

Synthesis and reactions of the novel sulfonium-methylidene complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(SMe}_2)\}]\text{SO}_3\text{CF}_3$

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Abstract

The reaction of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(SMe)}\}]$ ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$) with MeSO_3CF_3 forms the sulfonium-methylidene complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(SMe}_2)\}]\text{SO}_3\text{CF}_3$ (**3**). Compared to Casey's methylidyne complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CH})]\text{PF}_6$ (**1**), compound **3** appears to be more stable and easier to handle, still maintaining a reactivity centered at the μ -carbon. In fact **3** undergoes replacement of SMe_2 by a variety of nucleophiles X, at room temperature, affording the corresponding cationic $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(X)}\}]\text{SO}_3\text{CF}_3$ ($\text{X} = \text{NMe}_3, \text{PMe}_3, \text{PPh}_3, \text{PPh}_2$) or neutral $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(X)}\}]$ ($\text{X} = \text{H}^-, \text{MeO}^-, \text{CN}^-$) μ -methylidene derivatives, in good yield. The phosphonium complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(PPh}_2)\}]\text{SO}_3\text{CF}_3$ has been deprotonated with NEt_3 to yield the novel phosphino-methylidene complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(PPh}_2)\}]$. The presence of the SMe_2 moiety in **3** reduces, compared to **1**, the electrophilic character of the $\mu\text{-C}$ carbon, as evidenced by the reaction with styrene.

Keywords: Iron complexes; Sulfonium-methylidene complexes; Dinuclear complexes

1. Introduction

Several years ago $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CH})]\text{PF}_6$ (**1**) ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$), the first complex containing the bridging CH unit, was synthesized [1]. The μ -carbynyl carbon in **1** exhibits a powerful electrophilic character and its reactions with carbon and heteroatom nucleophiles result in the high yield synthesis of a variety of bridging alkylidene complexes [2]. However the potent electrophilic reactivity of **1** is related to its kinetic instability (CH_2Cl_2 solutions of **1** have half time of about 2 h at room temperature [1]) making its preparation and handling somewhat difficult. On the other hand it has been recently demonstrated that the sulfonium-alkylidene complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(CN)(SMe}_2)\}]\text{SO}_3\text{CF}_3$ (**2**) [3] provides an excellent route to the heteroatom-substituted μ -alkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(CN)(X)}\}]$ ($\text{X} = \text{OR}$ [4], NR_2 [5], PR_2 [6]) via SMe_2 replacement by the appropriate nucleophile. Therefore, the chemistry of **1** and **2** is similar, both of them being susceptible to

nucleophilic attack at the $\mu\text{-C}$ carbon to form alkylidene derivatives. In order to underline this point we have previously described the $\mu\text{-C}$ carbon in **2** as 'pseudo-alkylidyne' [5].

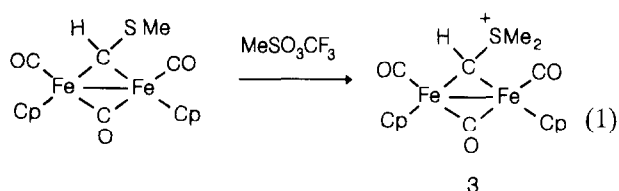
Herein we report the synthesis of the new sulfonium-methylidene complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(SMe}_2)\}]\text{SO}_3\text{CF}_3$ (**3**) and its reactivity with nucleophiles. Comparison with the corresponding reactions involving the methylidyne complex **1** or the cyano-sulfonium **2** will also be discussed.

2. Results and discussion

Reaction of the thiomethoxy-methylidene $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(SMe)}\}]$ [7] with an excess of MeSO_3CF_3 , in dichloromethane solution, resulted in the formation of the sulfonium $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)(SMe}_2)\}]\text{SO}_3\text{CF}_3$ (**3**) (Eq. (1)).

Compound **3** is a red crystalline solid, stable under N_2 (apparently indefinitely) and forms moderately air stable solutions in acetonitrile. Its spectroscopic data are similar to those of the strictly related cyano-sulfonium $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(CN)(SMe}_2)\}]$ -

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SO_3CF_3 (**2**) that has been similarly obtained by methylation of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{SMe})\}]$ [**3**]. The IR spectrum of **3** shows a $\nu(\text{CO})$ band pattern (1996s, 1961w and 1818m cm^{-1}) which is common to all of the related alkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{R})(\text{R}')\}]$ adopting a *cis*-conformation (cp ligands *cis* to each other). These frequencies are shifted to lower wavenumbers compared to those of the cyano-sulfonium **2** ($\nu(\text{CO})$ at 2013s, 1981w and 1835m cm^{-1}), because of the strong electron-withdrawing properties of the CN group in the latter complex. One single resonance for the cp ligands is observed in both the ^1H and ^{13}C NMR spectra of **3** (at δ 5.19 and 88.5, respectively), indicating the existence of one single *cis*-isomer in solution (presumably that bearing the SMe_2 group on the less hindered side of the molecule occupied by the CO ligands). Finally the presence of the $\mu\text{-C}(\text{H})(\text{SMe}_2)$ ligand is clearly evidenced by the occurrence of two resonances in the ^{13}C NMR spectrum (at δ 131.6 and δ 34.7) attributable to the $\mu\text{-C}$ and Me, respectively, and of one signal, in the ^1H NMR spectrum (at δ 9.53), in the range typical for the μ -alkylidene protons. The latter resonance occurs at considerably higher field compared to that of the μ -methylidyne proton in $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CH})]\text{PF}_6$ (**1**) ($\mu\text{-CH}$ at δ 22.8) [**1**]. In spite of these differences, both the sulfonium **3** and the methylidyne complex **1** react with NMe_3 affording the ammonium $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{NMe}_3)\}]\text{SO}_3\text{CF}_3$ (**4**), in comparable yield (about 80%) but, whereas the reaction with **1** must be performed at -78°C [**2b**], the NMe_3 was simply bubbled through a solution of **3** at room temperature. Similarly, we have found that the compound $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{PPh}_3)\}]^+$ (**5**), which has been previously obtained by reacting the in situ generated methylidyne **1** with PPh_3 at -20°C [**8**], can be conveniently obtained, in comparable yield, by reacting **3** with PPh_3 at room temperature. As a matter of fact the reactions of **3** with phosphines provide an excellent route to the new phosphonium-methylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{PR}_3)\}]\text{SO}_3\text{CF}_3$ ($\text{PR}_3 = \text{PMe}_3$ (**6**), PPhPh_2 (**7**)), that have been isolated as air stable red crystalline solids in about 85% yield. The reactions closely resemble those involving the cyano-sulfonium complex **2**, which correspondingly afforded the complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{PR}_3)\}]\text{SO}_3\text{CF}_3$ [**6**].

The IR spectra of **6** and **7** display the usual $\nu(\text{CO})$ band pattern (e.g. **6**: 1983s, 1948w and 1812m cm^{-1}) indicative of a *cis*-configuration. This geometry is confirmed by the occurrence of one single cp resonance in both the ^1H and ^{13}C NMR spectra (e.g. **6**: δ 5.11, 89.0). The key ^1H NMR spectral feature of these complexes is the low-field chemical shift of the $\mu\text{-C}(\text{H})$ proton, at about δ 9 ppm, which occurs as one doublet due to the coupling with phosphorus. In the complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{PPhPh}_2)\}]\text{SO}_3\text{CF}_3$ (**7**) the $\mu\text{-CH}$ proton is further coupled with the P–H proton of the PPhPh_2 moiety giving rise to a doublet of doublets ($J(\text{PH}) = 6$, $J(\text{HH}) = 18$ Hz). Similarly, the $\mu\text{-C}$ carbon gives rise to a doublet in the ^{13}C NMR spectra (e.g. **6**: δ 109.9, $J(\text{PC}) = 40$ Hz) which is comparable to the values reported for the μ -carbons of related phosphonium complexes [**6**] (e.g. for $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{PMe}_3)\}]\text{SO}_3\text{CF}_3$: δ 79.2, $J(\text{PC}) = 44$ Hz).

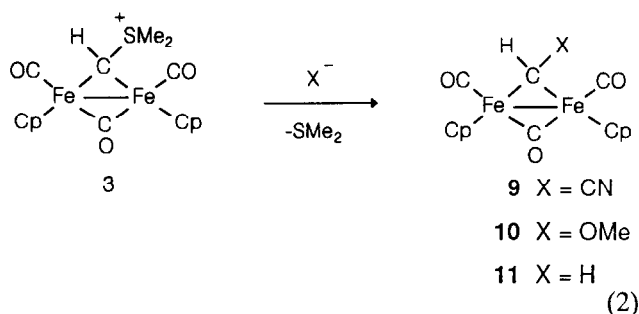
Reactions of **3** with phosphines or NMe_3 are almost immediate. We have also examined the reaction of **3** with SET_2 and found that exchange between SMe_2 and SET_2 occurs promptly (within the time necessary to record the ^1H NMR spectrum) generating an equilibrium mixture of **3** and $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{SET}_2)\}]\text{SO}_3\text{CF}_3$.

Although no kinetic studies have been performed, it seems reasonable to suppose that reactions proceed via SMe_2 dissociation to give **1** which then rapidly reacts. This hypothesis is supported by the observation that the rates of the above reactions appear to be unaffected by the nature of the nucleophiles and considering that, in the related compound $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{Br})\}]$, additions involving the $\mu\text{-C}$ carbon have been suggested to occur via bromide ionization to generate **1** [**2b**]. However the reactions of **3** with styrene or with equimolar amount of CN^- (see later discussion) are slower and, in the latter case, the reaction rate apparently depends on the CN^- concentration, therefore other possible mechanisms cannot be excluded.

Since we recently reported [**6**] that addition of NEt_3 to the phosphonium-alkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{PHRR}')\}]\text{SO}_3\text{CF}_3$ ($\text{R} = \text{R}' = \text{Et}$ or H ; $\text{R} = \text{H}$, $\text{R}' = \text{Cy}$ or Ph) results in deprotonation of the P atom, yielding neutral phosphinoalkylidene complexes, the compound $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{PPhPh}_2)\}]\text{SO}_3\text{CF}_3$ (**7**) has been treated with triethylamine affording, as expected the neutral $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{PPh}_2)\}]$ (**8**) almost quantitatively. Complex **8** exhibits the usual $\nu(\text{CO})$ band pattern (1984s, 1949w, 1816m cm^{-1}) and low-field resonance for the μ -methylidene proton (δ 11.6, $J(\text{PH}) = 11$ Hz). The resonance attributable to the μ -alkylidene carbon occurs at δ 159.3 ($J(\text{PC}) = 60$ Hz) in agreement

with the values found in related compounds (e.g. for $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{PPh})\}]$ δ 113.9, $J(\text{PC}) = 56$ Hz) [6a].

Like **2**, complex **3** reacts with Bu_4NCN , NaOMe and NaBH_4 undergoing displacement of the SMe_2 unit to give the corresponding neutral alkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{X})\}]$ ($\text{X} = \text{CN}$ (**9**), OMe (**10**), H (**11**)) (Eq. (2)).



Compound **3** appears to be less reactive compared to the cyano-sulfonium counterpart **2** since the latter directly reacts with alcohols (like methanol) [4], whereas **3**, under the same conditions is unreactive. Moreover reaction of **3** with CN^- requires several minutes to go to completion unless a twofold or higher excess of NBu_4CN is used, resulting in rapid formation of **9**.

Complexes **9**, **10** and **11** have been previously obtained by different routes. Compound $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{CN})\}]$ (**9**) has been prepared from **2** and NaBH_4 [5, 9]. Complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{OMe})\}]$ (**10**) was synthesized from $[\text{Fe}(\text{CO})(\text{PPh}_3)(\text{CHOMe})(\text{cp})]^+$ and $[\text{Fe}(\text{CO})_2(\text{cp})]^-$ [8], whereas several methods have been developed for obtaining $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CH}_2)]$ (**11**) including the reaction of $[(\text{CO})_2(\text{cp})\text{FeCH}_2\text{OAc}]$ with $[\text{Fe}(\text{CO})_2(\text{cp})]^-$ [1], preparation from $[\text{Fe}(\text{CO})_2(\text{cp})]_2$ and $(\text{Ph})_3\text{P}=\text{CH}_2$ [10] and from $\text{Me}_3\text{CCO}_2\text{CH}_2\text{Cl}$ and $[\text{Fe}(\text{CO})_2(\text{cp})]^-$ [11]. Compound **11** was also obtained by hydride addition to the methyldiene **1**: reaction with LiHBEt_3 reformed the methyldiene precursor **11** in low yield (10%) [1] whereas better results (60–70% yield) were obtained by use of NaBH_4 [8] or $[\text{HFe}(\text{CO})_4]^-$ [2b].

A comparison of these methods with that described in Eq. (2) indicates that the sulfonium-methyldiene complex **3** is to be considered a convenient precursor of methyldiene derivatives, providing a milder and easier way to handle the reagent compared to the methyldiene **1**. On the other hand, the reduced electrophilic character of **3** with respect to **1**, does not allow, to the same extent, certain peculiar reactions that have been shown to involve **1**, like the addition of alkenes to the methyldiene C–H bond [12]. As an example, we have found that **3**, upon treatment with a large excess of styrene, at room temperature for 24 h yields the alkenyldiene

complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-C}=\text{CHCH}_2\text{Ph})]$ (**12**) (29%), whereas, the corresponding reaction involving **1** immediately afforded the alkylidyne derivative $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CCH}_2\text{CH}_2\text{Ph})]^+$ (in 81% yield), which, in turn, was deprotonated leading to the formation of **12** (91%) [12c]. In the light of these considerations the sulfonium-methyldiene complex **3** should be viewed as a reagent complementary to **1**, since its reduced electrophilic reactivity can be advantageously employed in reactions with strong nucleophiles like amines, phosphines and hydrides.

A final consideration concerns the behavior shown by **3** with respect to other μ -methyldiene cations of the type $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{X})\}]^+$. In fact it is known that **1** forms 1:1 adducts with CO [2a], $\text{CNC}(\text{CH}_3)_3$ [13] or, as mentioned above, with NMe_3 and PPh_3 . Like **3** these adducts are more stable compared to **1**. Their reactivity has not been studied in detail, with the exception of the acylium $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{CO})\}]^+$ [12] but, apparently, they do not retain a reactivity centered at the $\mu\text{-C}$ carbon as is observed in **3**. For example the CO adduct $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{CO})\}]^+$ exhibits a remarkable electrophilic character, however addition of nucleophiles occurs at the acylium carbonyl carbon instead of involving the $\mu\text{-C}$ [2a,14].

3. Experimental

All reactions were routinely carried out under nitrogen by standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Instruments employed: IR, Perkin Elmer 983-G; NMR, Varian Gemini 200. Elemental analyses were determined by the Pascher Microanalytical Laboratory (Remagen, Germany). The compound $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{SMe})\}]$ was prepared according to a published method [7].

3.1. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{SMe}_2)\}]\text{SO}_3\text{CF}_3$ (**3**)

To a stirred solution of compound $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{SMe})\}]$ (0.94 g, 2.44 mmol) in dichloromethane (15 ml) was added a slight excess of $\text{CH}_3\text{SO}_3\text{CF}_3$ (0.42 g, 2.56 mmol). After 20 min Et_2O (15 ml) was added and a red precipitate was obtained. The solvent was then removed by cannula and the residue washed with Et_2O (15 ml). The red microcrystalline solid was dried under vacuum and stored under a nitrogen atmosphere affording compound **3** (1.22 g, 91%). *Anal.* Found: C, 37.3; H, 3.0. Calc. for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{Fe}_2\text{O}_6\text{S}_2$: C, 37.11; H, 3.11%. IR (cm^{-1} , CH_2Cl_2): $\nu = 1996\text{s}$, 1961w (CO); 1818m ($\mu\text{-CO}$). ^1H NMR (CD_3CN): $\delta = 9.53$ (s, 1H, $\mu\text{-CH}$), 5.19 (s, 10H, cp), 3.28 (s, 6H, $\mu\text{-CHSMe}$).

^{13}C NMR (CD_3CN): $\delta=260.1$ ($\mu\text{-CO}$), 209.3 (CO), 131.6 ($\mu\text{-CHSMe}_2$), 88.5 (cp), 34.7 (Me).

3.2. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)}\text{-}(\text{NMe}_3)\}]\text{SO}_3\text{CF}_3$ (**4**)

Through a stirred solution of **3** (0.26 g, 0.47 mmol) in MeCN (20 ml), NMe_3 was slowly bubbled for about 15 min. The mixture was stirred for 30 min then the volatile material was removed in vacuo. The residue was washed with Et_2O and crystallized from CH_2Cl_2 and Et_2O at -20°C . Yield 0.21 g (82%). Compound **4** was identified by comparison of its spectroscopic properties with those reported in the literature [2b].

3.3. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)}\text{-}(\text{PPh}_3)\}]\text{SO}_3\text{CF}_3$ (**5**)

Triphenylphosphine (0.12 g, 0.46 mmol) was added to a solution of **3** (0.22 g, 0.40 mmol) in MeCN (20 ml) and the mixture was stirred for 15 min. Then the volatile material was evaporated under reduced pressure, and the residue was washed with Et_2O , redissolved in CH_2Cl_2 , layered with Et_2O and crystallized at -20°C . Yield 0.26 g (88%). Compound **5** has been identified by comparison with the spectroscopic properties reported in the literature [8]. In addition we recorded its ^{13}C NMR spectrum (CD_3CN): $\delta=261.2$ ($\mu\text{-CO}$); 209.7 (d, $J(\text{CP})=6$ Hz, CO); 134.6, (d, $J(\text{CP})=8$ Hz), 133.4 (d, $J(\text{CP})=3$ Hz), 129.2 (d, $J(\text{CP})=11$ Hz), 125.6 (d, $J(\text{CP})=81$ Hz) Ph], 102.0 (d, $J(\text{CP})=29$ Hz, $\mu\text{-CHPPh}_3$), 89.8 (cp).

3.4. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)}\text{-}(\text{PMe}_3)\}]\text{SO}_3\text{CF}_3$ (**6**)

A solution of **3** (0.35 g, 0.64 mmol) in MeCN (20 ml) was reacted with PMe_3 (0.8 ml of a PMe_3/THF 1.0 M solution). The mixture was stirred for 15 min and then evaporated to dryness under reduced pressure. The red residue was washed with Et_2O , redissolved in MeCN, layered with Et_2O and crystallized at -20°C . Yield 0.34 g (95%). *Anal.* Found: C, 38.2; H, 3.8. Calc. for $\text{C}_{18}\text{H}_{20}\text{F}_3\text{Fe}_2\text{O}_6\text{PS}$: C, 38.32; H, 3.57%. IR (cm^{-1} , CH_2Cl_2): $\nu=1983\text{s}$, 1948w (CO), 1812m ($\mu\text{-CO}$). ^1H NMR (CD_3CN): $\delta=9.07$ (d, $J(\text{PH})=2$ Hz, 1H, $\mu\text{-CH}$), 5.11 (s, 10H, cp), 1.91 (d, $J(\text{PH})=13$ Hz, 9H, Me). ^{13}C NMR (CD_3CN): $\delta=262.0$ ($\mu\text{-CO}$), 211.9 (d, $J(\text{PC})=8$ Hz, CO), 109.9 (d, $J(\text{PC})=40$ Hz, $\mu\text{-CHPMe}_3$), 89.0 (cp), 14.3 (d, $J(\text{PC})=55$ Hz, Me).

3.5. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)}\text{-}(\text{PPh}_2)\}]\text{SO}_3\text{CF}_3$ (**7**)

Compound **7** was obtained by the procedure described for the synthesis of **5**, starting from **3** (0.35 g, 0.64

mmol) and PPh_2 (0.15 g, 0.80 mmol). Yield 0.51 g (95%). *Anal.* Found: C, 47.7; H, 3.7. Calc. for $\text{C}_{27}\text{H}_{22}\text{F}_3\text{Fe}_2\text{O}_6\text{PS}$: C, 48.10; H, 3.29%. IR (cm^{-1} , CH_2Cl_2): $\nu=1984\text{s}$, 1949w (CO), 1816m ($\mu\text{-CO}$). ^1H NMR (CD_3CN): $\delta=9.18$ (d of d, $J(\text{PH})=6$, $J(\text{HH})=18$ Hz, 1H, $\mu\text{-CHPPh}_2$), 8.2–7.8 (m, 10H, Ph), 7.04 (d of d, $J(\text{PH})=490$ Hz, $J(\text{HH})=18$ Hz, 1H, $\mu\text{-CHPPh}_2$), 4.98 (s, 10H, cp).

3.6. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)}\text{-}(\text{PPh}_2)\}]\text{SO}_3\text{CF}_3$ (**8**)

A solution of **7** (0.19 g, 0.28 mmol) in MeCN (15 ml) was treated with NET_3 (100 mg, 0.99 mmol). The mixture was stirred for 15 min, then the volatile material was removed in vacuo. The residue was redissolved in CH_2Cl_2 –petroleum ether (b.p. $40\text{--}70^\circ\text{C}$) (1:2) and the solution filtered on an alumina pad (3×3 cm). The filtered red solution was reduced to minimum volume, layered with pentane and cooled to -20°C affording red crystals of complex **8** (0.10 g, 68%). *Anal.* Found: C, 59.6; H, 4.0. Calc. for $\text{C}_{26}\text{H}_{21}\text{Fe}_2\text{O}_3\text{P}$: C, 59.58; H, 4.04%. IR (cm^{-1} , CH_2Cl_2): $\nu=1980\text{s}$, 1945w (CO), 1787m ($\mu\text{-CO}$). ^1H NMR (CDCl_3): $\delta=11.60$ (d, $J(\text{PH})=11$ Hz, 1H, $\mu\text{-CHPPh}_2$), 7.9–7.4 (m, 10H, Ph), 4.51 (s, 10H, cp). ^{13}C NMR (CD_2Cl_2): $\delta=270.6$ (d, $J(\text{PC})=15$ Hz, $\mu\text{-CO}$), 212.1 (CO), 159.3 (d, $J(\text{PC})=60$ Hz, $\mu\text{-C(H)PPh}_2$), 146.7, 133.1, 128.4 (Ph), 88.0 (cp).

3.7. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)}\text{-}(\text{CN})\}]\text{SO}_3\text{CF}_3$ (**9**)

Compound **3** (0.30 g, 0.55 mmol) was allowed to react with a slight excess of NBu_4CN (0.16 g, 0.60 mmol) in MeCN (15 ml) for 120 min. The solution was then evaporated to dryness in vacuo and the residue was redissolved in CH_2Cl_2 and filtered on an alumina pad. The red solution was evaporated to minimum volume and layered with hexanes and crystallized at -20°C to yield 0.15 g (74%) of complex **9** which has been identified by comparison with the spectroscopic properties reported in the literature [5, 9]. Reaction of **3** with a twofold or larger excess of NBu_4CN reduces the reaction time to a few minutes.

3.8. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C(H)}\text{-}(\text{OMe})\}]\text{SO}_3\text{CF}_3$ (**10**)

Compound **10** was prepared as described for **9** reacting **3** (0.28 g, 0.51 mmol) with NaOMe (5.5 ml of a NaOMe/MeOH 0.1 M solution) in MeCN (15 ml) for 15 min. Yield 0.14 g (75%). Compound **10** has been identified by comparison with the corresponding published spectroscopic data [8].

3.9. Synthesis of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CH}_2)]$ (**11**)

Compound **11** was prepared as described for **9** reacting **3** (0.30 g, 0.55 mmol) with NaBH_4 (30 mg, 0.58 mmol) in MeCN (15 ml) for 15 min. Yield 0.15 g (79%). Compound **11** has been identified by comparison with the spectroscopic data reported in the literature [1].

3.10. Reaction of **3** with styrene

A mixture of styrene (2 ml, 17.4 mmol) and **3** (0.26 g, 0.58 mmol) in MeCN (15 ml) was allowed to react at room temperature for 24 h. The volatile material was then removed under vacuum and the residue was chromatographed on an alumina column (10×3 cm) eluting with CH_2Cl_2 –hexanes (1:3). A first fraction containing some $[\text{Fe}_2(\text{CO})_4(\text{cp})_2]$ was discharged. A second red fraction was collected and evaporated to dryness under reduced pressure. The residue was crystallized from CH_2Cl_2 layered with n-pentane at -20°C yielding 74 mg (29%) of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-C}=\text{CHCH}_2\text{Ph})]$ (**12**). Complex **12** has been identified by comparison of its spectroscopic data with those reported in the literature [12c].

3.11. Reaction of **3** with SEt_2

To a CD_3CN solution (0.75 ml) of **3** (50 mg, 0.11 mmol) was added an equimolar amount of SEt_2 and the ^1H NMR recorded immediately after showing an equilibrium mixture of **3** and $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})(\text{SEt}_2)\}]\text{SO}_3\text{CF}_3$ (in approximately 1:0.6 ratio). The latter compound exhibits signals at $\delta=9.55$ (s, 1H, $\mu\text{-CH}$), 5.19 (s, 10H, cp) 3.61 (m, 4H, SCH_2CH_3), 1.62 (t, 6H, SCH_2CH_3).

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References

- [1] C.P. Casey, P.J. Fagan and W.H. Miles, *J. Am. Chem. Soc.*, **104** (1982) 1134.
- [2] (a) C.P. Casey, P.J. Fagan and V.W. Day, *J. Am. Chem. Soc.*, **104** (1982) 7360; (b) C.P. Casey, M. Crocker, P.C. Vosejпка, P.J. Fagan, S.R. Marder and M.A. Gohdes, *Organometallics*, **7** (1988) 670; (c) C.P. Casey, E.A. Austin and A.L. Rheingold, *Organometallics*, **6** (1987) 2157.
- [3] L. Busetto, V. Zanotti, S. Bordoni, L. Carlucci, V.G. Albano and D. Braga, *J. Chem. Soc., Dalton Trans.*, (1992) 1105.
- [4] L. Busetto, M.C. Cassani, V. Zanotti, V.G. Albano and D. Braga, *J. Organomet. Chem.*, **415** (1991) 395.
- [5] V.G. Albano, S. Bordoni, D. Braga, L. Busetto, A. Palazzi and V. Zanotti, *Angew. Chem., Int. Ed. Engl.*, **30** (1991) 847.
- [6] (a) L. Busetto, L. Carlucci, V. Zanotti, V.G. Albano and M. Monari, *Chem. Ber.*, **125** (1992) 1125; (b) M. Bassi, L. Carlucci and V. Zanotti, *Inorg. Chim. Acta*, **204** (1993) 171.
- [7] N.C. Schroeder, R. Funchess, R.A. Jacobson and R.J. Angelici, *Organometallics*, **8** (1989) 521.
- [8] S.C. Kao, P.P.Y. Lu and R. Pettit, *Organometallics*, **1** (1982) 911.
- [9] S. Aime, L. Cordero, R. Gobetto, S. Bordoni, L. Busetto, V. Zanotti, V.G. Albano, D. Braga and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, (1992) 2961.
- [10] R. Korswagen, R. Alt, D. Speth and M.L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **20** (1981) 1049.
- [11] M.E. Wright and G.O. Nelson, *J. Organomet. Chem.*, **263** (1984) 371.
- [12] (a) C.P. Casey and P. Fagan, *J. Am. Chem. Soc.*, **104** (1982) 4950; (b) C.P. Casey, M.W. Meszaros, S.R. Marder and P.J. Fagan, *J. Am. Chem. Soc.*, **106** (1984) 3680; (c) C.P. Casey, M.W. Meszaros, P.J. Fagan, R.K. Bly, S.R. Marder and E.A. Austin, *J. Am. Chem. Soc.*, **108** (1986) 4043; (d) C.P. Casey, M.W. Meszaros, P.J. Fagan, R.K. Bly and R.E. Colborn, *J. Am. Chem. Soc.*, **108** (1986) 4053; (e) C.P. Casey, M.W. Meszaros, R.E. Colborn, D.M. Roddick, W.H. Miles and M.A. Gohdes, *Organometallics*, **5** (1986) 1879.
- [13] C.P. Casey, M. Crocker, G.P. Niccolai, P.J. Fagan and M.S. Konings, *J. Am. Chem. Soc.*, **110** (1988) 6070.
- [14] C.P. Casey, M. Crocker and P.C. Vosejпка, *Organometallics*, **8** (1989) 278.