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Reactivity of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ towards unsaturated sulfur-containing compounds, SO_2, CS_2 and ArNCS: facile carbon–sulfur bond cleavage at the diiron centre

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Abstract

Photolysis of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) with SO_2, CS_2 and ArNCS leads to the formation of $[Fe_2(CO)_6(\mu\text{-}SO_2)(\mu\text{-dppm})]$ (**2**), $[Fe_4(CO)_{10}(\mu_3\text{-}S)(\mu\text{-}CS)(\mu\text{-dppm})_2]$ (**3**), $[Fe_2(CO)_3(CNAr)\{\mu\text{-}SC(NAr)C(O)S\}(\mu\text{-dppm})]$ (**4–5**) and $[Fe_2(CO)_4\{\mu\text{-}SC(N\text{-}p\text{-tolyl})C(O)S\}(\mu\text{-dppm})]$ (**6**), respectively. Complex **2** is a simple CO substitution product, while in **3** carbon–sulfur cleavage and coupling of diiron units has occurred. Dithiolate-bridged **4–6** also result from carbon–sulfur bond cleavage of one isothiocyanate and coupling of the sulfur with CO and a second isothiocyanate. Two isomers of complexes **3–6** are found and in thiolate-bridged **4–6** these interconvert as a result of inversion at the imine nitrogen, which has been monitored by VT NMR. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Sulfur dioxide; Carbon disulfide; Photolysis; Dimeric carbonyl

1. Introduction

While diiron nonacarbonyl displays a very rich and varied chemistry, it is characterised by the ease of cleavage of the diiron bond [1]. In order to study the chemistry of the diiron centre, then, we have utilised the diphosphine, bis(diphenylphosphino)methane (dppm), as a bridging ligand that holds the two iron atoms in close proximity, thus retaining the integrity of the diiron unit. Reactions of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) [2] with alkynes [3], allene [4], diazoalkanes [5], alkynyl phosphines [6], phospha-alkynes [7], acids [8], secondary phosphines [9] and diphosphines [10] have been carried out and in all cases the diiron core is retained. Given the high reactivity of $Fe_2(CO)_9$ towards sulfur-containing compounds we decided to investigate the reactivity of **1** towards small unsaturated sulfur-containing ligands and herein we describe the photochemical reactions of **1** with SO_2, CS_2 and ArNCS (Ar = Ph, *p*-tolyl) (Scheme 1).

2. Results and discussion

In keeping with previous studies [2–7,9,10], in the absence of UV irradiation $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) was unreactive towards a wide-range of organosulfur compounds; however, upon photolysis slow reactions took place. Photolysis of an SO_2-saturated THF solution of **1** for 16 h afforded the bridging SO_2 complex $[Fe_2(CO)_6(\mu\text{-}SO_2)(\mu\text{-dppm})]$ (**2**) in 90% yield. While SO_2 is known to bind to transition metals in a number of different ways, at the binuclear centre it invariably acts as a two-electron carbene-type bridging ligand [11]. This binding mode is formulated for **2** and is found in the parent carbonyl complex $[Fe_2(CO)_8(\mu\text{-}SO_2)]$ [12], while the analogous carbene complexes $[Fe_2(CO)_6(\mu\text{-}CR_2)(\mu\text{-dppm})]$ are also known [5,13]. Carbonyl bands of **2** in the IR spectrum are shifted by approximately 20 cm^{-1} to higher energies as compared to **1**, a result of the more electronegative nature of SO_2 versus CO, and suggesting that the diiron centre is less electron-rich in **2** versus **1**. Further bands at 1160 and 1027 cm^{-1} are assigned to $\nu_a(SO_2)$ and $\nu_s(SO_2)$, respectively. In the ^1H-NMR spectrum, the methylene protons are inequivalent, indicating that $\mu\text{-}SO_2$ lies at right angles to the diphosphine, a geometric disposition also adopted by

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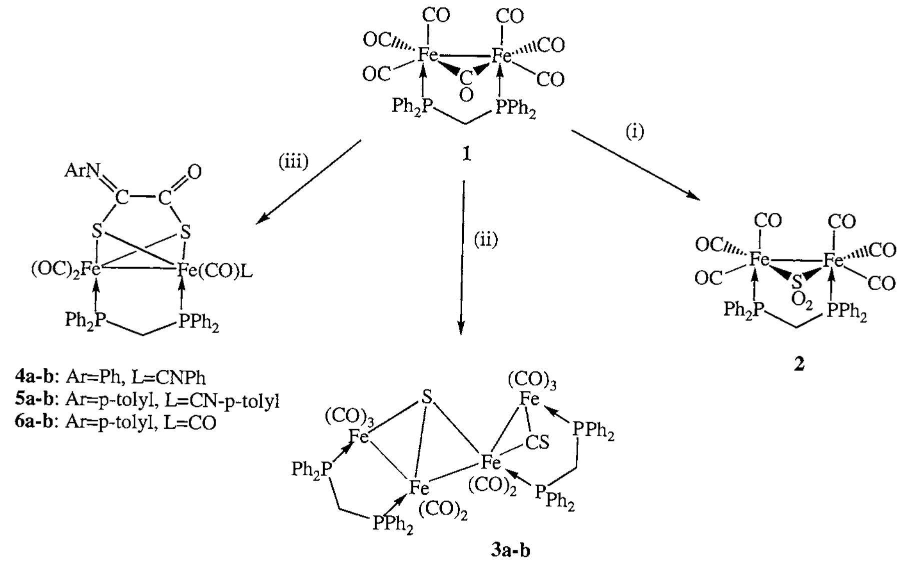
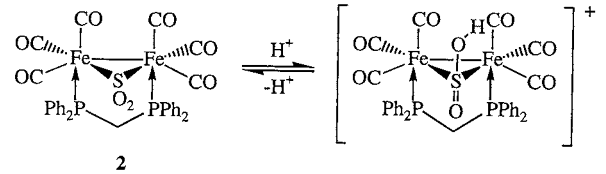


Scheme 1. (i) SO_2, *hv*, 16 h, (ii) CS_2, *hv*, 40 h, (iii) ArNCS, *hv*, 16 h.

μ-CO and the diphosphine in **1**, and rendering the two oxygen atoms inequivalent. In the ^{13}C-NMR spectrum, two signals for the *ipso* carbons confirm the relative disposition of SO_2 and diphosphine ligands, while in the low-field region of the spectrum, a single broad resonance centred at 208 ppm shows that the carbonyls undergo trigonal rotation on the NMR timescale. This process is probably the origin of the broadening of the ^{1}H-NMR spectrum, however, while the methylene protons broaden upon warming to 50°C, the chemical shift difference between them remains essentially unchanged, showing that the fluxional process does not involve movement of the bridging SO_2 group. This is in contrast to the fluxional behaviour of **1**, in which the five carbonyls (four terminal and one bridging) in the plane perpendicular to the diphosphine, undergo rapid scrambling which cannot be frozen out even at low temperature, and confirms the strong preference of SO_2 to adopt a bridging position.

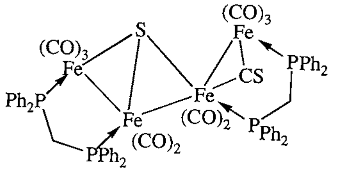


We have previously shown that **1** is readily protonated by $HBF_4 \cdot Et_2O$ to give $[Fe_2(CO)_6(\mu\text{-H})(\mu\text{-CO})(\mu\text{-dppm})][BF_4]$ [8]. Addition of $HBF_4 \cdot Et_2O$ to a dichloromethane solution of **2** results in a colour change from orange to pale yellow and a shift in the IR spectrum of the carbonyl bands to higher wavenumbers by about 20 cm^{-1}. This contrasts with the average shift of approximately 70 cm^{-1} in the terminal carbonyl bands of **1** upon protonation [8] and suggests that H^+ addition may occur not at the binuclear centre but rather at one of the oxygens of the SO_2 group. This is supported by ^{1}H-NMR studies, upon protonation by CF_3CO_2H in $CDCl_3$ no hydride signal was observed. Unfortunately we have not been able to unambiguously confirm this hypothesis as upon removal of excess acid **2** is regenerated. NMR studies show that inequivalent methylene sites are retained although signals are broadened at room temperature as a result of the trigonal rotation of carbonyls. At this temperature no signal could be observed for the added proton; however, warming to 50°C resulted in a significant sharpening of both phenyl and methylene signals together with the growth of a new broad signal at δ 8.79, which integrated to about 0.3H. We tentatively attribute these observations to the formation of $[Fe_2(CO)_6(\mu\text{-SO}_2H)(\mu\text{-dppm})][CF_3CO_2]$. Mononuclear SO_2H complexes have previously been prepared by Kubas et al. via insertion of SO_2 into a metal–hydrogen bond and one, namely $[CpMo(CO)_3(\eta^1\text{-S(O)OH})]$ ($Cp = \eta^5\text{-}C_5H_5$), has been crystallographically characterised [14]. These complexes are, however, quite unstable and readily lose SO_2, while the unique proton resonance (when observed) appears as a broad signal between δ 4.9–3.9. Since the SO_2 oxygens in **2** are inequivalent two sites of protonation are available and we favour addition to the more sterically accessible (as shown).

Unlike the clean reaction of **1** with SO_2, irradiation with CS_2 afforded a mixture of products which were separated by chromatography. The major component eluted as a blue–black band and is tentatively formulated as $[Fe_4(CO)_{10}(\mu_3\text{-S})(\mu\text{-CS})(\mu\text{-dppm})_2]$ **3a** (17%). A minor orange band followed closely afterwards affording **3b** (6%) and on the basis of the very similar spectroscopic data for **3a**–**b** we propose that they are isomers. Elemental analysis and mass spectrometry readily established the molecular formula. In each, all four phosphorus atoms are inequivalent and consist of two coupled pairs, the absence of coupling between pairs suggesting that no iron carries more than one phosphorus atom. The major spectroscopic difference between **3a–b** is found in their ^{31}P-NMR spectra. While **3a** is characterised by phosphorus–phosphorus coupling constants of 66.9 and 77.6 Hz, values of 74.5 and 92.3 Hz are seen in **3b**. Further, although chemical shifts of three of the resonances in both spectra match up well, the signal at 63.8 (J 77.6 Hz) ppm in **3a** is replaced by one at 74.2 (J 92.3 Hz) ppm in **3b**. We thus assume the isomers differ in the relative positions of dppm ligands, but cannot rule out other possibilities. In the carbonyl region of the IR spectrum the highest frequency band at 2043–2044 cm^{-1}, is characteristic of an '$Fe_2(CO)_5$' unit, while an absorption at 1093–1095 cm^{-1} is attributed to a thiocarbonyl [15] and provides strong evidence for carbon–sulfur bond scission. Unfortunately due to their poor solubility, we have been unable to confirm the presence of a thiocarbonyl ligand by ^{13}C-NMR.

Thiocarbonyls can bind to polynuclear metal centres in a variety of different ways, contributing between two and six electrons [15]. The increasing donor capacity leads to a decrease in the frequency of the C–S vibration. The 1093–1095 cm^{-1} band is in the region expected for a doubly bridging CS ligand, although we cannot completely rule out the possibility that it binds in a μ_3-CS fashion. We can, however, rule out binding modes in which sulfur is also metal bound as these are generally seen at wavenumbers of >1000 cm^{-1} [15]. Based on the assumption that the thiocarbonyl acts as a two-electron and the sulfido a four-electron donor, then the original CS_2 contributes a total of six electrons to the cluster. As '$Fe_4(CO)_{10}(dppm)_2$' is a 60-electron fragment, we conclude that **3** is a 66-electron cluster and if electron-precise is characterised by three metal–metal interactions.

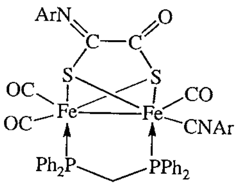
Based on the above, the structure shown is suggested, although it should be emphasised that this is quite speculative and repeated attempts to grow X-ray quality crystals of either **3a** or **3b** have been unsuccessful. Thus, we have little precise information concerning the position of either the thiocarbonyl or the sulfido moieties, or the relative disposition of the diphosphines. The hapticity of sulfur is also unknown and we favour μ_3-coordination as it is common in cluster chemistry and seen in related clusters formed from the reaction of $Fe_3(CO)_{12}$ with CS_2 [16,17]. Thus, $Fe_3(CO)_{12}$ reacts with CS_2 at 80°C and under 10 atm CO/Ar to afford both tetranuclear [$Fe_4(CO)_{12}(\mu_3\text{-S})(\mu_4\text{-CS})$] [16] and pentanuclear [$Fe_5(CO)_{13}(\mu_3\text{-S})_2(\mu_4\text{-CS})$] [17] clusters containing μ_4-CS and μ_3-S ligands. While the μ_4-CS ligands are bound somewhat differently in each of these clusters, an IR band is seen below 1000 cm^{-1} in both [Fe_4-η^3-C-η^1-S 963 cm^{-1} [16]; Fe_5-η^2-C-η^2-S 921 cm^{-1} [17]], whereas in **3** there are no absorptions in this region of the spectrum. On this basis we have ruled out the possibility that **3** is a derivative of [$Fe_4(CO)_{12}(\mu_3\text{-S})(\mu_4\text{-CS})$] although the proposed structure has many similar characteristics. Reaction of other metal carbonyls with CS_2 has also lead to carbon–sulfur bond scission and the generation of thiocarbonyl and sulfido ligands [18]. Conditions used are often quite harsh; however these may be required to remove tightly bound carbonyl ligands rather than reflecting the strength of the carbon–sulfur bond.



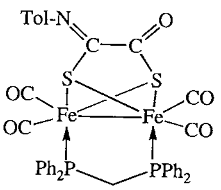
3a-b

The mode of formation of **3a–b** is unclear. Reaction of $Fe_2(CO)_9$ with CS_2 is known to produce the side-bound CS_2 complex [$Fe(CO)_4(\eta^2\text{-S–C=S})$] [19], a phosphine derivative of which has been crystallographically characterised [20]. The latter react readily with 16-electron metal fragments to produce binuclear complexes in which the CS_2 bridges metal centres via an η^2-CS, η^1-S coordination mode and donates a total of four electrons to each metal centre [21]. Under photolysis, [$Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-dppm})$] (**1**) readily loses between 1 and 3 mol of CO [2–9] and it is possible that CS_2 bridges between binuclear centres in a related fashion. Further loss of CO requires that the donor capacity of the CS_2 unit increase and complexes are known in which CS_2 donates up to six electrons, with both carbon–sulfur bonds remaining intact [22]. However, this may place unfavourable geometric constraints which carbon–sulfur bond scission could help relieve.

Carbon–sulfur bond cleavage also occurs upon reaction of **1** with aryl isothiocyanates (ArNCS; Ar=Ph, *p*-tolyl). Photolysis of toluene solutions with a slight excess of the isothiocyanate resulted in a slow reaction which afforded a mixture of products from which the major constituents were isolated and characterised as dithiolate-bridged products [$Fe_2(CO)_3(CNAr)\{\mu\text{-SC(NAr)C(O)S}\}(\mu\text{-dppm})$] (**4**–**5**) and [$Fe_2(CO)_4\{\mu\text{-SC(N-}p\text{-tolyl)C(O)S}\}(\mu\text{-dppm})$] (**6**). Formulation as tricarbonyl–isocyanide and tetracarbonyl complexes, respectively was made on the basis of the IR spectra, the isocyanide coming at characteristically low frequency (**4**, 2087; **5**, 2092 cm^{-1}). Further, for all complexes low frequency C=O (1605–1593 cm^{-1}) and C=N (1504–1484 cm^{-1}) bands were also observed suggesting of the presence of ketonic carbonyl and imine functionalities respectively. On this basis and supported by analytical and mass spectral results the above formulations are made.



4a-b (Ar=Ph)
5a-b (Ar=Tol)



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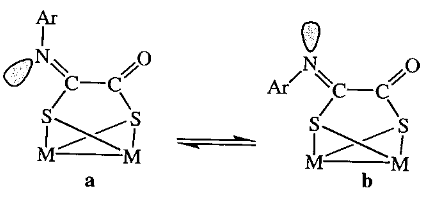
It was clear from the NMR data that all three products were a mixture of two isomers **a**–**b** between a 3:1 and 6:1 ratio, and VT NMR studies have shown that these interconvert. As it gives the simplest spectra, discussion will focus around tetracarbonyl **6**. In the ^{31}P-NMR spectrum, at low temperature (253 K) two distinct resonances are observed in a 5.3:1 ratio (**6a**:**6b**). Each isomer is represented by only a single phosphorus resonance suggesting a plane of symmetry bisecting the two phosphorus and iron atoms. Upon warming to 323 K, the peaks broaden to a single resonance at 57.2 ppm showing that the two isomers are in fast exchange at this temperature. These changes are mirrored in the ^{1}H-NMR spectra, the methylene and methyl regions being most informative. At 253 K, four virtual quartets are clearly observed between δ 4.36–3.68 showing that for each isomer the methylene protons are inequivalent, while two methyl resonances are also observed. In contrast, but in keeping with the isomers being in exchange at higher temperatures, at 323 K a single methyl resonance is seen while the four methylene protons collapse into two broad peaks. A number of possible processes could be envisaged to account for these observations, however, as a similar process operates for all three complexes, isocyanide fluxionality can be discounted. This leaves inversion at the imine moiety as the most likely reason and indeed such a process is known to have a substantial energy barrier. Thus we believe that the isomers seen for complexes **4**–**6** relate to the different aryl positions on the imine and given the large steric nature of the diphosphine, it seems reasonable to suggest that the major isomer is that in which the aryl group points away from this.



Formation of **4**–**5** involves loss of three carbonyls from **1** and addition of two equivalents of aryl isothiocyanate. One of the isothiocyanates remains intact and couples with a carbonyl via formation of a new carbon–carbon bond. The second undergoes sulfur–carbon bond cleavage with the resulting sulfur also coupling to a carbonyl, while the generated isocyanide binds to iron. Clearly, it is not possible to predict the order of events leading to the generation of dithiolate-bridged complexes. Isothiocyanates have previously been shown to add to low-valent metal centres via carbon–sulfur bond scission [23,24]. Thus, addition of RNCS to [CpCo(CO)(PPh$_3$)] affords [Cp$_3$Co$_3$(μ$_3$-S)(μ$_3$-CNR)] [23], while thermolysis of PhNCS and [Cp$_2$Ru$_2$(CO)$_2${μ-C(O)C(Ph)=C(Ph)}] yields [Cp$_2$Ru$_2$(CO)$_2$(μ-CO){μ-C(O)C(Ph)=C(Ph)C(=NPh)}] [24]. It is noteworthy that in both of these examples and in the formation of **4**–**6** it is always the sulfur–carbon bond that is cleaved. Formation of thiolate-bridged complexes is not unexpected as a large number of related diiron species have previously been prepared and are very stable.

In conclusion, this work has extended the already rich photochemical reactivity of [Fe$_2$(CO)$_6$(μ-CO)(μ-dppm)] (**1**) to yield some otherwise inaccessible new organoiron complexes. All the organosulfur compounds used were heterocumulene type species, and the positive outcome suggests that other members of this class of compound may also be worthy of study. We have tried to extend the reactivity of **1** to saturated sulfur-containing species with limited success. Thus, H$_2$S reacts readily but does not produce any tractable products while no significant reaction was noted with disulfides RSCH$_2$SR (R=Ph, Me).

3. Experimental

3.1. General procedures

General experimental methods have been described previously [9]. Complex **1** was prepared by the literature method [10]. All reactions were carried out in dry degassed solvents under a nitrogen atmosphere but work-up was carried out in air unless otherwise stated. UV photolysis was carried out using a Hanovia medium-pressure mercury lamp.

3.2. Reaction with SO$_2$

A THF solution (200 cm^3) of **1** (0.50 g, 0.72 mmol) was purged with SO$_2$ for 10 min in order to form a saturated solution. This was then irradiated for 16 h resulting in the formation of a dark-brown solution. Volatiles were removed under reduced pressure to give a brown solid. This was washed with 40–60 light-petroleum and crystallised upon addition of hexanes to a dichloromethane solution to give brown [Fe$_2$(CO)$_6$(μ-SO$_2$)(μ-dppm)] (**2**) (0.47 g, 90%). IR (CH$_2$Cl$_2$) ν(CO) 2068s, 2026s, 2007m, 1981m, 1960sh cm^{-1}; (KBr) 2064m, 2023m, 1998s, 1973s, 1160s (SO$_2$), 1123m, 1095m, 1073w, 1027s (SO$_2$), 998m cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ 7.62–7.10 (m, 20H, Ph), 3.89 (q, J 13.2, 1H,

CH_2), 2.89 (q, *J* 13.0, 1H, CH_2). ^{13}C-NMR ($CDCl_3$) 208.7 (br, CO), 133.6 (t, *J* 29.4, C_i), 132.8 (t, *J* 23.9, C_i). 132.3 (m, C_m), 131.2 (d, *J* 18.4, C_o), 128.8 (t, *J* 4.2, C_p), 128.6 (t, *J* 4.9, C_p), 31.2 (t, *J* 20.3, CH_2) ppm. ^{31}P-NMR ($CDCl_3$) 64.1 (s) ppm; mass spectrum (FAB^+) *m*/*z* 728 [M^+]. Anal. Calc. for $Fe_2C_{31}H_{22}O_8P_2S_1$: C, 51.10; H, 3.02; S, 4.40. Found: C, 49.78; H, 2.91; S, 4.39%.

3.3. Protonation of **2**

Addition of a drop of $HBF_4{\cdot}Et_2O$ to a dichloromethane solution (10 cm^3) of **2** (30 mg) resulted in an immediate colour change from orange to yellow and the development of new bands in the IR spectrum; ν(CO) (CH_2Cl_2) 2088s, 2050s, 2033m, 2010m cm^{-1}. Upon removal of the solvent, washing with diethyl ether resulted in the removal of excess acid concomitant with regeneration of **2** (as shown by IR). Addition of a drop of CF_3CO_2H to **2** (20 mg) in $CDCl_3$ led to the generation of a yellow solution. ^{1}H-NMR ($CDCl_3$) (303 K) δ 7.61–7.29 (br, 20H, Ph), 3.89 (br, 1H, CH_2), 3.16 (br, 1H, CH_2); (333 K) δ 8.79 (br, 0.3H, SO_2H), 7.61–7.29 (m, Ph, 20H), 3.97 (q, *J* 12.2, 1H, CH_2), 3.10 (q, *J* 11.5, 1H, CH_2).

3.4. Reaction with CS_2

Carbon disulfide (1 cm^3) was added to a toluene solution (250 cm^3) of **1** (0.50 g, 0.72 mmol) via a degassed syringe. The reaction mixture was irradiated for 40 h. Volatiles were removed under reduced pressure and the resulting solid was absorbed onto alumina. Column chromatography on alumina with 40–60 light-petroleum resulted in the separation of a number of bands. Elution with 10% dichloromethane gave a minor brown band (ca. 10 mg): IR (CH_2Cl_2) ν(CO) 1999m, 1982s, 1951m cm^{-1}. Elution with 25% dichloromethane afforded a minor brown band (ca. 10 mg): IR (CH_2Cl_2) ν(CO) 2009s, 1996s, 1974m, 1962m, 1932w cm^{-1}. Elution with 45% dichloromethane gave a minor brown band (ca. 10 mg): IR (CH_2Cl_2) ν(CO) 2005m, 1982m, 1950m cm^{-1}. Elution with 55% dichloromethane gave a blue–black band which afforded [$Fe_4(CO)_{10}(\mu_4$-η^2,η^2,η^3-$CS_2)(\mu$-dppm$)_2$] (**3a**) (82 mg, 17%) as a dark solid. Dark blue–black crystals were obtained upon slow diffusion of light-petroleum into a dichloromethane solution. IR (CH_2Cl_2) ν(CO) 2043s, 2005s, 1978vs, 1958s, 1945s, 1909m, 1889w, 1605w cm^{-1}; IR (methylcyclohexane) 2048s, 2012s, 1990vs, 1980s, 1965m, 1950s, 1937w, 1918s, 1897w; IR (KBr) 2037s, 2003s, 1978vs, 1956s, 1942s, 1911s, 1889m, 1885m, 1460m, 1435m, 1093m cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 7.65–6.70 (m, 40H, Ph), 4.13 (brq, *J* 9.3, 1H, CH_2), 3.55 (brq, *J* 8.0, 1H, CH_2), 3.33 (brq, *J* 9.3, 1H, CH_2), 2.86 (brq, *J* 8.3, 1H, CH_2). ^{31}P-NMR ($CDCl_3$) 78.2 (d, *J* 66.9), 63.8 (d, *J* 77.6), 62.8 (d, *J* 66.9), 57.8 (d, *J* 77.6) ppm; mass spectrum (FAB^+) *m*/*z* 1348 [M^+], 1124 [M^+-8CO], 1096 [M^+-9CO], 1068 [M^+-10CO]. Anal. Calc. for $Fe_4C_{61}H_{44}O_{10}P_4S_2CH_2Cl_2$: C, 51.92; H, 3.21; P, 8.65; S, 4.47. Found: C, 52.49; H, 3.45; P, 8.54; S, 4.37%. Elution with 60% dichloromethane gave an orange band **3b** (30 mg, 6%): IR (CH_2Cl_2) 2044s, 2008s, 1980s, 1962s, 1942s, 1911m, 1889w, 1095m cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 7.84–6.90 (m, 40H, Ph), 4.07 (brq, 1H, CH_2), 3.53 (brq, 1H, CH_2), 3.29 (brq, 1H, CH_2), 2.93 (brq, 1H, CH_2). ^{31}P-NMR ($CDCl_3$) 78.4 (d, *J* 74.5), 74.2 (d, *J* 92.3), 64.1 (d, *J* 74.5), 59.9 (d, *J* 92.3) ppm. Mass spectrum (FAB^+) *m*/*z* 1348 [M^+], 1305 [M^+-CS], 1081 [$M^+-CS-8CO$].

3.5. Reaction with PhNCS

A toluene solution (250 cm^3) of **1** (0.50 g, 0.72 mmol) and PhNCS (0.3 cm^3) was irradiated for 16 h resulting in the formation of a dark solution. Removal of volatiles under reduced pressure gave a dark solid, which was absorbed onto alumina. Column chromatography on alumina with light-petroleum gave a number of bands. Eluting with 70% dichloromethane gave an orange band which afforded [$Fe_2(CO)_3$(CNPh) {μ-SC-(NPh)C(O)S) (μ-dppm)] (**4**) (70 mg, 11%) as a mixture of isomers **4a**:**4b** (3:1 by ^{1}H-NMR). IR (CH_2Cl_2) ν(CO) 2087m (C≡N), 1971s, 1928s, 1915sh, 1605m (C=O), 1586m (C=N) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 7.70–6.50 (m, 30H, Ph), 4.46 (q, *J* 11.2, 1H, CH_2, **4a**), 4.26 (q, *J* 12.8, IH, CH_2, **4b**), 3.76 (q, *J* 11.3, 1H, CH_2, **4a**), 3.66 (q, *J* 12.8, 1H, CH_2, **4b**). ^{13}C-NMR ($CDCl_3$) 220.14 (d, *J* 26.7, CO), 213.0 (d, *J* 3.8, CO), 210.2 (s, CO), 178.70 (d, *J* 28.8, CNPh), 162.63 (s, C=O), 146.06 (s, C=NPh), 140–120 (m, Ph), 49.14 (t, *J* 22.5, CH_2), 48.83 (t, *J* 21.8, CH_2, **4b**) ppm. ^{31}P-NMR ($CDCl_3$) 65.8 (d, *J* 57.1, **4a**), 65.3 (s, **4b**), 63.8 (d, *J* 57.1, **4a**) ppm. Anal. Calc. for $Fe_2C_{43}H_{32}O_4P_2S_2N_2$: C, 58.76; H, 3.64; N, 3.19; S, 7.29. Found: C, 58.46; H, 3.66; N, 3.09; S, 7.20%. Further elusion with 35% dichloromethane gave a yellow band (ca. 15 mg): IR (CH_2Cl_2) ν(CO) 2111w (C≡N), 2033s, 1989m, 1712w cm^{-1}.

3.6. Reaction with p-tolylNCS

A THF solution (150 cm^3) of **1** (0.50 g, 0.72 mmol) and *p*-tolylNCS (0.5 cm^3) was irradiated for 16 h, resulting in the formation of a deep-red–black solution. Removal of volatiles under reduced pressure gave a dark solid, which was absorbed onto alumina. Column chromatography on alumina with light-petroleum gave a number of bands. Eluting with 40% dichloromethane gave a blue band (ca. 10 mg): IR (CH_2Cl_2) ν(CO) 2099m (C≡N), 2014m, 1990m, 1962s, 1945m cm^{-1}. Eluting with 50% dichloromethane gave an orange band which afforded [$Fe_2(CO)_4${μ-SC(N-*p*-tolyl)-

C(O)S}(μ-dppm)] (**6**) (60 mg, 10%) as a mixture of isomers (**6a**:**6b** 5.3:1 by ^{31}P-NMR). Orange crystals were obtained upon slow diffusion of light-petroleum into a dichloromethane solution: IR (CH_2Cl_2) ν(CO) 1987m, 1948s, 1912s, 1605w (C=O), 1483w (C=N) cm^{-1}. ^{1}H-NMR ($CDCl_3$) (323 K) δ 7.63–6.97 (m, 24H, Ph), 4.24 (br, 1H, CH_2), 3.73 (br, 1H, CH_2), 2.32 (s, 3H, Me); (253 K) δ 7.64–6.96 (m, 24H, Ph), 4.36 (q, *J* 11.3, 1H, CH_2, **6a**), 4.12 (q, *J* 10.9, 1H, CH2, **6b**), 3.74 (q, *J* 11.3, 1H, CH_2, **6a**), 3.68 (q, *J* 11, 1H, CH_2, **6b**), 2.37 (s, 3H, CH3, **6b**), 2.35 (s, 3H, CH_3, **6a**). ^{31}P-NMR ($CDCl_3$) (323 K) 57.2 (s); (253 K) 57.6 (s, **6a**), 57.1 (s, **6b**) ppm. Mass spectrum (FAB$^+$) *m*/*z* 790 [M$^+$ − CO], 761 [M$^+$ − 2CO]. Anal. Calc. for $Fe_2C_{38}H_{29}O_5P_2S_2N_1$: C, 55.81; H, 3.55; N, 1.71. Found: C, 56.03; H, 3.82; N, 1.68%. Eluting with 65% dichloromethane gave an orange band which afforded [$Fe_2(CO)_3$(CN-*p*-tolyl){μ-SC(N-*p*-tolyl)C(O)S}(μ-dppm)] (**5**) (60 mg, 9%) as a mixture of isomers **5a**:**5b** (6:1 by ^{1}H-NMR). Orange crystals were grown by slow diffusion of light-petroleum into a dichloromethane solution: IR (CH_2Cl_2) ν(CO) 2092m (C≡N), 1970s, 1926s, 1920sh, 1593m (C=O), 1504w (C=N) cm^{-1}. ^{1}H-NMR ($CDCl_3$) (323 K) δ 7.68–6.96 (m, 26H, Ph), 6.56 (br, 2H, Ph), 4.37 (br, 1H, CH_2), 3.79 (br, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.30 (s, 3H, CH_3); (253 K) δ 7.71–6.92 (m, 26H, Ph), 6.52 (d, *J* 7.4, 2H, Ph, **5b**), 6.43 (d, *J* 7.6, 2H, Ph, **5a**), 4.48 (q, *J* 11.9, 1H, CH_2, **5a**), 4.29 (br, 1H, CH_2, **5b**), 3.75 (q, *J* 11.7, 1H, CH_2, **5a**), 3.63 (m, 1H, CH_2, **5b**), 2.37 (s, 3H, CH_3, **5b**), 2.34 (s, 3H, CH_3, **5a**), 2.29 (s, 3H, CH_3, **5b**), 2.27 (s, 3H, CH_3, **5a**). ^{31}P-NMR ($CDCl_3$) (293 K) 65.9 (d, *J* 57.4, **5a**), 65.5 (s, **5b**), 64.0 (d, *J* 57.4, **5a**); (323 K) 60.1 (br), 58.7 (brd, *J* 62); (253 K) 61.10 (d, *J* 56.7, **5a**), 60.50 (d, *J* 42.7, **5b**), 58.28 (d, *J* 56.7, **5a**), 58.16 (d, *J* 42.7, **5b**) ppm. Mass spectrum (FAB$^+$) *m*/*z* 906 [M$^+$], 879 [M$^+$ − CO], 677 [M$^+$ − 5CO]. Anal. Calc. for $Fe_2C_{45}H_{36}O_4P_2S_2N_2$: C, 59.60; H, 3.97; N, 3.09. Found: C, 60.11; H, 4.56; N, 3.07%. Eluting with 100% dichloromethane gave a yellow band (ca. 10 mg): IR (CH_2Cl_2) ν(CO) 2117s (C≡N), 2067w, 2032m, 1973m cm^{-1}.

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