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Journal of Organometallic Chemistry 672 (2003) 22–28

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Thiocarbyl ligands via elimination of pentafluorobenzene at a diiron centre: crystal structures of $[Fe_2(CO)_4\{\mu\text{-SC(Ph)=CH}\}(\mu\text{-dppm})]$ and $[Fe_2(CO)_4\{\mu\text{-SCH=C(Ph)C(O)}\}(\mu\text{-dppm})]$

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Received 13 January 2003; received in revised form 12 February 2003; accepted 12 February 2003

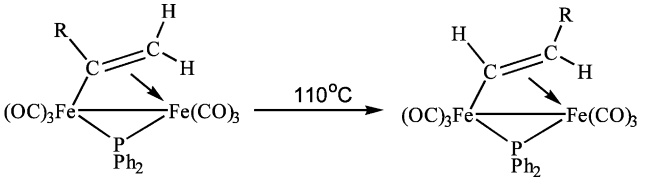
Abstract

Reaction of $[Fe_2(CO)_6\{\mu\text{-O=C–C(Ph)=CH}_2\}(SC_6F_5)]$ with bis(diphenylphosphino)methane (dppm) at 110 °C affords the alkenyl complex $[Fe_2(CO)_4(\mu\text{-HC=CHPh})(\mu\text{-SC}_6F_5)(\mu\text{-dppm})]$ together with the novel complexes $[Fe_2(CO)_4\{\mu\text{-SC(Ph)=CH}\}(\mu\text{-dppm})]$ and $[Fe_2(CO)_4\{\mu\text{-SCH=C(Ph)C(O)}\}(\mu\text{-dppm})]$ resulting from elimination of pentafluorobenzene. Both have been characterised crystallographically, the hydrocarbyl units acting as six-electron donors. The thioalkyne complex $[Fe_2(CO)_4\{\mu\text{-SC(Ph)=CH}\}(\mu\text{-dppm})]$ exists as *cis* and *trans* isomers. Both are fluxional and interconvert at higher temperatures as shown by 2D NMR.

Keywords: Thiocarbonyl; Iron; Pentafluorophenylthiol; Thioalkyne

1. Introduction

Since the first reported synthesis and characterisation of σ-π alkenyl complexes by Stone and co-workers in 1961 [1], this class of compound has undergone extensive study. Our interest in this area is twofold. Firstly, we have shown that the activation barrier to the well-known 'windshield wiper' fluxionality depends significantly upon the position of substituents on the alkenyl moiety, with unsubstituted and α-substituted alkenyls showing high activation barriers, while β-substitution leads to a significant reduction [2]. Secondly, we have recently discovered the novel α-β isomerisation of monosubstituted alkenyl complexes at a diiron centre [3].



To date we have focused exclusively on phosphido-bridge stabilised diiron alkenyl complexes, primary since they are stable and the phosphorus nucleus provides a useful NMR handle. In contrast, Seyferth [4,5] and co-workers [6] have been concerned with related thiolate-bridged diiron complexes. In general the two types of complex seem to behave in a similar manner with the phosphido-bridge analogues having enhanced stability. We have recently been interested in determining whether α-β alkenyl isomerisation at a dinuclear centre is a general process and the thiolate-bridged diiron complexes were chosen as a starting point. The full results of this work [7] will be reported elsewhere, but here we detail some unusual findings when we used pentafluorothiophenol in order to probe the effect of an electron-withdrawing group at sulfur. This gave rise to some quite different chemistry, culminating in the facile elimination of pentafluorobenzene and leading to the preparation of unusual thiocarbyl units.

2. Results and discussion

In an attempt to prepare $[Fe_2(CO)_6(\mu\text{-PhC=CH}_2)(\mu\text{-SC}_6F_5)]$ (**1**) we carried out the reaction of $[Fe_2(CO)_6(\mu\text{-}$

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0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00135-9

$SC_6F_5)(\mu$-CO)][Et_3NH] with phenylethyne following Seyferth's procedure [4]. Chromatography yielded a dark red oil, shown by ^1H-NMR spectroscopy to be an inseparable mixture of [$Fe_2(CO)_6(\mu$-PhC=$CH_2)(\mu$-$SC_6F_5)$] (**1**), [$Fe_2(CO)_6(\mu$-HC=CHPh)$(\mu$-$SC_6F_5)$] (**2**) and [$Fe_2(CO)_6\{\mu$-O=C–C(Ph)=$CH_2\}(\mu$-$SC_6F_5)$] (**3**) in an approximate 7:1:40 ratio. The two alkenyl complexes were identified only on the basis of ^1H-NMR spectroscopy, the hydrocarbyl protons appearing in positions characteristic of α (**1**, δ 3.08, 2.17) and β (**2**, δ 8.62, 4.48, J_{HH} 14.3 Hz) alkenyl ligands respectively. Formation of the α,β-unsaturated acyl complex [$Fe_2(CO)_6\{\mu$-O=C–C(Ph)=$CH_2\}(\mu$-$SC_6F_5)$] (**3**) as the major reaction product was unexpected. Seyferth and others have observed formation of acyl complexes from similar reactions but generally these lose CO readily to yield alkenyl complexes. The μ-SC_6F_5 group appears to stabilise the acyl unit and even after reflux in toluene for 4h there was no evidence of CO loss. Indeed, under these conditions the small amounts of **1** and **2** disappeared and we were able to obtain a purer sample of **3**. We have noted the decomposition of other thiolate-bridged alkenyl complexes under similar conditions and conclude that they are less thermally stable than their phosphido-bridged analogues. Characterisation of **3** was straightforward, location of the phenyl group on the β-carbon being concluded from the observation of singlets at δ 7.61 and 6.41 in the ^1H-NMR spectrum. In the ^{19}F-NMR spectrum, three signals assigned to *ortho* (−131.6, dt, J 25.4, 5.6 Hz), *meta* (−159.7, m) and *para* (−148.1, dt, J 19.8, 2.8 Hz) fluorines were observed. Interestingly, in the mass spectrum a molecular ion was not observed, the heaviest ion at m/z 414 corresponding to loss of pentafluorobenzene.

Heating a toluene solution of **3** and dppm at 110 °C resulted in a slow reaction over 18 h leading to isolation after chromatography of [$Fe_2(CO)_4(\mu$-HC=CHPh)$(\mu$-$SC_6F_5)(\mu$-dppm)] (**4**), [$Fe_2(CO)_4\{\mu$-SC(Ph)=CH$\}(\mu$-dppm)] (**5**) and [$Fe_2(CO)_4\{\mu$-SCH=C(Ph)C(O)$\}(\mu$-dppm)] (**6**), the first two complexes being inseparable. Further, in the ^{31}P-NMR spectrum it was apparent that **5** consisted of *trans* (**5a**) and *cis* (**5b**) isomers in an approximate 2:1 ratio, isomerism relating to the relative disposition of sulfur and phosphorus atoms. Complexes **5a** and **6** were characterised by X-ray crystallography the results of which are summarised in Figs. 1 and 2, respectively.

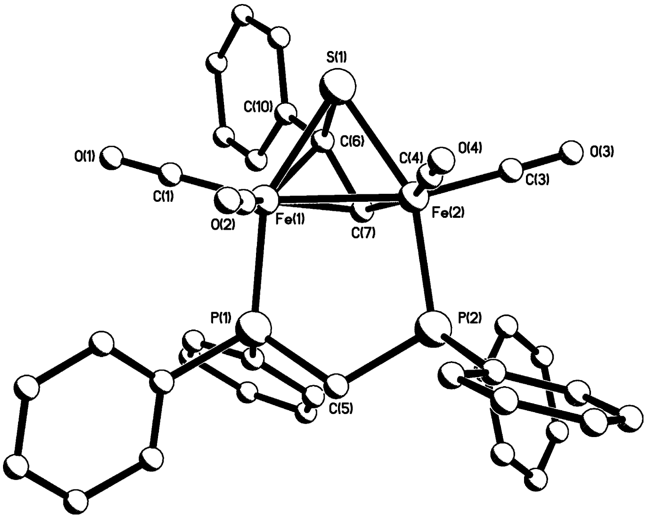
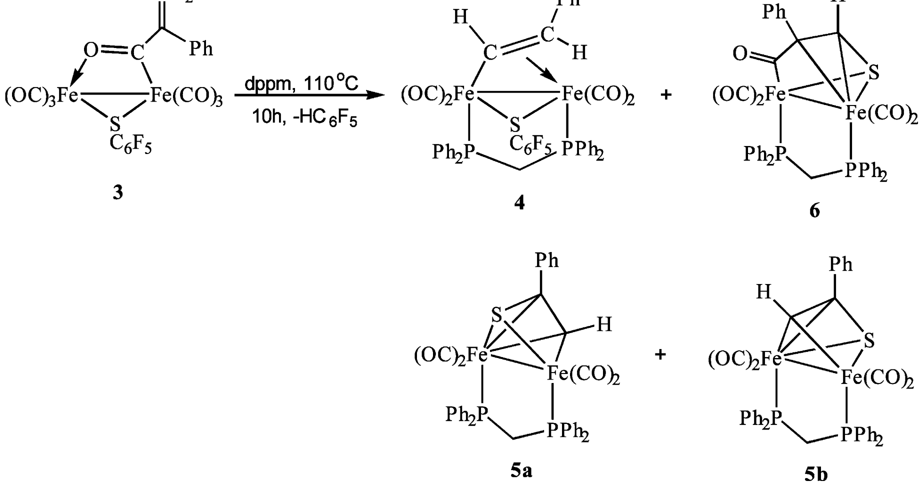


Fig. 1. Molecular structure of *cis*-[$Fe_2(CO)_4\{\mu$-SC(Ph)=CH$\}(\mu$-dppm)] (**5a**) with selected bond lengths (Å) and angles (°); Fe(1)–Fe(2) 2.5129(13), Fe(1)–S(1) 2.2544(17), Fe(2)–S(1) 2.2772(18), Fe(1)–P(1) 2.1927(16), Fe(2)–P(2) 2.1927(16), Fe(1)–C(6) 2.085(6), Fe(1)–C(7) 2.111(5), Fe(2)–C(7) 1.937(7), S(1)–C(6) 1.739(6), C(6)–C(7) 1.415(8), Fe(1)–S(1)–Fe(2) 67.36(5), Fe(1)–C(7)–Fe(2) 76.6(2), P(1)–Fe(1)–S(1) 151.13(7), P(2)–Fe(2)–S(1) 153.07(8).

Both consist of a diiron centre spanned by a diphosphine and new thiocarbyl groups resulting from the loss of pentafluorobenzene. In **5**, CO has also been lost with formation of a new sulfur–carbon bond to the phenyl-



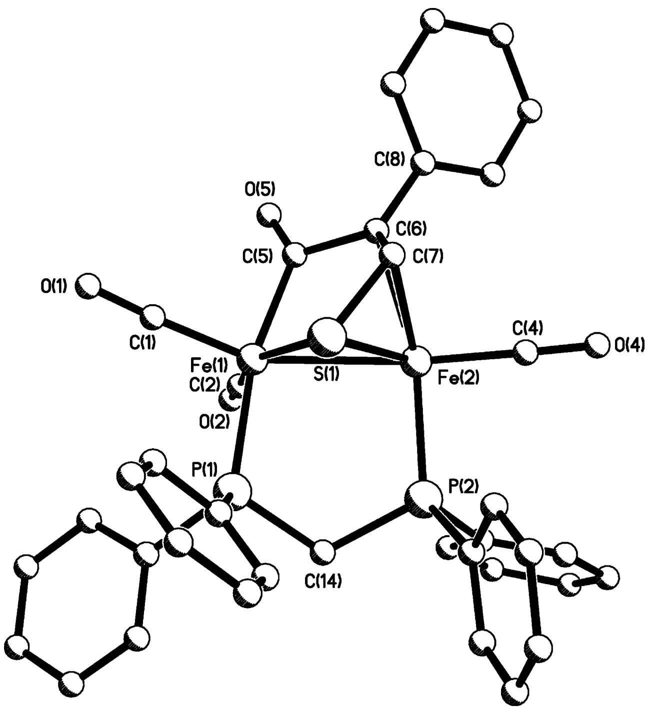


Fig. 2. Molecular structure of $[Fe_2(CO)_4\{\mu\text{-}SCH{=}C(Ph)C(O)\}(\mu\text{-}dppm)]$ (**6**) with selected bond lengths (Å) and angles (°); Fe(1)–Fe(2) 2.6413(5), Fe(1)–S(1) 2.2100(8), Fe(2)–S(1) 2.2513(8), Fe(1)–P(1) 2.2470(8), Fe(2)–P(2) 2.2181(8), Fe(1)–C(5) 1.964(3), Fe(2)–C(6) 2.214(3), Fe(2)–C(7) 2.061(3), S(1)–C(7) 1.734(3), C(5)–C(6) 1.520(4), C(6)–C(7) 1.394(4), C(5)–O(5) 1.214(3), Fe(1)–S(1)–Fe(2) 72.60(2), P(1)–Fe(1)–S(1) 86.81(3), P(2)–Fe(2)–S(1) 97.59(3).

substituted carbon, while in **6**, CO is retained and the new carbon–sulfur bond is to the unsubstituted carbon centre. In both complexes sulfur bridges the diiron centre somewhat asymmetrically [**5a**, Fe(1)–S(1) 2.254(2), Fe(2)–S(1) 2.513(1) Å; **6**, Fe(1)–S(1) 2.209(1), Fe(2)–S(1) 2.251(1) Å] and the formal carbon–carbon double bond binds to a single metal centre [**5a**, Fe(1)–C(6) 2.085(6), Fe(1)–C(7) 2.111(5) Å; **6**, Fe(2)–C(6) 2.217(4), Fe(2)–C(7) 2.069(4) Å]. In **5a**, the second iron atom is also bound to C(7) [Fe(2)–C(7) 2.111(5) Å] which can be considered as a functionalised μ-alkylidene, while in **6** the carbonyl is retained but is now bound only through the carbon atom [Fe(1)–C(5) 1.971(5) Å]. Both new hydrocarbyl ligands are six-electron donors thus bringing the EAN to the expected 34-electron count. A clear difference between the two complexes is the relative orientation of sulfur and phosphorus centres, being approximately *trans* in **5a** and *cis* in **6**. Further, on the basis of spectroscopic data and the fluxional behaviour of isomers **5a** and **5b**, we assign the latter as containing a cis disposition of sulfur and phosphorus atoms.

Spectroscopic data for **5a** and **6** are consistent with the structures elucidated crystallographically. For **6**, two sharp doublets are seen in the room temperature ^{31}P-NMR spectrum at 61.3 and 37.9 ppm (J_{PP} 87 Hz), the unique proton appearing as a singlet at δ 6.91 in the ^{1}H-NMR spectrum. Complexes **4**, **5a** and **5b** were initially obtained as a mixture (ca. 1:2:4), although a clean sample of **5a/5b** was obtained after recrystallisation. Consequently, $[Fe_2(CO)_4(\mu\text{-}HC{=}CHPh)(\mu\text{-}SC_6F_5)(\mu\text{-}dppm)]$ **4** was only characterised on the basis of ^{1}H, ^{19}F and ^{31}P-NMR spectra. Given the absence of fluorine in **5**, the presence of a $\mu\text{-}SC_6F_5$ ligand in **4** was easily confirmed by ^{19}F-NMR spectroscopy. Designation as the β-isomer was made on the basis of the characteristic positions of the alkenyl protons in the ^{1}H-NMR spectrum, with further support coming from the relatively low barrier to alkenyl fluxionality (see below) which we have previously noted for β-alkenyl complexes [2]. In the context of our previous observations regarding α,β alkenyl isomerisation at the diiron centre [3], it is noteworthy that the β-alkenyl isomer is produced here from the α-substituted unsaturated acyl complex **3**. Unfortunately, in the absence of crystallographic data we cannot discern whether the diphosphine lies trans to the thiolate or alkenyl bridge. At 213 K, two sharp sets of doublets are seen in the ^{31}P-NMR spectrum of **5**, at 42.4 and 32.7 ppm (J_{PP} 70 Hz) (**5a**) and 62.8 and 50.3 ppm (J_{PP} 56 Hz) (**5b**), while in the ^{1}H-NMR spectrum (253 K) the unique thiocarbyl protons are observed at δ 6.21 (d, J 6.2 Hz) (**5a**) and 6.13 (t, J 12.8 Hz) (**5b**). The larger coupling to phosphorus in the latter suggests that the unique proton lies *trans* to the diphosphine and assignment of isomers in solution is made on this basis.

A number of reports have previously appeared on diiron thioalkyne complexes. Schrauzer and co-workers [8] prepared $[Fe_2(CO)_6\{\mu\text{-}SC(R){=}CR\}]$ (R = H, Ph) from the reaction of iron carbonyls with 1,2,3-thiadiazoles, and Petillon and co-workers [9] synthesised $[Fe_2(CO)_6\{\mu\text{-}SC(CF_3){=}CCF_3\}]$ in 20% yield from the thermal reaction of $Fe_3(CO)_{12}$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)\{\mu\text{-}S(Me)C(CF_3)C(CF_3)\}]_2$. Most pertinent to our work is the preparation of $[Fe_2(CO)_6\{\mu\text{-}SC(Ph){=}CH\}]$ by Huttner and co-workers [10] from the reaction of $Fe_3(CO)_{12}$ with ^{t}BuSH and PhC_2H at 75 °C. This is the parent of **5** and the unique proton appears at δ 7.60. A number of crystallographic studies have been reported on related diiron thioalkyne complexes [8–13], general features being similar to those in **5a**. Thioacyl complexes akin to **6** are also known. Huttner and co-workers [13] found that reduction of $[Fe_2(CO)_6\{\mu\text{-}SC(Ph){=}CH\}]$ by sodium amalgam in the presence of ^{t}BuLi followed by oxidation by iodine afforded $[Fe_2(CO)_6\{\mu\text{-}SC(Ph){=}CHC(O)\}]$ in 19% yield. Interesting, the latter loses CO rapidly and quantitatively at 70 °C to regenerate $[Fe_2(CO)_6\{\mu\text{-}SC(Ph){=}CH\}]$. Further, Pétillon and co-workers [12] have noted that reaction of $[Fe_2(CO)_6\{\mu\text{-}SC(CF_3){=}CCF_3\}]$ with dppm at 70 °C proceeds via an η^1-bonded intermediate to afford both $[Fe_2(CO)_4\{\mu\text{-}SC(CF_3){=}CCF_3\}(\mu\text{-}dppm)]$ and $[Fe_2(CO)_4\{\mu\text{-}SC(CF_3){=}C(CF_3)C(O)\}(\mu\text{-}dppm)]$.

Here it was not clarified whether CO loss from the latter also occurred, although on the basis of Huttner's results it appears likely. Huttner and co-workers have crystallographically characterised [$Fe_2(CO)_6${μ-SC(Ph)=CHC(O)}] [13] and structural features are very similar to those in **6**.

As previously alluded to, NMR spectra of complexes **4**, **5a** and **5b** were temperature dependent. In order to probe their fluxionality a number of variable temperature and 2D-NMR experiments were carried out, ^{31}P-NMR data proving most informative. At low temperature (213 K) each appeared as a set of sharp doublets. Warming to 273 K resulted in the broadening of signals assigned to **5a** and **5b**, both coalescing at approximately 308 K. At temperatures higher than 333 K, spectra become complex but it appeared that signals due to **5a** and **5b** coalesced. Interconversion of **5a** and **5b** was confirmed by a 2D ^{31}P-NMR spectrum at 283 K, which showed strong crosspeaks for all four phosphorus atoms. Signals for **4** remained sharp to 300 K but began to broaden above this temperature. Unfortunately, due to the changes occurring with **5a/5b** we were unable to obtain a clear coalescence temperature and can only estimate a value of 343 K. That the two phosphorus centres in **4** were equivalencing was confirmed in the 2D experiment.

Changes to the NMR spectra of **4** are readily associated with 'windshield wiper' alkenyl fluxionality and the estimated $\Delta G^{\#}$ of 58.3 ± 1 kJ mol^{-1} compares well with values for related dppm-bridged diiron alkenyl complexes [2,7]. In order to account for the NMR properties of **5a** and **5b** we invoke two fluxional processes, namely: (i) equivalencing of phosphorus centres in each isomer via a 'tethered windshield wiper' process; and (ii) the interconversion of *cis* and *trans* isomers via a planar hydrocarbyl transition state (Fig. 3). From the coalescence temperature of 308 K we estimate $\Delta G^{\#}$ values of 51.7 ± 1 and 52.3 ± 1 kJ mol^{-1} for the tethered 'windshield wiper' fluxionality in **5a** and **5b**, respectively. As they are the same (within error) it suggests that the relative orientation of the dppm ligand had little effect. Interestingly, in the X-ray structure of **5a** there are two molecules in the asymmetric unit relating to the two optical isomers of the 'windshield wiper' fluxionality and there are no significant differences in bond lengths and angles. The second proposed fluxional process is more unusual. Interconversion of cis and trans isomers can be envisaged to occur in two ways; through a planar transition state (shown) or via a trigonal-twist at both iron centres. While the latter process is common for monodentate phosphines and phosphites, as far as we are aware it is unknown for dppm, probably as a result of the steric strain introduced in a transition-state in which one phosphorus lies in the plane and the second at right angles to it. Thus we favour the first option, that is via a planar transition state. In this process the methylene protons on the diphosphine would be equivalenced, and this is confirmed by ^{1}H-NMR spectroscopy, a sharp methylene triplet being observed at 373 K. In previous work, Hickey et al. [11] noted a single room temperature carbonyl resonance for [$Fe_2(CO)_6${μ-SC(Ph)=CPh}], suggestive of the equivalencing of iron centres and thus appears that a 'tethered windshield wiper' process may be general in this class of complexes.

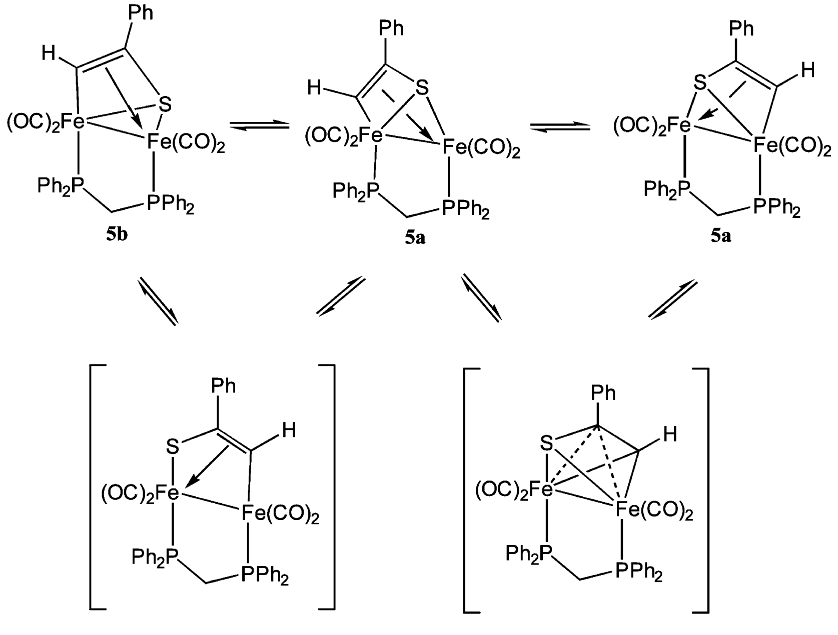


Fig. 3. Fluxional processes occurring in thioalkyne complexes: (i) equivalencing of phosphorus centres in each isomer via a 'tethered windshield wiper' process; (ii) the interconversion of *cis* and *trans* isomers via a planar hydrocarbyl transition state.

The precise mode of formation of **5a**/**5b** and **6** is unknown. Given the thermal stability of $[Fe_2(CO)_6\{\mu\text{-}O{=}C{-}C(Ph){=}CH_2\}(SC_6F_5)]$ (**3**) it is clear that dppm coordination is a prerequisite for pentafluorobenzene loss. In related systems, both Pétillon and Huttner have observed evidence of monodentate diphosphine coordination prior to binding of the second phosphorus centre. Certainly in **3**, the oxygen-bound metal centre should be the more substitutionally labile leading to a preference for monodentate coordination. The latter may then introduce adverse steric effects, however, it is still difficult to see why pentafluorobenzene loss would be facile when the proton associated with it lies on a carbon so distant from the binuclear centre. This may be circumvented by coordination of the olefinic bond to the metal centre, and indeed we have recently observed such five-electron α-β unsaturated acyl complexes at the phosphido-bridge stabilised diiron centre [14]. Here, coordination of the carbon–carbon double bond was also found to lead to the twisting of the C–O vector out of the plane of the metal–metal bond with a lengthening of the Fe–O bond. After elimination of pentafluorobenzene the sulfido-bridge generated could attack either the substituted or non-substituted hydrocarbyl centre leading to **5a**/**5b** (after CO loss) or **6**, respectively. Why CO loss upon attack at the unsubstituted centre should be so much slower than at the substituted centre remains unknown, however, heating **6** at 110 °C for 18 h resulted in no significant change.

3. Experimental

3.1. General

All reactions were carried out under nitrogen using standard vacuum line techniques and dried and degassed solvents. Chromatography was carried out on deactivated alumina (6% w/w distilled water) wet packed with light-petroleum unless otherwise stated. The solution to be separated was added to alumina (3–5 g) and the solvent removed under reduced pressure. The resulting solids were then deposited on top of the prepared column and separation effected by elution with progressively more polar solvents. IR spectra were recorded on a Nicolet 205 FTIR spectrometer. NMR spectra were recorded on Bruker AMX400 and Avance500 spectrometers and internally referenced to residual solvent peaks (^1H, ^{13}C) or externally to $P(OMe)_3$ (^{31}P) or $CFCl_3$ (^{19}F). Mass spectra were recorded on VG 7070 high resolution and VG Analytical ZAB2F spectrometers and elemental analyses were performed in house.

3.2. *Synthesis of $[Fe_2(CO)_6\{\mu\text{-}O{=}C{-}C(Ph){=}CH_2\}(\mu\text{-}SC_6F_5)]$ (3)*

To a THF solution (30 cm^3) of $Fe_3(CO)_{12}$ (1.52 g, 3.02 mmol) and triethylamine (0.42 cm^3, 3.00 mmol), pentafluorobenzethiol (0.60 cm^3, 3.00 mmol) was added dropwise by syringe. This led to gas evolution and heating of the solution. The resulting solution was stirred for 20 min during which a colour change and further gas evolution were noted. To this was added phenylethyne (0.30 cm^3, 3.00 mmol). The solution was stirred at 50 °C for 2 h and turned deep red. Volatiles were removed under reduced pressure and chromatography gave a red band eluting with light-petroleum (40–60 °C) which afforded **3** as a red oil (0.55 g, ca. 30%). NMR spectra revealed trace impurities of $[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}SC_6F_5)]$ (**1**) and $[Fe_2(CO)_6(\mu\text{-}HC{=}CHPh)(\mu\text{-}SC_6F_5)]$ (**2**). Heating a toluene solution of this mixture (ratio **3**:**1**:**2** ca. 40:7:1) for 2 h resulted in the disappearance of **1** and **2** (as shown by ^1H-NMR spectroscopy).

3: $\nu(CO)(C_6H_{14})$ 2079vs, 2040vs, 2004vs, 1987m cm^{-1}; $^1H(CDCl_3)$ δ 7.61 (s, 1H, $C{=}CH_2$), 7.5–7.1 (m, 5H, Ph), 6.41 (s, 1H, $C{=}CH_2$); $^{19}F(CDCl_3)$ −131.6 (dt, *J* 25.4, 5.6 Hz, *ortho*), −148.1 (dt, *J* 19.8, 2.8 Hz, *para*), −159.7 (m, *meta*); mass spectrum (FAB) *m*/*z* 414 $[M-C_6F_5H]$, 386, 358, 304. **1**: $^1H(CDCl_3)$ δ 3.08 (s, $C{=}CH_2$), 2.17 (s, $C{=}CH_2$); **2**: $^1H(CDCl_3)$ δ 8.62 (d, *J* 14.3 Hz, CH), 4.47 (d, *J* 14.3 Hz, CHPh).

3.3. *Reaction of **3** with bis(diphenylphosphino)methane (dppm)*

A toluene solution (80 cm^3) of **3** (0.20 g, 0.33 mmol) and dppm (0.15 g, 0.39 mmol) was heated at reflux for 18 h. Volatiles were removed under reduced pressure and chromatography was carried out. A red band eluting with light-petroleum: dichloromethane (4:1) afforded an inseparable mixture (ratio **4**:**5a**:**5b** ca. 1:2:4) of $[Fe_2(CO)_4(\mu\text{-}HC{=}CHPh)(\mu\text{-}SC_6F_5)(\mu\text{-dppm})]$ (**4**) and $[Fe_2(CO)_4\{\mu\text{-}SC(Ph){=}CH\}(\mu\text{-dppm})]$ (**5a**–**b**) as a red powder (0.12 g, ca. 49.%). A second red band eluting with light-petroleum: dichloromethane (7:3) afforded $[Fe_2(CO)_4\{\mu\text{-}SCH{=}C(Ph)C(O)\}(\mu\text{-dppm})]$ (**6**) as a red powder (0.05 g, 20%). Crystals of **5** and **6** suitable for X-ray crystallography were grown by slow diffusion of methanol into a saturated dichloromethane solution.

4: $^1H(CDCl_3)$ (253 K) δ 7.8–6.9 (m, Ph), 6.21 (dd, *J* 9.9, 1.6 Hz, 1H, CH), ca.4.41 (obscured 1H, PCH_2P), ca. 3.75 (obscured, 1H, PCH_2P), 1.54 (m, 1H, $C{=}CHPh$); $^1H(C_7D_8)(383K)$ δ 4.03 (dt, *J* 13.4, 10.2 Hz, 1H, CH_2), 3.75 (q, *J* 10.2 Hz, 1H, CH_2) other signals obscured; $^{19}F(CDCl_3)$ −126.7 (ddd, *J* 142.9, 16.9, 2.8 Hz, *ortho*), −155.9 (t, *J* 22.6 Hz, *para*), −162.8 (m, *meta*); $^{31}P(CDCl_3)$ (213 K) 46.2 (d, *J* 72 Hz), 35.5 (d, *J* 72 Hz).

5: ν(CO)(C_6H_{14}) 2002s, 1969vs, 1947m, 1918w cm^{-1}; mass spectrum (FAB) *m*/*z* 742 [M], 715 [M−CO], 686 [M−2CO], 658 [M−3CO], 630 [M−4CO], 528 [M−4CO−PhC=CH_2]; Anal. Calc. for $Fe_2C_{37}H_{28}O_4P_2S.C_6H_{14}$: C, 59.87; H, 3.80. Found C, 60.16; H, 3.21%. $^1H(C_7D_8)$ (383 K) δ 3.80 (t, *J* 10.2 Hz, 2H, CH_2); **5a**: $^1H(CDCl_3)$ (253 K) δ 7.8–6.9 (m, Ph), 6.79 (d, *J* 6.8 Hz, 1H, CH), 4.41 (dt, *J* 13.3, 9.7 Hz, 1H, PCH_2P), 3.80 (dt, *J* 13.8, 10.4 Hz, 1H, PCH_2P); $^{31}P(CDCl_3)$ (213 K) 42.4 (d, *J* 70 Hz), 32.7 (d, *J* 70 Hz); **5b**: $^1H(CDCl_3)$ (253 K) δ 7.8–6.9 (m, Ph), 6.13 (t, *J* 12.8 Hz, 1H, CH), 4.13 (dt, *J* 14.2 Hz, 10.9, 1H, PCH_2P), 3.28 (dt, *J* 14.3, 10.8 Hz, 1H, PCH_2P); $^{31}P(CDCl_3)$ (213 K) 62.8 (d, *J* 56 Hz), 50.3 (d, *J* 56 Hz).

6: ν(CO)(CH_2Cl_2) 2006s, 1971vs, 1947s, 1923m (KBr) 1592m (C=O) cm^{-1}; $^1H(CDCl_3)$ δ 7.68–7.05 (m, 25H, Ph), 6.91 (s, 1H, CH), 3.83 (dt, *J* 14.1, 10.6 Hz, 1H, PCH_2P), 2.75 (dt, *J* 14.1, 10.6 Hz, 1H, PCH_2P); $^{31}P(CDCl_3)$ 61.3 (d, *J* 87 Hz), 37.9 (d, *J* 87 Hz); mass spectrum (FAB) *m*/*z* 771 [M], 742 [M−CO], 715 [M−2CO], 686 [M−3CO], 659 [M−4CO], 630 [M−5CO], 528 [M−5CO−PhC=CH_2]; Anal. Calc. for $Fe_2C_{38}H_{28}O_5P_2S.0.5CH_2Cl_2$: C, 57.21; H, 3.45. Found C, 58.07; H, 4.07%.

3.4. X-ray data collection and solution

For **5a** and **6** a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) at 293 ± 2 K. Data reduction was carried out with SAINT+ and absorption correction applied using the programme SADABS. Structures were solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were generally placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package.

Crystallographic data for **5a**: red block, dimensions $0.20 \times 0.16 \times 0.14$ mm^3, monoclinic, space group Pn, $a = 12.9893(8)$, $b = 17.7810(11)$, $c = 14.4629(9)$ Å, $\beta = 91.992(1)°$, $V = 3338.4(4)$ Å^3, $Z = 4$, $F(000) = 1520$, $D_{calc} = 1.477$ g cm^{-3}, $\mu = 1.067$ mm^{-1}, $T_{max}/T_{min} = 0.865/0.815$. A total of 20 993 reflections were collected, 10 645 unique [$R_{int} = 0.0160$] of which 9148 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0307$, $wR_2 = 0.0909$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0366$, $wR_2 = 0.1004$ (all data), for 837 parameters.

Crystallographic data for **6**: red needle, dimensions $0.48 \times 0.12 \times 0.10$ mm^3, monoclinic, space group $P2_1/n$, a = 12.6688(9), $b = 14.0346(10)$, $c = 20.9741(15)$ Å, $\beta = 98.578(2)°$, $V = 3687.5(5)$ Å^3, $Z = 4$, $F(000) = 1744$, $D_{calc} = 1.540$ g cm^{-3}, $\mu = 1.119$ mm^{-1}, $T_{max}/T_{min} = 0.896/0.616$. A total of 23 300 reflections were collected, 8679 unique [$R_{int} = 0.0379$] of which 5971 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0451$, $wR_2 = 0.1052$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0752$, $wR_2 = 0.1179$ (all data), for 489 parameters.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 200679 and 200678 for **5a** and **6**, respectively. 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).

Acknowledgements

We thank Dr Abil E. Aliev for help with the 2D NMR experiments.

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