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PREPARATION AND REACTIVITY OF THE NEW CYCLOPENTADIENYL-BRIDGED COMPLEX $(Me_2SiCH_2CH_2SiMe_2)(C_5H_4Fe(CO)_2)_2$

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Summary

A new metal–metal bonded binuclear iron system $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2]_2$ (**2**) has been prepared by treating two equivalents of NaCp with one equivalent of $ClSi(Me)_2CH_2CH_2SiClMe_2$ obtaining the intermediate $(C_5H_5)Si(Me)_2CH_2CH_2Si(Me)_2(C_5H_5)$ which then is directly allowed to react with $Fe(CO)_5$ giving **2** in 30% yield. From this cyclopentadienyldisilyl linked system three new binuclear iron complexes are formed. Treatment of **2** with Na/Hg in THF produces the dianion $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2{}^-]_2$ which is quenched with CH_3I giving $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_4H_4Fe(CO)_2CH_3]_2$ (**4**) in 76% yield. Complex **2** is oxidized with 1.2 equivalent of I_2 to give $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ (**5**) in 85% yield. Photolysis of **5** (1 equiv.) and PPh_3 (3 equiv.) results in the formation of the bis-substituted compound $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)(PPh_3)I]_2$ (**6**). These four new binuclear iron complexes are characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy.

Introduction

Binuclear transition-metal complexes which are linked by a non-interactive, non-dissociating ligand are attractive models for studying the interactions of two metal reaction sites. Recently considerable attention is being focused on the synthesis of unbridged and bridged binuclear metal–metal bonded complexes [1,2]. In our laboratory a system which has been the focal point of the binuclear transition-metal studies is the cyclopentadienyl-bridged system $Me_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2]_2$ (**1**). The chemistry of **1** has been explored by Wegner and co-workers [3], and more recently we have prepared and examined the reactivity of derivatives of **1** such as $Me_2Si[\eta^5\text{-}C_5H_4Fe(CO)(L)I]_2$ (L = CO, PPh_3, $P(OPh)_3$) [4] and $Me_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5)]_2$ [5].

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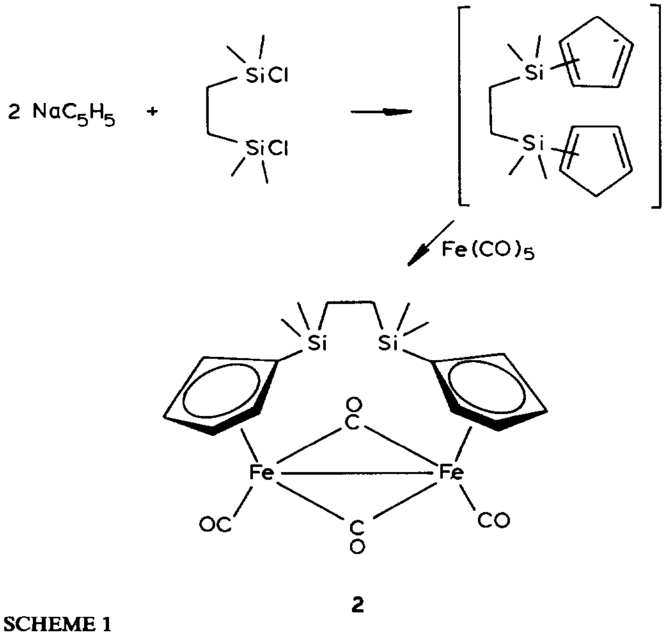
We wish to report in this paper the synthesis and characterization of the new binuclear iron complex $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2]_2$ (**2**). In addition, the preparations of three key derivatives of **2** are described.

Results and discussion

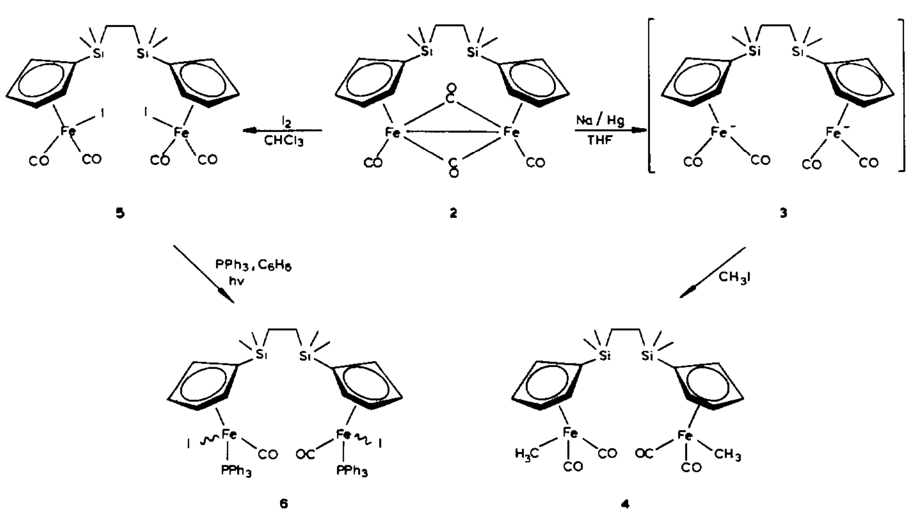
Preparation of $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2]_2$ (**2**). The strategy for the synthesis of **2** is very similar to that reported previously for **1** [5]. Two equivalents of NaC_5H_5 are treated with one equivalent of $ClSi(Me)_2CH_2CH_2SiClMe_2$ at 0°C in THF. The assumed product, $(C_5H_5)Si(Me)_2CH_2CH_2Si(Me)_2(C_5H_5)$, is never isolated but merely treated directly with $Fe(CO)_5$ in refluxing xylene/THF (5/1, v/v) for 12 h (Scheme 1). Complex **2** is typically isolated after work-up in ~ 30% yield as an air-stable, brick-red powder. This dimer displays spectroscopic data (IR, NMR) analogous to the related system **1**. The relatively high yield of **2** as compared to **1** (~ 15%) indicates that the additional ethylene unit and dimethylsilyl group in the cyclopentadienyl-bridge are beneficial in the synthesis.

Synthesis of derivatives of 2. Treatment of **2** with Na/Hg in THF for 30 min produces the dianion $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2^-]_2$ (**3**) (Scheme 2). The dianion can then be cleanly alkylated by treatment with 2.5 equivalent of CH_3I. The dimethyl product, $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2CH_3]_2$ (**4**), is isolated in analytically pure form in 76% yield by medium pressure chromatography (alumina III, benzene/ hexane, 1/1, v/v). This reaction provides direct experimental evidence for the presence of the dianion **3**. It also demonstrates that this new system can be efficiently dialkylated.

Complex **2** is readily oxidized with 1.2 equivalent of I_2 in refluxing $CHCl_3$ [6] to afford the diiodide $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ (**5**). Complex **5** is purified by column chromatography (alumina III, CH_2Cl_2/hexane, 7/3, v/v) to



SCHEME 1



SCHEME 2

give **5** as an air-stable brown solid in 85% isolated yield. Photolysis of a benzene solution containing **5** (1 equivalent) and PPh_3 (3 equivalent) for 4 h results in formation of the bis-substituted compound $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4\text{-}Fe(CO)(PPh_3)I]_2$ (**6**). Complex **6** is purified by recrystallization from acetone/hexane at −28°C over several hours. The two asymmetric iron centers in **6** give rise to the possibility of diastereomers. In the related complex $Me_2Si[\eta^5\text{-}C_5H_4Fe(CO)(PPh_3)I]_2$ diastereomers are formed in ca. a 1/1 ratio and can be separated and unambiguously identified by their NMR spectra [7]. In the case of **6** if both the diastereomers are present, they are not discernible from either NMR (^1H, ^{13}C, ^{31}P) or IR spectroscopic data.

Experimental

General data. All manipulations of complexes and solvents are carried out using standard Schlenk techniques under an atmosphere of purified argon or nitrogen. Solvents are degassed and purified by distillation under nitrogen from standard drying agents [8]. Spectroscopic measurements use the following instrumentation: ^1H NMR, Bruker WM 250 FT (at 250 MHz); ^{13}C NMR, Bruker WM 250 FT (at 62.9 MHz); ^{31}P NMR, Bruker WM 250 FT (at 101.3 MHz); IR, Perkin-Elmer 983; NMR chemical shifts are reported in δ versus Me_4Si assigning the $CDCl_3$ resonance in ^{13}C spectra to be at 77.00 ppm. Carbon-13 spectra are run with ^1H decoupling and resonances may be assumed to be singlets unless multiplicity is specified. Phosphorus-31 chemical shifts are relative to external 85% H_3PO_4 with downfield chemical shifts reported as positive. The NaH, PPh_3, and $Fe(CO)_5$ are purchased from Alfa and used as received. The disilyl reagent 1,1,4,4,-tetramethyl-1,4-dichlorodisilylethylene is purchased from Petrarch Systems, stored at −20°C, and used without further purification. The alumina (Woelm N32-63) for the medium pressure chromatography is purchased from Universal Scientific and deactivated to grade III. Medium pressure chromatography utilizes a column 15 × 500 mm unless otherwise specified. NMR solvents are routinely degassed by three consecutive freeze-pump-thaw cycles and stored under nitrogen. Samples for NMR spectroscopy are passed through a Celite plug contained in a disposable pipet to obtain optimum resolution.

Preparation of $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ *(2).* To a mixture of THF (100 ml) and NaH (98%, 6.0 g, 250 mmol) is added a THF (25 ml) solution containing cyclopentadiene (25 ml, 303 mmol) dropwise over a time of ~ 2 h. The resulting burgundy-colored solution is then slowly cannulated into a chilled (0°C) THF (25 ml) solution of $ClSi(Me)_2CH_2CH_2SiClMe_2$ (25 g, 116 mmol) over a 20 min period. Agitation by swirling the flask containing the disilyl reagent in an ice water bath is required due to large amounts of NaCl being formed. After the addition is complete, xylene (250 ml) is added and the mixture agitated at 0°C for an additional 15 min. The reaction mixture is filtered using a medium porosity fritted-glass funnel into a Schlenk round bottom flask containing xylene (200 ml). The precipitate on the filter is washed with additional xylene (100 ml). To the clear yellow filtrate is added $Fe(CO)_5$ (33 ml, 245 mmol), and this mixture is refluxed for 10–12 h under nitrogen. The purple reaction mixture is allowed to cool, filtered to remove decomposition material, and then the solvent is removed in vacuo. (Caution! Unreacted $Fe(CO)_5$ should be collected by an efficient low temperature trap.) The crude product is treated with pentane (200 ml) and placed at −25°C for ~ 12 h. The mixture is filtered and the solid washed with pentane until the washes appear faint red to give **2** as a brick red powder in ~ 30% (~ 17.0 g). **2**: ^1H NMR (δ, $CDCl_3$): 4.86 (dd, 4, J 1.9 Hz, C_5H_4), 4.45 (bs, 4, C_5H_4), 0.72 (s, 4, CH_2CH_2), 0.33, 0.32 (s, s, 12, $SiCH_3$); ^{13}C NMR (δ, $CDCl_3$): 94.50, 92.91 (C_5H_4), 90.99 (C_5H_4-carbons bound to Si), 8.75 (CH_2CH_2), −3.06 ($SiCH_3$); IR (cm^{-1} in CH_2Cl_2): ν(CO) 1993, 1951, 1772.

Preparation of $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2CH_3]_2$ *(4).* A THF (50 ml) solution of 2 (1.00 g, 2.0 mmol) is stirred over sodium-amalgam (1% sodium, 30 g) for 30 min. The THF solution is cannulated away from the Na/Hg into a separate flask and CH_3I (0.40 ml, 0.91 g, 6.4 mmol) is added via syringe. The mixture is stirred for an additional 15 min to ensure complete reaction. The solvent is removed in vacuo, the residue extracted with benzene (~ 5 ml) and placed on a column (alumina III, 2 × 10 cm). Elution with hexane/benzene (1/1, v/v) gives an initial yellow band and a slower moving red band (not collected). The yellow band is collected and the solvent removed in vacuo to give crude **4**. Final purification of **4** is achieved by medium pressure chromatography (alumina III, benzene/hexane, 1/1, v/v). The yellow band is collected and the solvent removed to afford analytically pure **4** (0.80 g, 76%): ^1H NMR (δ, $CDCl_3$): 4.80 (dd, 4, J 1.9 Hz, C_5H_4), 4.73 (dd, 4, J 1.9 Hz, C_5H_4), 0.59 (s, 4, CH_2CH_2), 0.21 (s, 12, $SiCH_3$), 0.11 (s, 6, $FeCH_3$); ^{13}C NMR (δ, $CDCl_3$): 217.55 (CO), 92.75, 87.63 (C_5H_4), 86.74 (C_5H_4-carbons bound to Si), 8.72 (CH_2CH_2 and $FeCH_3$), −3.08 ($SiCH_3$), IR(cm^{-1} in CH_2Cl_2): ν(C≡O) 2003, 1944. Anal. Found: C, 50.32; H, 5.77. $C_{22}H_{30}Fe_2O_4Si_2$ calcd.: C, 50.20; H, 5.75%.

Preparation of $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ *(5).* Complex **2** (0.50 g, 1.0 mmol) is treated with I_2 (0.31 g, 1.2 mmol) in refluxing $CHCl_3$ for 30 min. The reaction mixture is cooled and washed with 10% aq. $Na_2S_2O_3$. The organic layer is separated and dried over $MgSO_4$. The solvent is removed in vacuo and crude product dissolved in a minimum of CH_2Cl_2. Column chromatography (alumina III) utilizing first hexane as an eluent followed by CH_2Cl_2/hexane (7/3, v/v) gives a single brown band. Collection of the band and removal of the solvent yields **5** (0.64 g, 85%): ^1H NMR (δ, $CDCl_3$): 5.10, 5.03 (m, m, 8, C_5H_4), 0.71 (s, 4, CH_2CH_2), 0.31 (s, 12, $SiCH_3$); ^{13}C NMR (δ, $CDCl_3$): 213.40 (CO), 93.55 (C_5H_4), 85.84

(C_5H_4-carbons bound to Si), 85.26 (C_5H_4), 8.57 (CH_2CH_2), −2.98($SiCH_3$); IR (cm^{-1} in CH_2Cl_2): ν(C≡O) 2037, and 1993. Anal. Found: C, 32.01; H, 3.28; I, 33.73. $C_{20}H_{24}Fe_2I_2O_4Si_2$ calcd.: C, 32.03; H, 3.23; I. 33.84%.

Preparation of $[Me_2SiCH_2CH_2SiMe_2][\eta^5\text{-}C_5H_4Fe(CO)(PPh_3)I]_2$ *(6).* A benzene (50 ml) solution containing **5** (0.50 g, 0.7 mmol) and PPh_3 (0.55 g, 2.1 mmol) is irradiated (450 W med. pressure Hg lamp) in a Pyrex flask for 4 h. The resulting green solution is filtered and the solvent removed in vacuo. The crude product is column chromatographed (alumina III, benzene), the green band is collected, and the solvent removed. The green oil is then dissolved in acetone (~ 5 ml) and treated with hexanes (~ 20 ml). The mixture is set aside at −25°C for 12 h. The mixture is filtered and the green powder dried in vacuo to give pure **6** (0.68 g, 80%): ^1H NMR (δ, $CDCl_3$): 7.53, 7.36 (bs's, 30, C_6H_5), 5.43 (bs, 2, C_5H_4), 4.57 (bs, 2, C_5H_4), 3.74 (bs, 4, C_5H_4), 0.78 (s, 4, CH_2CH_2), 0.40, 0.39 (s, s, 12, $SiCH_3$); ^{13}C NMR (δ, $CDCl_3$): 221.59 (d, *J* 29 Hz, CO), 136.63 (d, *J* 9.6 Hz, *ortho*-C_6H_5), 130.01 (*para*-C_6H_5), 128.08 (d, *J* 9.6 Hz, *meta*-C_6H_5), 102.95, 87.82, 84.54 (C_5H_4), 81.28 (C_5H_4-carbons bound to Si), 78.91 (C_5H_4), 8.85 (CH_2CH_2), −2.67 ($SiCH_3$);^{31}P NMR ($CDCl_3$) 69.73; IR (cm^{-1} in CH_2Cl_2): ν(C≡O) 1948. Anal. Found: C, 53.38; H, 4.51; I, 20.88. $C_{54}H_{54}Fe_2I_2O_4P_2Si_2$ calcd.: C, 53.22; H, 4.47; I, 20.83%.

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