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Note

Hindering the formation of ferrocenes: mono(cyclopentadienyl)halo iron complexes [Fe(C_5R_5)X] containing a sterically bulky cyclopentadienyl ligand

Jun Okuda *

Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Duesbergweg 10–14, D-55099 Mainz, Germany

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Abstract

The reaction of lithium 1,2,4-tris(trimethylsilyl)cyclopentadienide Li(Si_3Cp) with ferrous halide FeX_2 (X = Cl, Br, I) in THF at − 95 °C gives a thermally extremely sensitive compound that can be regarded as a functional equivalent for the 14-electron fragment [Fe(Si_3Cp)X]. Experiments to trap this species with TMEDA gives thermally sensitive, colorless, paramagnetic crystals of the composition [LiFe(Si_3Cp)Cl_2($TMEDA)_3$]. Trimethylphosphite gives isolable 18-electron half-sandwich complexes [Fe(Si_3Cp){P($OMe)_3$}$_2$X]. [Fe(Si_3Cp)X] is also formed by reducing the ferric derivative [Fe(Si_3Cp)Cl_2] with zinc. Analogous reactivity towards ferrous halides is observed for the lithium derivatives of the similarly bulky 1,2-bis(trimethylsilyl)-4-*tert*-butyl- and 2,4-di-*tert*-butyl-1-trimethylsilylcyclopentadienide, Li($BuSi_2Cp$) and Li(Bu_2SiCp). Trapping with carbon monoxide gives complexes of the type [Fe($Bu_nSi_{3-n}Cp$)($CO)_2$X]. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Half-sandwich complexes; Bulky cyclopentadienyl ligand

1. Introduction

The original synthesis of ferrocene, [Fe(η^5-$C_5H_5)_2$], by Kealy and Pauson [1] can be rationalized by the in situ reduction of ferric chloride to ferrous chloride followed by a double nucleophilic substitution of the two chloro ligands against cyclopentadienide anions. A logical intermediate on the way to ferrocene would be a species of the type [Fe(C_5H_5)Cl] that contains only one cyclopentadienyl ligand and undergoes further substitution by a cyclopentadienide anion. Such an intermediate will be synthetically most useful [2], e.g. for the preparation of mixed ring ferrocenes [Fe(η^5-C_5H_5)(η^5-C_5R_5)]. There is some evidence that by using the C_5Me_5 (Cp*) ligand, 14- or 16-electron stable complexes of the type [FeCp*(X)] or [FeCp*(L)(X)] are accessible [3–9].

We have been interested in utilizing multiply trimethylsilyl-substituted cyclopentadienyl ligands as sterically bulky analogs of the cyclopentadienyl ligand without strong electronic perturbation as found in Cp* [10]. Previously we reported evidence for the formation of a colorless, thermally sensitive half-sandwich species [Fe(Si_3Cp)Cl] ($Si_3Cp = C_5H_2(SiMe_3)_3$-1,2,4) [11–13]. This species furnishes 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)ferrocene Fe($Si_3Cp)_2$ in moderate yields when warmed above − 30 °C in what we believe is a shift in a Schlenk-type ligand disproportionation [11]. Further reactions of the intermediate include the formation of mixed ferrocenes [Fe(Si_3Cp)(η^5-C_5R_5)] [11] or cationic arene complexes [Fe(Si_3Cp)(η^6-C_6R_6)]$^+$ [13], each with one Si_3Cp ligand (Scheme 1). This intermediate [Fe(Si_3Cp)Cl] (in associated form or as an ate complex) can be also be trapped with carbon monoxide to afford the stable 18-electron complex [Fe(Si_3Cp)Cl($CO)_2$] in high yield [11a]. We describe here, some further studies involving these thermally extremely sensitive species.

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* Tel.: + 49-6131-392-3737; fax: + 49-6131-392-5605.
E-mail address: okuda@mail.uni-mainz.de (J. Okuda).

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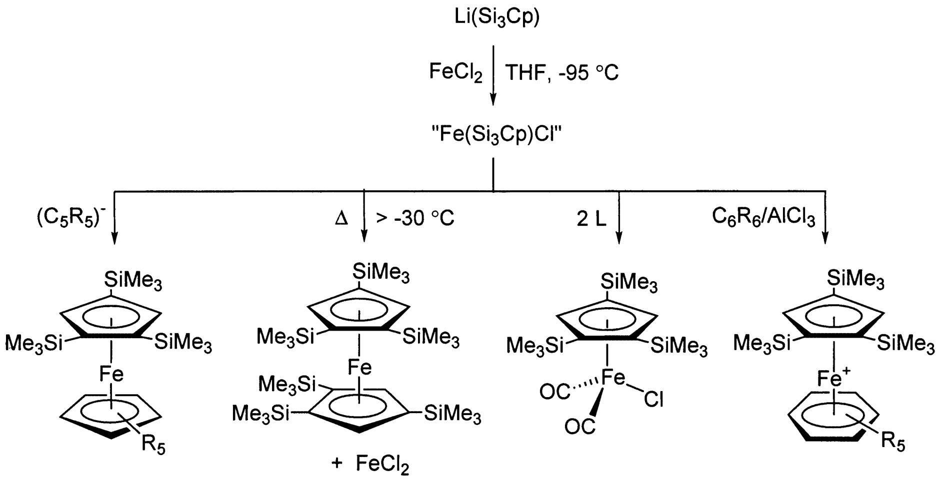
2. Results and discussion

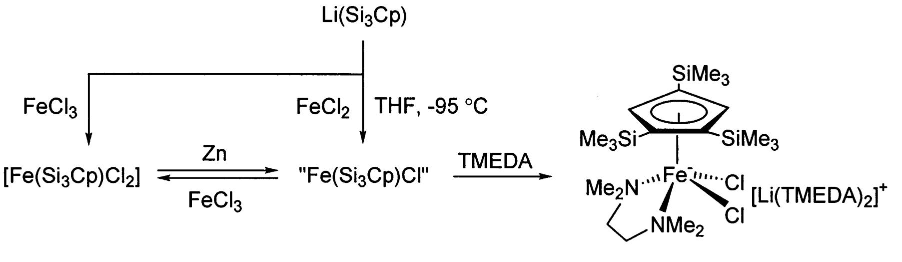
When a THF solution of lithium 1,2,4-tris(trimethylsilyl)cyclopentadienide Li($\mathrm{Si_3Cp}$) is reacted with a suspension of ferrous chloride at −95 °C in an equimolar ratio, ferrous chloride completely dissolves and a colorless solution is formed that develops with traces of oxygen, a greenish color, probably due to the formation of a ferric species [14] (Scheme 2). Numerous attempts to isolate a crystalline material from this thermally and oxidation-sensitive solution failed; upon removal of the solvent, a honey-like, pentane-soluble, paramagnetic residue is obtained that defies crystallization. A variety of ligands (1,2-dimethoxyethane, 1,4-dioxane, crown ether) were also added in order to sequester lithium, but only in the case of TMEDA (TMEDA = N,N',N'',N'''-tetramethylethylenediamine) could a highly thermally labile, colorless, crystalline material be obtained that could be analyzed. The composition [$\mathrm{LiFe(Si_3Cp)Cl_2(TMEDA)_3}$] may hint at an ate complex containing [$\mathrm{Fe(Si_3Cp)Cl_2(TMEDA)}$]$^-$, although the presence of a half-sandwich iron complex [$\mathrm{Fe(Si_3Cp)Cl(TMEDA)}$] with a three-legged piano-stool geometry in analogy to the Cp* complex reported by Jonas et al., [7] as well as to a structurally characterized magnesium complex [$\mathrm{Mg(Si_3Cp)Br(TMEDA)}$] [15] also seems probable (with co-crystallized [$\mathrm{Li(TMEDA)_2}$]Cl). The paramagnetism of the compound is in agreement with a high-spin ferrous center. Unfortunately, magnetic susceptibility measurement was hampered by its thermal instability. Reactions of Li($\mathrm{Si_3Cp}$) with ferrous bromide and iodide result in similar observations as with the chloride, whereas with $\mathrm{Fe(acac)_2}$ no stable half-sandwich complex was obtained.

When anhydrous ferric chloride is added to the colorless THF solution of [$\mathrm{Fe(Si_3Cp)Cl}$] at −78 °C, an intense green solution forms from which upon rapid work-up at low temperatures, dark-blue paramagnetic crystals of [$\mathrm{Fe(Si_3Cp)Cl_2}$] are obtained. This ferric complex rapidly decomposes above −40 °C, but can be directly synthesized by the reaction of ferric chloride with Li($\mathrm{Si_3Cp}$) in THF at −95 °C. It decomposes above −40 °C to give a dihydrofulvalene derivative besides ferrous chloride [14]. While it fails to form any half-sandwich complex with ligands such as bipyridyl or acetylacetone, it smoothly undergoes reduction with zinc powder in THF at −40 °C to give back the colorless [$\mathrm{Fe(Si_3Cp)Cl}$] (trapped with CO).

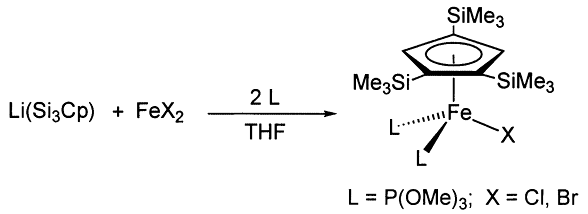
A good ligand to trap this thermal intermediate turns out to be trimethylphosphite that gives air-sensitive, turquoise crystals of [$\mathrm{Fe(Si_3Cp)X\{P(OMe)_3\}_2}$] (X = Cl, Br) in high yields, as previously mentioned for the homologous iodo complex [12] (Scheme 3). Both complexes have been completely characterized by elemental



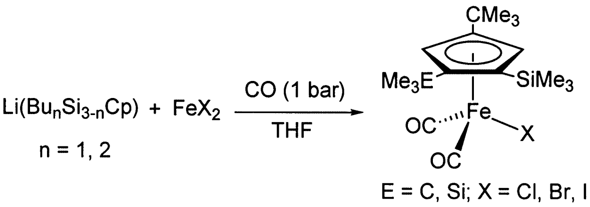
Scheme 1.



Scheme 2.



Scheme 3.

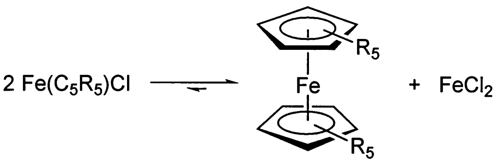


Scheme 4.

Table 1
Values for ν(CO) (in pentane) and δ(CO) of the dicarbonyl complexes

Compound	ν(CO) (cm^{-1})	δ(CO) (ppm)
$(Si_3Cp)Fe(CO)_2Cl$ [a]	2042, 2000	214.4
$(Si_3Cp)Fe(CO)_2Br$ [a]	2038, 1998	214.5
$(Si_3Cp)Fe(CO)_2I$ [a]	2030, 1991	215.5
$(Si_3Cp)Fe(CO)_2CH_3$ [a]	1993, 1938	218.4
$(BuSi_2Cp)Fe(CO)_2Cl$	2040, 1998	214.7
$(BuSi_2Cp)Fe(CO)_2Br$ [b]	2036, 1995	214.9
$(BuSi_2Cp)Fe(CO)_2I$	2028, 1988	215.7
$(Bu_2SiCp)Fe(CO)_2Cl$	2038, 1996	214.8, 215.4
$(Bu_2SiCp)Fe(CO)_2Br$	2034, 1993	214.9, 215.4
$(Bu_2SiCp)Fe(CO)_2I$	2027, 1987	214.8, 215.4
$(Si_2Cp)Fe(CO)_2Cl$ [c]	2046, 2004	214.5
$(Bu_2Cp)Fe(CO)_2Cl$ [c]	2042, 2000	214.9

[a] Ref. [11a].
[b] Ref. [16].
[c] Ref. [24].



Scheme 5.

analysis, ^1H-, ^{13}C-, and ^{31}P-NMR spectroscopy as well as by mass spectrometry. The purple product observed using trimethylphosphine could not be isolated in pure form due to its extreme air-sensitivity. The halobis(trimethylphosphite) complexes $[Fe(Si_3Cp)X\{P(OMe)_3\}_2]$ react with CO to form highly pentane-soluble, brown carbonyl complexes $[Fe(Si_3Cp)Cl(CO)\{P(OMe)_3\}]$ (X = Cl, $\nu = 1966$ cm^{-1}, X = Br, $\nu = 1964$ cm^{-1}). In the ^{13}C-NMR spectra, the carbonyl group of the chloro and bromo complex resonates at 221.4 and 221.6 ppm, respectively, both with $^3J(P,C) = 51$ Hz. The complexes are chiral and configurationally stable on the NMR timescale. Furthermore, it adopts a conformation that places the bulky trimethylphosphite ligand below the 2- and 4-trimethylsilyl group, giving rise to two well-separated ring protons only one of which shows a coupling to the phosphorus atom with $^3J(P,H) = 4.9$ Hz.

The utilization of the related bulky ligands 1,2-bis(trimethylsilyl)-4-*tert*-butyl- [16] and trimethylsilyl-2,4-di-*tert*-butylcyclopentadienyl [17], $BuSi_2Cp$ and trimethylphosphite, results in an observation analogous to that for the Si_3Cp ligand. Thus, the lithium derivative $Li(Bu_nSi_{3-n}Cp)$ ($n = 1,2$) is treated with ferrous halides in THF at −95 °C to give analogous intermediates $[Fe(Bu_nSi_{3-n}Cp)X]$. They are colorless, paramagnetic, and similarly thermally sensitive, but can be trapped with carbon monoxide to give in good yields, isolable 18-electron half-sandwich complexes of the type $[Fe(Bu_nSi_{3-n}Cp)(CO)_2X]$ (X = Cl, Br, I) (Scheme 4). The complete series of the complexes could be isolated in high yields and fully characterized by elemental analysis, mass spectrometry, IR and NMR spectroscopy. For the complexes containing the planar chiral Bu_2SiCp ligand, two ^{13}C-NMR resonances are recorded for the diastereotopic carbonyl ligands. As can be seen from Table 1, there is a small, but significant trend to lower wavenumbers upon increasing the number of the electron-donating *tert*-butyl groups [10]. A similar trend is observed for the series $Cl > Br > I$, indicating a slight increase in back bonding to the CO ligands. The ^{13}C-NMR chemical shifts, on the other hand, remain fairly constant.

3. Conclusions

Reaction of the sterically bulky cyclopentadienide with ferrous halides gives a colorless, paramagnetic species that can be considered to be a functional equivalent for the mono(cyclopentadienyl)iron(II) fragment $[Fe(C_5R_5)X]$. While detailed structural description requires definitive characterization by crystallographic analysis, the bonding of the cyclopentadienyl ligand at a ferrous center carrying only weak field ligands appears to be ionic and thus labile [18]. Due to the exceedingly high thermodynamic stability of ferrocenes, it is quite obvious that the Schlenk-type ligand redistribution according to Scheme 5 is far on the right side. Recently, Jonas et al., showed that the greenish-yellow complex [FeCp*(TMEDA)Cl] readily undergoes disproportionation to give decamethylferrocene and ferrous chloride [7]. Of course, the equilibrium is directly related to the bonding stability of the sandwich complex, as Köhler et al. observed for the various manganese analogs of the type $[Mn(C_5R_5)X]_2$ [19].

Finally, the decomposition of the product [Fe-(C_5R_5)X_2] from the reaction of ferric chloride with the bulky cyclopentadienide, in principle, realizes the original intention of Kealy and Pauson to oxidatively couple cyclopentadienide to give fulvalene [20,21]. Obviously, the steric bulk of the cyclopentadienyl ligand without pronounced electronic perturbation may effectively impede the formation of the thermodynamically stable ferrocenes.

4. Experimental

4.1. General considerations

All experiments were performed under nitrogen using standard Schlenk techniques. Et_2O, THF, and pentane were purified by distillation from sodium/benzophenone ketyl. Toluene was distilled over sodium sand. 2,5,5,-Tris(trimethylsilyl)cyclopentadiene [22], 2-*tert*-butyl-5,5-bis(trimethylsilyl)cyclopentadiene-2,4 [16], 2,4-di-*tert*-butyl-1-trimethylsilylcyclopentadiene [17], ferrous chloride [23], and FeX_2(DME) (X = Br, I) [3] were prepared according to literature procedures. $FeCl_2(THF)_{1.5}$ was obtained by recrystallizing ferrous chloride from THF. All other reagents were commercially available and purified appropriately. NMR spectra were recorded on a JEOL JNM-GX 270 or 400 spectrometer in C_6D_6 at 298 K. Chemical shifts for ^1H- and ^{13}C-spectra were referenced internally using the residual solvent resonances and reported relative to Me_4Si. IR spectra were recorded on a Nicolet 5-DX, mass spectra were recorded on a Varian 311A spectrometer. Melting points were determined in sealed tubes and are not corrected. Elemental analyses were performed by the microanalytical laboratory of the Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg University.

4.2. Reaction of lithium 1,2,4-tris(trimethylsilyl)cyclopentadienide with ferrous chloride

To a suspension of $FeCl_2(THF)_{1.5}$ (2.35 g, 10 mmol), was added dropwise at − 95 °C, 10 ml of 1 M THF solution of lithium 1,2,4-tris(trimethylsilyl)cyclopentadienide Li(Si_3Cp) in 50 ml of THF. The reaction mixture was allowed to warm to − 40 °C with stirring. At − 40 °C, the solvent was removed in vacuo, the residue extracted with 50 ml of pentane, cooled to − 18 °C, and the extracts were quickly filtered through a cooled glasfrit layered with kieselguhr. The clear solution was treated with 2.67 g (23 mmol) of *N*,*N*′,*N*″,*N*‴-tetramethylethylenediamine, concentrated, and cooled to − 40 °C to give colorless crystals, rapidly decomposing above − 18 °C; yield 300 mg (40%). Anal. Found: C, 47.87; H, 9.88; N, 10.76; Cl, 8.71; Fe, 7.90; Li, 1.00. Calc. for $C_{32}H_{77}Cl_2N_6FeLiSi_3$ (MW 764.0): C, 50.31; H, 10.16; N, 11.00; Cl, 9.28; Fe, 7.31; Li, 0.91%.

4.3. Chlorobis(trimethylphosphite){η⁵-1,2,4-tris(trimethylsilyl)cyclopentadienyl}iron

To a suspension of $FeCl_2(THF)_{1.5}$ (940 mg, 4.0 mmol) in 50 ml of THF, was added 40 ml of a 0.1 M solution of Li(Si_3Cp) in THF (4.0 mmol) at − 95 °C within 30 min. The pale-green solution was allowed to slowly warm to − 50 °C. After recooling to − 95 °C, a solution of trimethylphosphite (1.0 g, 8.0 mmol) in 40 ml of THF was added dropwise over a period of 30 min. The blue reaction mixture was allowed to attain room temperature (r.t.) and to stir for 2 h. All volatiles were removed in vacuo, the residue extracted with 3 × 15 ml of pentane and the extracts filtered through kieselguhr. The filtrate was concentrated and cooled to − 40 °C to give highly air-sensitive blue crystals; yield 1.85 g (75%), m.p. (dec.) 73 °C. ^1H-NMR: $\delta = 0.10$ (s, 9H, $SiCH_3$), 0.66 (s, 18H, $SiCH_3$), 3.54 (vt, 18H, $POCH_3$), 5.05 (vt, 2H, C_5H_2). $^{13}C\{^1H\}$-NMR: $\delta = 0.10$ ($SiCH_3$), 1.74 ($SiCH_3$), 53.20 (vt, $POCH_3$), 65.01, 97.33, 98.20 (ring C). ^{31}P-NMR: $\delta = 171.4$. IR (cm^{-1}, KBr): ν 2970 ms, 1244 ms, 1087 s, 1074, 1049 vs, 1031 s, 841 vs, 770 s, 754 s, 730 m, 555 mw. EIMS (70 eV); *m*/*z* (relative intensity): 618 ([M^+], 5), 546 ([$M^+ - SiMe_3$], 2). Anal. Found: C, 38.59; H, 7.63; Cl, 5.75. Calc. for $C_{20}H_{47}ClFeO_6P_2Si_3$ (MW 621.1): C, 38.68; H, 7.63; Cl, 5.71%.

4.4. Bromobis(trimethylphosphite){η⁵-1,2,4-tris(trimethylsilyl)cyclopentadienyl}iron

Using $FeBr_2$(DME) and following a procedure analogous to that described to prepare the chloro derivative, dark-green crystals are obtained from diethyl ether–pentane; yield 80%, m.p. (dec.) 124 °C. ^1H-NMR: $\delta = 0.18$ (s, 9H, $SiCH_3$), 0.64 (s, 18H, $SiCH_3$), 3.50 (vt, 18H, $POCH_3$), 4.82 (vt, 2H, C_5H_2). $^{13}C\{^1H\}$-NMR: $\delta = 0.32$ ($SiCH_3$), 2.40 ($SiCH_3$), 54.06 (vt, $POCH_3$), 72.35, 95.58, 95.74 (ring C). ^{31}P-NMR: $\delta = 174.4$. IR (KBr, cm^{-1}): ν 2970 ms, 2849 m, 1245 s, 1087 s, 1073 s, 1050 vs, 1037 s, 1019 s, 812 m, 838 vs, 772 s, 756 s, 705 m. EIMS (70 eV); *m*/*z* (relative intensity): 712 ([M^+], 1), 588 ([$M^+ - P(OMe)_3$], 5), 464 ([$M^+ - 2\ P(OMe)_3$], 6). Anal. Found: C, 35.87; H, 7.08; Br, 11.90. Calc. for $C_{20}H_{47}BrFeO_6P_2Si_3$ (MW 665.6): C, 36.09; H, 7.12; Br, 12.01%.

4.5. Iodobis(trimethylphosphite){η⁵-1,2,4-tris(trimethylsilyl)cyclopentadienyl}iron

This compound was described in Ref. [12].

4.6. Carbonyl(chloro)(trimethylphosphite){η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl}iron

A solution of 620 mg (1.0 mmol) of [Fe(Si_3Cp){P(OMe)$_3$}$_2$Cl] in 10 ml of Et_2O was treated at 0 °C with carbon monoxide. The color of the solution instantaneously turned brown. After stirring for 5 min at r.t., the solvent was removed and the oily residue crystallized at -78 °C to give brown crystals; yield 515 mg (98%), m.p. 75 °C, dec. > 120 °C. ^{1}H-NMR: $\delta = 0.32$ (s, 18H, $SiCH_3$), 0.53 (s, 9H, $SiCH_3$), 3.43 (d, ^3J(P,H) = 10 Hz, 9H, $POCH_3$), 4.74 (dd, ^4J(H,H) = 1.5 Hz, ^3J(H,H) = 4.9 Hz, 1H, C_5H_2), 5.56 (d, ^4J(H,H) = 1.5 Hz, 1H, C_5H_2). ^{13}C{^{1}H}-NMR: $\delta = -0.14$ ($SiCH_3$), 0.94 ($SiCH_3$), 1.20 ($SiCH_3$), 53.57 (d, ^2J(P,C) = 9 Hz, $POCH_3$), 86.05, 89.07, 96.85, 97.99, 114.21 (ring C), 221.44 (d, ^2J(P,C) = 51 Hz, CO). ^{31}P-NMR: $\delta = 168.6$. IR (pentane, cm^{-1}): ν 1966. IR (KBr, cm^{-1}): ν 2954 m, 1953 vs, 1260 sh, 1255 s, 1095 m, 1056 br s, 1041 s, 1018 s, 841 vs, 779 m, 758 s. EIMS (70 eV); m/z (relative intensity): 496 ([$M^+ - CO$], 12), 372 ([$M^+ - CO - P(OMe)_3$], 20), 357 ([$M^+ - CO - Me - P(OMe)_3$], 26). Anal. Found: C, 41.00; H, 7.34; Cl, 6.66. Calc. for $C_{18}H_{38}ClFeO_4PSi_3$ (MW 525.0): C, 41.18; H, 7.30; Cl, 6.75%.

4.7. Bromo(carbonyl)(trimethylphosphite){η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl}iron

Using [Fe(Si_3Cp){P(OMe)$_3$}$_2$Br] and following a procedure analogous to that described to prepare the chloro derivative, brown crystals were obtained; yield 95%, m.p. 84 °C, dec. > 135 °C. ^{1}H-NMR: $\delta = 0.28$ (s, 9H, $SiCH_3$), 0.37 (s, 9H, $SiCH_3$), 0.53 (s, 9H, $SiCH_3$), 3.42 (d, ^3J(P,H) = 10 Hz, 9H, $POCH_3$), 4.64 (dd, ^4J(H,H) = 1.5 Hz, ^3J(H,H) = 3.9 Hz, 1H, C_5H_2), 5.60 (d, ^4J(H,H) = 1.5 Hz, 1H, C_5H_2). ^{13}C{^{1}H}-NMR: $\delta = 0.09$ ($SiCH_3$), 0.94 ($SiCH_3$), 1.35 ($SiCH_3$), 53.83 (d, ^2J(P,C) = 9 Hz, $POCH_3$), 86.36, 88.79, 94.19, 98.30, 115.27 (ring C), 221.57 (d, ^2J(P,C) = 51 Hz, CO). ^{31}P-NMR: $\delta = 170.2$. IR (pentane, cm^{-1}): ν 1964. IR (KBr, cm^{-1}): ν 2952 m, 1954 vs, 1252 s, 1056 br s, 1041 s, 1020 s, 839 vs, 779 s, 758 s, 728 m. EIMS (70 eV); m/z (relative intensity): 570 ([M^+], 1), 542 ([$M^+ - CO$], 10), 418 ([$M^+ - CO - P(OMe)_3$], 8), 403 ([$M^+ - CO - Me - P(OMe)_3$], 8). Anal. Found: C, 37.98; H, 6.49; Br, 13.86. Calc. for $Cl_8H_{38}BrFeO_4PSi_3$ (MW 569.5): C, 37.96; H, 6.73; Br, 14.03%.

4.8. (Carbonyl)iodo(trimethylphosphite){η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl}iron

This compound was described in Ref. [12].

4.9. Chloro(dicarbonyl){η^5-4-tert-butyl-1,2-bis-(trimethylsilyl)cyclopentadienyl}iron

This compound was prepared by using lithium {4-*tert*-butyl-1,2-bis(trimethylsilyl)cyclopentadienide} Li($BuSi_2$Cp) and $FeCl_2(THF)_{1.5}$ following an analogous procedure as described for the preparation of the Si_3Cp derivative [11a] and obtained as orange–red crystals; yield 71%, m.p. 106 °C, dec. > 150 °C. ^{1}H-NMR: $\delta =$ 0.23 (s, 18H, $SiCH_3$), 1.17 (s, 9H, CCH_3), 4.95 (s, 2H, ring H). ^{13}C{^{1}H}-NMR: $\delta = 0.67$ ($SiCH_3$), 31.31 ($\mathit{C}CH_3$), 31.44 ($C\mathit{C}H_3$), 91.78 (C-1,2), 99.15 (C-3,5), 118.72 (C-4), 214.71 (CO). IR (pentane, cm^{-1}): ν 2040, ν(CO) 1998. IR (KBr, cm^{-1}): ν 3066 mw, 2975 s, 2771 m, 2901 m, 2027 vs, 1983 vs, 1459 m, 1363 m, 1258 s, 1247 s, 1180 ms, 980 s, 904 m, 842 vs, 757 s, 575 s, 541 ms, 457 m. CIMS; m/z (relative intensity): 412 ([M^+], 1), 377 ([$M^+ - Cl$], 100), 356 ([$M^+ - 2$ CO], 80), 341 ([$M^+ - 2$ CO $-$ Me], 40). Anal. Found: C, 49.54; H, 7.26; Cl, 7.90. Calc. for $C_{17}H_{29}ClFeO_2Si_2$ (MW 412.9): C, 49.45; H, 7.08; Cl, 8.59%.

4.10. Bromo(dicarbonyl){η^5-4-tert-butyl-1,2-bis-(trimethylsilyl)cyclopentadienyl}iron

This compound was reported in Ref [16].

4.11. (Dicarbonyl)iodo{η^5-4-tert-butyl-1,2-bis-(trimethylsilyl)cyclopentadienyl}iron

This compound was prepared by using Li($BuSi_2$Cp) and FeI_2(DME) following an analogous procedure as described for the preparation of the Si_3Cp derivative [11a] and obtained as dark-brown crystals; yield 83%, m.p. 113 °C, dec. > 150 °C. ^{1}H-NMR: $\delta = 0.24$ (s, 18H, $SiCH_3$), 1.21 (s, 9H, CCH_3), 5.07 (s, 2H, ring H). ^{13}C{^{1}H}-NMR: $\delta = 0.81$ ($SiCH_3$), 31.43 ($\mathit{C}CH_3$), 31.89 ($C\mathit{C}H_3$), 90.40 (C-1,2), 98.46 (C-3,5), 119.09 (C-4), 215.73 (CO). IR (pentane, cm^{-1}): ν 2028, ν(CO) 1988. IR (KBr, cm^{-1}): ν 2976 ms, 2955 s, 2902 m, 2018 vs, 1976 vs, 1459 m, 1363 m, 1258 s, 1247 s, 1181 ms, 982 s, 904 m, 840 vs, 757 s, 573 s, 547 ms, 457 m. CIMS (70 eV); m/z (relative intensity): 504 ([M^+], 5), 476 ([$M^+ -$ CO], 35), 448 ([$M^+ - 2$ CO], 100), 433 ([$M^+ - 2$ CO $-$ Me], 40), 477 ([$M^+ - I$], 94), 304 ([$M^+ - I - SiMe_3$]). Anal. Found: C, 40.45; H, 5.68; I, 24.53. Calc. for $C_{17}H_{29}FeIO_2Si_2$ (MW 504.3): C, 40.49; H, 5.80; I, 25.16%.

4.12. Chloro(dicarbonyl){η^5-2,4-di-tert-butyl-1-(trimethylsilyl)cyclopentadienyl}iron

This compound was prepared by using lithium {2,4-di-*tert*-butyl-1-(trimethylsilyl)cyclopentadienide} Li(Bu_2SiCp) and $FeCl_2(THF)_{1.5}$ following an analogous procedure as described for the preparation of the Si_3Cp derivative [11a] and obtained as orange crystals; yield 70%, m.p. 93 °C, dec. > 160 °C. ^{1}H-NMR: $\delta = 0.33$ (s, 9H, SiCH$_3$), 1.00 (s, 9H, CCH$_3$), 1.19 (s, 9H, CCH$_3$), 4.00 (d, ^{4}J(H,H) = 1.7Hz, 1H, ring H], 5.15 (s, 1H, ring H). ^{13}C{^{1}H}-NMR: $\delta = 1.85$ (SiCH$_3$), 31.13 (*C*CH$_3$), 31.36 (C*C*H$_3$), 31.79 (C*C*H$_3$), 32.08 (*C*CH$_3$), 83.16, 83.28, 103.61, 114.39, 119.43 (ring C), 214.84, 215.37 (CO). IR (pentane, cm^{-1}): ν 2038, ν(CO) 1996. IR (KBr, cm^{-1}): ν 2973 ms, 2964 s, 2958 m, 2926 m, 2905 m, 2025 vs, 1980 vs, 1459 m, 1367 m, 1258 s, 1247 s, 1180 ms, 980 s, 904 m, 842 vs, 757 s, 608 m, 575 m, 544 ms, 457 m. EIMS (70 eV); m/z (relative intensity): 396 ([M$^+$], 1), 369 ([M$^+$ − CO], 2), 340 ([M$^+$ − 2 CO], 38), 325 ([M$^+$ − 2 CO − Me], 40). Anal. Found: C, 54.55; H, 7.16; Cl, 8.69. Calc. for $C_{18}H_{29}ClFeO_2Si$ (MW 396.8): C, 54.48; H, 7.37; Cl, 8.93%.

4.13. Bromo(dicarbonyl){η^5-2,4-di-tert-butyl-1-(trimethylsilyl)cyclopentadienyl}iron

This compound was prepared by using Li(Bu$_2$SiCp) and FeBr$_2$(DME) following an analogous procedure as described for the preparation of the Si$_3$Cp derivative [11a] and obtained as red crystals; yield 87%, m.p. 103 °C, dec. > 150 °C. ^{1}H-NMR: $\delta = 0.34$ (s, 9H, SiCH$_3$), 1.00 (s, 9H, CCH$_3$), 1.23 (s, 9H, CCH$_3$), 4.38 (d, ^{4}J(H,H) = 1.7 Hz, 1H, ring H), 5.25 (s, 1H, ^{4}J(H,H) = 1.7 Hz, ring H). ^{13}C{^{1}H}-NMR: $\delta = 1.93$ (SiCH$_3$), 31.33 (*C*CH$_3$), 31.40 (*C*CH$_3$), 31.55 (C*C*H$_3$), 31.40 (C*C*H3), 80.80, 82.89, 103.77, 114.51, 118.54 (ring C), 214.92, 215.41 (CO). IR (pentane, cm^{-1}): ν 2034, ν(CO) 1993. IR (KBr, cm^{-1}): ν 2970 ms, 2964 s, 2958 m, 2926 m, 2905 m, 2027 vs, 1980 vs, 1459 m, 1367 m, 1251 s, 1247 s, 1180 ms, 980 s, 904 m, 846 vs, 757 s, 608 m, 575 m, 544 ms, 457 m. EIMS (70 eV); m/z (relative intensity): 440 ([M$^+$], 1), 412 ([M$^+$ − CO], 1), 384 ([M$^+$ − 2 CO], 38), 369 ([M$^+$ − 2 CO − Me], 36). Anal. Found: C, 48.63; H, 6.75; Br, 18.14. Calc. for $C_{18}H_{29}BrFeO_2Si$ (MW 441.3): C, 48.99; H, 6.62; Br, 18.11%.

4.14. (Dicarbonyl)iodo{η^5-2,4-di-tert-butyl-1-(trimethylsilyl)cyclopentadienyl}iron

This compound was prepared by using Li(Bu$_2$SiCp) and FeI$_2$(DME) following an analogous procedure as described for the preparation of the Si$_3$Cp derivative [11a] and obtained as brown crystals; yield 73%, m.p. 123 °C, dec. > 170 °C. ^{1}H-NMR: $\delta = 0.35$ (s, 9H, SiCH$_3$), 1.01 (s, 9H, CCH$_3$), 1.20 (s, 9H, CCH$_3$), 4.47 (d, ^{4}J(H,H) = 1.9 Hz, 1H, ring H), 5.37 (s, 1H, ^{4}J(H,H) = 1.9 Hz, ring H). ^{13}C{^{1}H}-NMR: $\delta = 1.85$ (SiCH$_3$), 31.13 (*C*CH$_3$), 31.36 (C*C*H$_3$), 31.79 (C*C*H$_3$), 32.08 (*C*CH$_3$), 83.16, 83.28, 103.61, 114.39, 119.43 (ring C), 214.84, 215.37 (CO). IR (pentane, cm^{-1}): ν 2027, ν(CO) 1987. IR (KBr, cm^{-1}): ν 2973 ms, 2965 s, 2958 m, 2926 m, 2905 m, 2020 vs, 1972 vs, 1459 m, 1367 m, 1258 s, 1250 s, 1180 ms, 980 s, 904 m, 843 vs, 757 s, 608 m, 575 m, 565 ms. EIMS (70 eV); m/z (relative intensity): 488 ([M$^+$], 17), 460 ([M$^+$ − CO], 10), 432 ([M$^+$ − 2 CO], 38), 417 ([M$^+$ − 2 CO − Me], 40), 360 ([M$^+$ − I], 6). Anal. Found: C, 44.29; H, 6.01; I, 25.80. Calc. for $C_{18}H_{29}IFeO_2Si$ (MW 489.0): C, 44.22; H, 5.98; I, 26.10%.

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