deviations in parentheses refer to the last significant digit

Bond lengths

Fe–S(1)	2.322(1)	C(7)–C(8)	1.462(4)
Fe–C(1)	1.796(4)	C(8)–C(9)	1.321(5)
Fe–C(2)	1.812(4)	C(9)–C(16)	1.463(5)
Fe–C(3)	1.823(4)	C(10)–C(11)	1.377(6)
Fe–C(5)	2.211(4)	C(10)–C(15)	1.387(6)
Fe–C(6)	2.091(4)	C(11)–C(12)	1.384(6)
Fe–C(7)	2.194(4)	C(12)–C(13)	1.348(8)
S(1)–C(4)	1.738(4)	C(13)–C(14)	1.356(10)
O(1)–C(1)	1.133(5)	C(14)–C(15)	1.401(6)
O(2)–C(2)	1.131(5)	C(16)–C(17)	1.378(5)
O(3)–C(3)	1.126(5)	C(16)–C(21)	1.388(6)
O(4)–C(4)	1.215(5)	C(17)–C(18)	1.380(7)
C(4)–C(7)	1.510(5)	C(18)–C(19)	1.349(9)
C(5)–C(6)	1.398(5)	C(19)–C(20)	1.360(7)
C(5)–C(10)	1.481(5)	C(20)–C(21)	1.382(6)
C(6)–C(7)	1.421(4)		

Bond angles

S(1)–Fe–C(1)	174.6(1)	Fe–C(3)–O(3)	176.0(4)
S(1)–Fe–C(2)	89.4(1)	S(1)–C(4)–O(4)	127.4(3)
C(1)–Fe–C(2)	94.3(2)	S(1)–C(4)–C(7)	109.1(3)
S(1)–Fe–C(3)	83.8(1)	O(4)–C(4)–C(7)	123.4(3)
C(1)–Fe–C(3)	91.3(2)	Fe–C(5)–C(6)	66.4(2)
C(2)–Fe–C(3)	107.3(2)	Fe–C(5)–C(10)	102.2(3)
S(1)–Fe–C(5)	85.3(1)	C(6)–C(5)–C(10)	123.8(3)
C(1)–Fe–C(5)	98.8(2)	Fe–C(6)–C(5)	75.8(2)
C(2)–Fe–C(5)	87.9(2)	Fe–C(6)–C(7)	74.6(2)
C(3)–Fe–C(5)	161.1(2)	C(5)–C(6)–C(7)	125.1(3)
S(1)–Fe–C(6)	93.2(1)	Fe–C(7)–C(4)	94.6(2)
C(1)–Fe–C(6)	88.0(2)	Fe–C(7)–C(6)	66.7(2)
C(2)–Fe–C(6)	124.9(1)	C(4)–C(7)–C(6)	119.5(3)
C(3)–Fe–C(6)	127.6(2)	Fe–C(7)–C(8)	120.5(3)
C(5)–Fe–C(6)	37.8(1)	C(4)–C(7)–C(8)	119.1(3)
S(1)–Fe–C(7)	71.8(1)	C(6)–C(7)–C(8)	119.7(3)
C(1)–Fe–C(7)	106.3(2)	C(7)–C(8)–C(9)	127.1(3)
C(2)–Fe–C(7)	151.0(2)	C(8)–C(9)–C(16)	126.3(3)
C(3)–Fe–C(7)	92.7(2)	C(5)–C(10)–C(11)	124.2(3)
C(5)–Fe–C(7)	69.2(1)	C(5)–C(10)–C(15)	117.5(4)
C(6)–Fe–C(7)	38.6(1)	C(11)–C(10)–C(15)	118.2(4)
Fe–S(1)–C(4)	84.5(1)	C(10)–C(11)–C(12)	120.5(4)
Fe–C(1)–O(1)	177.5(4)	C(11)–C(12)–C(13)	120.9(5)
Fe–C(2)–O(2)	175.0(4)	C(12)–C(13)–C(14)	120.0(5)
C(13)–C(14)–C(15)	120.3(5)	C(16)–C(17)–C(18)	121.3(5)
C(10)–C(15)–C(14)	119.9(5)	C(17)–C(18)–C(19)	120.6(4)
C(9)–C(16)–C(17)	120.4(4)	C(18)–C(19)–C(20)	119.8(5)
C(9)–C(16)–C(21)	122.6(3)	C(19)–C(20)–C(21)	120.2(5)
C(17)–C(16)–C(21)	117.0(4)	C(16)–C(21)–C(20)	121.1(4)

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