(η⁵-C₅H₅)-Ring alkylation reaction with the C₅H₅ anion: towards the construction of tri-Fe complex
Fe{[µ,η⁵:η⁴-5-exo-(1'-C₅H₄)C₅H₅]Fe(CO)₂(PPh₃)}₂

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Abstract

The reaction of (η⁵-C₅H₅)Fe(CO)I with C₅H₅M (M = Na, Li) in the presence of PPh₃ gives the Cp-ring alkylation η⁴-Fe products 10a,b. The compounds 10a,b could be deprotonated with n-BuLi to generate 12. When 12 reacts with FeCl₃, the reaction produces the tri-Fe complex 6, Fe{[µ,η⁵:η⁴-5-exo-(1'-C₅H₄)C₅H₅]Fe(CO)(PPh₃)}₂, whose hydride abstraction with Ph₃CPF₆ results in 13, [Fe{[µ,η⁵:η⁴-1-(1'-C₅H₄)C₅H₅]Fe(CO)(PPh₃)}₂][PF₆]₂. A similar strategy was applied in the preparation of penta-Fe complex 17. Fe{[µ-η⁵-C₅H₅-1,3-((C₅H₅-5-endo)-η⁴Fe(CO)(PPh₃)]₂}, which has four η⁴-Fe arms attached to a ferrocene core. The compound 12, upon treatment with the W(CO)₆(EtCN), then MeI sequence, gives the dimetallc η⁴-Fe, η⁴-W complex 17. The endo-hydride of 17 could be abstracted with Ph₃CPF₆ to result in 18 whose reaction with C₅H₅Na proceeds smoothly with the Cp-ring alkylation and gives η⁴-Fe products 19a,b. Treatment of 19a,b with n-BuLi, followed by the W(CO)₆(EtCN), then MeI sequence yields the trimetallc η⁴-W, η²-Fe, η⁴-W complex 20. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cp-ring alkylation; Three-component reaction; Ferrocenediy1-bridged tri-Fe complex; Electron-transfer chain catalysis; Carbon nucleophile; Hydride abstraction

1. Introduction

At −78 °C, the reaction of RLi (R = n-Bu, s-Bu, Me, Ph) and half-sandwich halide complex (η⁵-C₅H₅)Fe(CO)₂X (X = Cl, Br, and I) in the presence of phosphine PR₃ (R' = Ph, PhMe, PhMe₂, Me₃) produces (η⁴-exo-RC₅H₅)Fe(CO)(PR₃) (1) (Scheme 1) [1,2]. The overall three-component reaction is the Cp-ring alkylation that shifts the bonding mode of metal to ring from (η⁵-C₅H₅) to (η⁴-exo-RC₅H₅), the metal center being concurrently reduced from Fe(II) to Fe(0). The Cp-ring addition reaction is usually accompanied by a minor CO addition that gives the acyl complex (η⁵-C₅H₅)Fe(CO)(PR₃)C(O)R (2) as a by-product.

As one example, the reaction of (η⁵-C₅H₅)Fe(CO)I with BuLi in the presence of Ph₂PCH₂CH₂PPh₂ (= dppe) results in products of both Cp-ring butylation and CO butylation [3]. There are two PPh₃ groups in dppe to serve as the phosphine ingredient in three-component reaction. The isolated dppe-bridging products are as follows: (η⁴-exo-ButC₅H₅)Fe(CO)₂[µ,η⁴:η¹-dppe]-((η⁴-exo-ButC₅H₅)Fe(CO)₂ (3, 55%), (η⁴-exo-ButC₅H₅)Fe(CO)₂[µ,η¹:η¹-dppe](η⁴-C₅H₅)Fe(CO)(O)Bu (4, 18%), and (η⁴-C₅H₅)Fe(CO)(O)Bu[µ,η¹:η¹-dppe](η⁴-C₅H₅)Fe(CO)(O)Bu (5, 1%). The two PPh₃ groups of dppe seem to proceed independently with the Cp-ring butylation and/or CO butylation, such that the three dppe-bridging species are collected in a statistic ratio, as shown in Scheme 2. Accordingly, the Cp-ring butylation is ca. seven to eight times more favorable than the CO butylation, e.g. an anionic carbon nucleophile prefers the Cp-ring to CO.

Since its discovery half a century ago [4], ferrocene, an electron-rich molecule, has displayed a variety of intriguing physical and chemical properties. Complexes with a ferrocenyl group (Fc) directly bonded to a metal...
are known, among which lithioferrocenes provide key intermediates for further elaboration [5]. The reaction between metal halides and FeLi [6], the ferrocenyl transfer from Fe₃Hg [7], and the thermal or photo-induced decarbonylation of ferrocenoyl complexes [8] are inter alia useful methods for the preparation of ferrocenyl derivatives.

The above three-component reaction has been extended to that of two equivalents of (η⁵-C₅H₅)Fe(CO)₂I, 1,1'-dilithioferrocene, and two equivalents of PPh₃ (see Scheme 3) [9]. It has been found that under this condition, the substitution of the iodide on (η⁵-C₅H₅)Fe(CO)₂I by PPh₃ is much faster than nucleophilic Fc-addition at the Fe-center or at a CO ligand of (η⁵-C₅H₅)Fe(CO)₂I. The reaction thus proceeds through the intermediate [(η⁵-C₅H₅)Fe(CO)₃PPh₃] and results in the interesting ferrocenediyl-bridged tri-

Fe complex (η⁵-C₅H₅)Fe(CO)(PPh₃)[μ-C:η⁵-C(O)C₅-H₄]Feμ,η⁴:5-exo-(1'-C₅H₅)C₅H₅Fe(CO)₃(PPh₃) (7, 51%), with the 1,1'-dilithioferrocene participating twice in the nucleophilic Fe-additions: at the Cp-ring and at a CO ligand of [(η⁵-C₅H₅)Fe(CO)₂PPh₃]. This reaction, however, results in only a smaller amount of double-end η⁴-Fe tri-Fe complex Fe{μ,η⁴:5-exo-(1'-C₅H₅)C₅H₅Fe(CO)₃(PPh₃)}₂ (6, 13%) and no double-end CO-alkylation product Fe{μ,η⁴:5-C-C₅H₅}CO(PPh₃)(η⁵-C₅H₅)₂ (8). A rationale for the absence of the last product has been proposed [9].

Here we would like to report the alternative preparation of the double-end η⁴-Fe tri-Fe complex 6 that, a minor by-product with the 1,1'-dilithioferrocene reaction, could seemingly be prepared by constructing the η⁴-Fe arms first and the ferrocene core second.
2. Experimental

2.1. General

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques. All solvents were distilled from an appropriate drying agent [10]. Infrared spectra were recorded in CHCl₃ using CaF₂ optics on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. The ¹H- and ¹³C-NMR spectra were obtained on Bruker AC200/AC300/AMX400 spectrometers, with chemical shifts reported in δ values, downfield positive, relative to the residual solvent resonance of CDCl₃ (¹H 7.26, ¹³C 77.0). The ³¹P-NMR spectra were obtained on Bruker AC200/AC300 spectrometers using 85% H₃PO₄ as an external standard (δ 0.00). Mass spectra were obtained on a VG system, model 70-250S spectrometer. Microanalytical data were obtained with the use of a Perkin–Elmer 240C elemental analyzer independently operated by the Institute of Chemistry, Academia Sinica. (η⁵-C₅H₅)Fe(CO)₂I was prepared according to the literature procedure [11]. Other reagents were obtained from commercial sources, e.g. Aldrich, Merck, Strem, etc. and used without further purification.

2.2. Reaction of C₅H₅Na with 1:1
(η⁵-C₅H₅)Fe(CO)₂I/PPh₃

Three equivalents of C₅H₅Na (2 M, 15 ml) were added dropwise into a solution of (η⁵-C₅H₅)Fe(CO)₂I (3.04 g, 10 mmol) and PPh₃ (2.62 g, 10 mmol) in 150 ml of THF at −78 °C. The color of solution changed from black to orange-red during the addition. After being warmed to room temperature (r.t.), the solution was quenched with H₂O (200 ml) and extracted with Et₂O (100 ml × 2). The organic layer, combined with the ethereal extracts, was dried over MgSO₄ and then evaporated to dryness under vacuum. The oily residue was purified by chromatography using a SiO₂ column with EtOAc/hexane = 1:7 as an eluent. The following three bands separated in the order of appearance: unreacted PPh₃, yellow [η⁴-5-exo-(1'-C₅H₅)C₅H₅]Fe(CO)₂(PPh₃) and [η⁴-5-exo-(2'-C₅H₅)C₅H₅]Fe(CO)₂(PPh₃) (10a,b: 2.95 g, 60%), and yellow 1,3'-C₅H₅[(C₅H₅/5-exo-η⁴)Fe(CO)₂(PPh₃)] and 1,4'-C₅H₅[(C₅H₅/5-exo-η⁴)Fe(CO)₂(PPh₃)] (11a,b: 0.75 g, 16%). In the process of purification, two sets of ¹H-NMR data were differentiated when one component was more concentrated than the second.

10a: IR (CHCl₃, cm⁻¹) 1969 (s), 1913 (s); ¹H-NMR (C₅D₅) δ 2.62 (b, 2H, −CH−CHCH(CH₃)−), 2.56 (b, 2H, C₅H₅), 3.87 (s, 1H, −CH−CHCH(CH₃)−), 4.92 (b, 2H, −CH−CHCH(CH₃)−), 5.81 (b, 1H, C₅H₅), 6.02 (d, 1H, JHH = 1.3 Hz, C₅H₅), 6.27 (d, 1H, JHH = 1.9 Hz, C₅H₅), 6.97–7.50 (m, 15H, Ph); ³¹P-NMR (C₅D₅) δ 73.8 (s). 10b: ¹H-NMR (C₅D₅) δ 2.43 (b, 2H, −CH−CHCH(CH₃)−), 2.56 (b, 2H, C₅H₅), 3.92 (b, 1H, −CH−CHCH(CH₃)−), 5.00 (b, 2H, −CH−CHCH(CH₃)−), 5.57 (b, 1H, C₅H₅), 6.04 (d, 1H, JHH = 1.2 Hz, C₅H₅), 6.29 (d, 1H, JHH = 1.8 Hz, C₅H₅), 6.97–7.50 (m, 15H, Ph). Anal. Calc. for C₃₀H₂₄FeO₄P (mixture of 10a,b): C, 71.44; H, 5.00. Found: C, 71.76; H, 5.08%.

11a: IR (CHCl₃, cm⁻¹) 1971 (s), 1911 (s); ¹H-NMR (C₅D₅) δ 2.29 (b, 2H, C₅H₅), 2.52 (b, 4H, −CH−CHCH(CH₃)−), 3.80 (b, 2H, −CH−CHCH(CH₃)−), 5.00 (b, 2H, −CH−CHCH(CH₃)−), 5.57 (s, 1H, −CH−CHCH(CH₃)−), 6.04 (d, 1H, JHH = 1.2 Hz, C₅H₅), 6.29 (d, 1H, JHH = 1.8 Hz, C₅H₅), 6.97–7.50 (m, 15H, Ph). Anal. Calc. for C₃₀H₂₄FeO₄P (mixture of 10a,b): C, 71.44; H, 5.00. Found: C, 71.76; H, 5.08%.
2.3. Preparation of 11a.b from 10a.b

n-BuLi (1.6 M in n-hexane, 2.0 ml, 3.2 mmol) was added dropwise via a syringe into a yellow solution of mixtures of 10a.b (1.52 g, 3.0 mmol) in 20 ml of THF at 0 °C. The color of solution changed from yellow to orange-red. After being stirred for 1 h, the in-situ generated lithium reagent was cannula-transferred into the suspension solution of [[(η^5-C₅H₅)Fe(CO)₂PPh₃]⁺ [I⁻] in 50 ml of THF at −78 °C. The solution was then warmed to r.t. over 2 h. The resulting brown solution was quenched with H₂O (200 ml) and extracted with Et₂O (100 ml x 2). The organic layer, combined with the ethereal extracts, was dried over MgSO₄ and then evaporated to dryness under vacuum. The oily residue was purified by chromatography using a SiO₂ column with CH₂Cl₂/hexane = 1:2.5 as an eluent. The following three bands separated in the order of appearance: PPh₃, unreacted 10a.b, and yellow 11a.b (1.25 g, 44%).

2.4. Preparation of 6 from 10a.b

A solution of 10a.b (0.756 g, 1.5 mmol) in THF (20 ml) was treated with n-BuLi (1.6 M in n-hexane, 1.0 ml, 1.6 mmol) at 0 °C. After the stirring was stopped for 1 h, anhydrous FeCl₃ (0.146 g, 0.90 mmol) was added in one portion via a cured tube. The mixture was then refluxed for 15 h. The solvent was removed under vacuum to give a black residue, which was purified by SiO₂ column chromatography with 1:2 CH₂Cl₂/hexane as an eluent to give yellow 6 (0.31 g, 39%) and some unidentified compounds.

6: IR (CH₂Cl₂, cm⁻¹) 1967 (s), 1906 (s); ¹H-NMR (CDCl₃) δ 2.43 (b, 2H, −CH₂−CHCH₃), 3.36 (b, 1H, −CH₂−CHCH₂H), 3.61, 3.72 (2H x 2, C₅H₅), 5.05 (b, 2H, −CH₃−CHCH₂H), 7.36−7.41 (m, 15H, Ph); ¹³C-NMR (CDCl₃) δ 54.5 (s, −CH₂−CHCH₂H), 55.9 (s, −CH₃−CHCH₂H), 66.3, 67.3 (s, C₅H₅), 82.0 (s, −CH₂−CHCH₂H), 95.1 (s, C₅H₄NO₂), 128.1, 128.3, 129.6, 132.9, 133.1, 135.9, 136.6 (m, Ph), 219.5 (d, Jpc = 14 Hz, CO); ³¹P-NMR (CDCl₃) δ 74.1 (s); MS (m/z) [M⁺] 1062 (parent ion). Anal. Calc. for C₅₀H₄₆Fe₂O₄P₂: C, 67.82; H, 4.55. Found: C, 67.57; H, 4.70%.

2.5. Reaction between 6 and Ph₃CPF₆

A mixture of 6 (0.136 g, 0.13 mmol) and Ph₃CPF₆ (0.12 g, 0.31 mmol) was dissolved in 10 ml of CH₂Cl₂. The solution gradually became purple. After being stirred for 30 min, the mixture was added with H₂O. The CH₂Cl₂ layer was collected. The H₂O layer was extracted with CH₂Cl₂ for several times. The organic layers were combined and dried over MgSO₄. The by-product Ph₃CH was removed during recrystallization/filtration procedure from CH₂Cl₂ and n-hexane. The precipitate was washed with Et₂O (20 ml x 2) and dried under vacuum to result in a red complex [Fe{(μ-Fe)(η⁵-C₅H₅)C₅H₅}Fe(CO)₂(PPh₃)]₂[PF₆]₂ (13, 0.15 g, 86%).

13: IR (CH₂Cl₂, cm⁻¹) 2047 (vs), 2008 (s), 1996(s); ¹H-NMR (acetone-d₆) δ 4.58, 4.93 (b, 2H x 2, C₅H₅Fe), 5.37, 5.74 (b, 2H x 2, C₅H₅FePPh₃), 7.26−7.61 (m, Ph); ³¹P-NMR (acetone-d₆) δ 67.3 (s), −144.1 (sept). Anal. Calc. for C₅₀H₄₆Fe₂P₂O₄: C, 52.55; H, 4.85. Found: C, 52.14; H, 4.69%.

2.6. Preparation of Fe{μ-η⁵-C₅H₅-1,3-[(C₅H₅-5′-exo-η⁴)Fe(CO)₃(PPh₃)]}₂ (15) and attempted reaction between 15 and Ph₃CPF₆

A solution of 11a.b (0.706 g, 0.75 mmol) in THF (15 ml) was treated with n-BuLi (1.6 M in n-hexane, 0.5 ml) at 0 °C and stirred for 1 h. Anhydrous FeCl₃ (0.15 g, 0.9 mmol) was added in one portion via a curved tube to this brown solution. After being refluxed for 16 h, the solvent was removed under vacuum to give a black residue, which was purified by SiO₂ column chromatography with CH₂Cl₂/n-hexane = 3/2 as an eluent to afford yellow 15 (0.12 g, 17%). Some unidentified compounds were also obtained which were cationic in nature as shown by the IR peaks at ca. 2050 and 2010 cm⁻¹.

15: IR (CH₂Cl₂, cm⁻¹) 1967 (s), 1906 (s); ¹H-NMR (CDCl₃) δ 2.65 (m, 4H, −CH₂−CHCH₂H), 3.21 (s, 1H, C₅H₅Fe), 3.35 (s, 1H, C₅H₅Fe), 3.60 (b, 2H, −CH₂−CHCH₂H), 5.04 (m, 4H, −CH₂−CHCH₂H), 7.00−7.06, 7.51−7.61 (m, 30H, Ph); ¹³C-NMR (CDCl₃) δ 55.6 (s, −CH₂−CHCH₂H), 56.2 (s, −CH₂−CHCH₂H), 57.6, 66.0 (s, C₅H₅), 82.4 (s, −CH₂−CHCH₂H), 94.6 (s, C₅H₄NO₂), 128.4, 128.8, 129.0, 133.3, 133.4, 136.8, 137.1 (Ph), 220.2 (d, Jpc = 11 Hz, CO), 220.3 (d, Jpc = 11 Hz, CO); ³¹P-NMR (CDCl₃) δ 73.1 (s). Anal. Calc. for C₅₀H₄₄Fe₂O₄P₂: C, 68.14; H, 4.47. Found: C, 68.47; H, 4.71%.

The reaction of 15 and four equivalents of Ph₃CPF₆ gave a number of cationic species on the basis of IR (2050 and 2010 cm⁻¹) and ³¹P-NMR (δ 62−68) spectra. As the cationic species were not differentiating enough, detailed assignment of spectroscopic property for each cationic species was not yet possible.
2.7. Fe(CO)$_2$(PPh$_3$)[μ-(η$^4$-C$_6$H$_4$)]-5-exo-(1'-C$_6$H$_4$-η$^5$)]-M(CO)$_2$Me, M = W, Mo (17, 17)

(a) M = W. A solution of 10a,b (0.756 g, 1.5 mmol) in THF (20 ml) was treated with n-BuLi (1.6 M in n-hexane, 1.0 ml) at 0 °C and stirred for 1 h. W(CO)$_3$(EtCN)$_3$ (0.866 g, 2.0 mmol) was then added in one portion via a curved tube to the brown solution. The solution became clear after being warmed up to room temperature and was further stirred for 30 min. MeI (1.0 ml) was added dropwise via a syringe. After the mixture was stirred overnight, the solvent was removed under vacuum to give a brownish residue, which was purified by SiO$_2$ column chromatography with CH$_2$Cl$_2$/n-hexane = 1/3 as an eluent to afford unreacted starting materials (0.1 g) and yellow 17 (0.9 g, 76%).

17. IR (CH$_2$Cl$_2$, cm$^{-1}$) 2011 (s), 1974 (s), 1916 (vs); $^1$H-NMR (C$_6$D$_6$) $\delta$ 0.46 (s, 3H, Me), 2.36 (b, 2H, –CH–CH$_2$C$_5$H$_4$), 3.34 (b, 1H, –CH–CHCH$_2$C$_5$H$_4$), 4.27 (s, 4H, C$_6$H$_4$), 4.81 (b, 2H, –CH–CHCH$_2$C$_5$H$_4$), 7.00–7.05, 7.44–7.49 (m, 15H, Ph); $^{13}$C-NMR (C$_6$D$_6$) $\delta$ 33.5 (s, Me), 52.6 (s, –CH–CHCH$_2$C$_5$H$_4$), 54.8 (s, –CH–CHCH$_2$C$_5$H$_4$), 82.1 (s, –CH–CHCH$_2$C$_5$H$_4$), 89.3, 89.8 (s, C$_6$H$_4$), 119.4 (d, $J_{PC} = 5.0$ Hz, C$_5$H$_4$), 128.5, 128.7, 130.0, 133.1, 133.8, 135.6 (Ph), 217.7 (s, $J_{W_C} = 30$ Hz, CO$_{unseparated}$), 219.2 (d, $J_{PC} = 14$ Hz, CO), 230.7 (s, CO); $^{31}$P-NMR (C$_6$D$_6$) $\delta$ 73.6 (s); MS (m/z) [M$^+$] 786 (parent ion). Anal. Calc. for C$_{34}$H$_{27}$FeO$_5$PW: C, 51.94; H, 3.46. Found: C, 51.79; H, 3.52%.

(b) M = Mo. A procedure similar to the preparation of 17 was used, employing Mo(CO)$_3$(MeCN)$_3$ instead of W(CO)$_3$(EtCN)$_3$. The final purification by SiO$_2$ column chromatography with CH$_2$Cl$_2$/n-hexane = 1/3 as an eluent afforded yellow 17' (0.5 g, 72%).

17'. IR (CH$_2$Cl$_2$, cm$^{-1}$) 2015 (s), 1973 (s), 1918 (vs); $^1$H-NMR (C$_6$D$_6$) $\delta$ 0.38 (s, 3H, Me), 2.40 (b, 2H, –CH–CH$_2$C$_5$H$_4$), 3.34 (b, 1H, –CH–CHCH$_2$C$_5$H$_4$), 4.29 (s, 4H, C$_6$H$_4$), 4.83 (b, 2H, –CH–CHCH$_2$C$_5$H$_4$), 7.01–7.03, 7.44–7.49 (m, 15H, Ph); $^{13}$C-NMR (C$_6$D$_6$) $\delta$ –21.0 (s, Me), 52.8 (s, –CH–CHCH$_2$C$_5$H$_4$), 55.0 (s, –CH–CHCH$_2$C$_5$H$_4$), 82.1 (s, –CH–CHCH$_2$C$_5$H$_4$), 90.6, 91.0 (s, C$_6$H$_4$), 121.3 (s, C$_5$H$_4$), 128.5, 128.6, 130.0, 133.2, 133.3, 136.1, 136.5 (Ph), 219.2 (s, $J_{PC} = 15$ Hz, CO), 227.9 (s, CO$_{unseparated}$), 241.1 (s, CO); $^{31}$P-NMR (C$_6$D$_6$) $\delta$ 73.7 (s); MS (m/z) [M$^+$] 698 (parent ion). Anal. Calc. for C$_{34}$H$_{27}$FeO$_5$PMo: C, 58.48; H, 3.90. Found: C, 58.19; H, 3.82%.

2.8. {Fe(CO)$_2$(PPh$_3$)[μ-(η$^4$-C$_6$H$_4$)]-5-exo-(1'-C$_6$H$_4$)}(CO)$_2$Me -> MePF$_6$ (18)

A mixture of 17 (0.91 g, 1.16 mmol) and Ph$_3$CPF$_6$ (0.49 g, 1.26 mmol) was dissolved in 20 ml of CH$_2$Cl$_2$. The color of solution changed gradually from orange to yellow, accompanied by the formation of a yellow precipitate after 30 min. After being stirred for 1 h, the volume of solution was reduced to about half the original volume in vacuo. Et$_2$O (30 ml) was then added. The precipitate was filtered and washed with Et$_2$O until the washings were colorless, resulting in a yellow-orange powder 18 (1.01 g, 94%).

18. IR (CH$_2$Cl$_2$, cm$^{-1}$) 2055 (m), 2132 (s), 1932 (vs); $^1$H-NMR (acetone-d$_6$) $\delta$ 0.35 (s, 3H, Me), 5.55, 5.84 (vt, $J_{HH} = 2$ Hz, 2H × 2, C$_5$H$_4$Fe), 6.11, 6.24 (vt, $J_{HH} = 2$ Hz, 2H × 2, C$_5$H$_4$W), 7.53–7.68 (m, 15H, Ph); $^{13}$C-NMR (acetone-d$_6$) $\delta$ –30.8 (s, Me), 84.1, 90.1 (s, C$_5$H$_4$Fe), 96.2, 96.4 (s, C$_5$H$_4$W), 98.5, 104.3 (s, C$_5$H$_4$), 130.5, 130.7, 133.2, 133.8, 133.9, 136.1, 136.5 (Ph); $^{31}$P-NMR (acetone-d$_6$) $\delta$ 67.0 (s), –138.3 (sept); MS (m/z) [M$^+$] 698 (parent ion). Anal. Calc. for C$_{34}$H$_{27}$FeO$_5$PF$_6$: C, 43.87; H, 2.82. Found: C, 44.10; H, 2.85%.

2.9. Reaction of C$_6$H$_4$Na with 18

A suspension of 18 (1.01 g, 1.09 mmol) in 30 ml of THF was treated with C$_6$H$_4$Na (2.0 M in THF, 0.6 ml) at $-78$ °C. The mixture became clear after the addition was completed and was further stirred for 2 h. After being warmed up to r.t., the solution was quenched with MeOH and then pumped dry to give an oily residue. Purification by SiO$_2$ column chromatography with CH$_2$Cl$_2$/n-hexane = 1/1 as an eluent afforded yellow 18 as an unseparated isomers, each with very complicated $^1$H-NMR spectrum, corresponding to 1'- or 2'-substitution on the cyclo pentadienene without metal.

19a,b. IR (CH$_2$Cl$_2$, cm$^{-1}$) 2008 (s), 1971 (s), 1918 (vs); $^{31}$P-NMR (C$_6$D$_6$) $\delta$ 73.6 (s). MS (m/z) [M$^+$] 850 (parent ion). Anal. Calc. for C$_{39}$H$_{32}$FeO$_5$PW: C, 55.09; H, 3.67. Found: C, 55.40; H, 3.87%.

2.10. Fe(CO)$_4$(PPh$_3$)[μ-(η$^4$-C$_6$H$_4$)]-5-exo-(η$^5$-C$_6$H$_4$)W(CO)$_2$Me -> MePF$_6$ (18)

A solution of 19a,b (0.595 g, 0.7 mmol) in THF (20 ml) was treated with n-BuLi (1.6 M in n-hexane, 0.5 ml) at 0 °C and stirred for 30 min. W(CO)$_3$(EtCN)$_3$ (0.28 g, 0.65 mmol) was added in one portion via a curved tube to this brown solution. It became clear after being warmed up to r.t. and was further stirred for 30 min. MeI (1.0 ml) was then added dropwise via a syringe. The solution was stirred for additional 30 min. Then the solvent was removed under vacuum to give a brownish residue, which was purified by SiO$_2$ column chromatography with CH$_2$Cl$_2$/n-hexane = 1/3 as an elu-
ent to afford unreacted starting materials (0.2 g) and yellow 20 (0.3 g, 57%).

20: IR (CHCl₃, cm⁻¹) 2010 (s), 1974 (m), 1918 (vs); ¹H-NMR (CD₂Cl₂) δ 0.43, 0.45 (s, 3H × 2, Me), 1.85 (m, 1H, H₅), 3.40 (m, 1H, H₆), 4.27, 4.34, 4.37, 4.50, 4.55, 4.63, 4.78, 4.80 (m, 1H × 8, C₅H₆W), 4.76 (m, 1H, H₇), 5.10 (m, 1H, H₅), 7.04–7.08, 7.34–7.40 (m, 15H, Ph); ³¹P-NMR (CD₂Cl₂) δ 73.6 (s). Anal. Calc. for C₄₃H₂₃FeO₇P₂W₂: C, 45.61; H, 2.94. Found: C, 45.80; H, 3.09%.

3. Results and discussion

3.1. [(η⁵-C₅H₅)Fe(CO)₂PPh₃][I⁻] as the intermediate for Cp-ring and/or CO alkylation

The preparation of the η⁴-Fe compounds in three-component reaction is actually a two-stage transformation (Schemes 1–3), in which the ionic [(η⁵-C₅H₅)Fe(CO)₂PPh₃][I⁻] is the intermediate product that receives the carbon nucleophile at the Cp-site or the CO-site. The mechanism for in-situ, facile production of [(η⁵-C₅H₅)Fe(CO)₂PPh₃][I⁻] from (η⁵-C₅H₅)Fe(CO)₂I and PPh₃ is an electron-transfer chain catalytic replacement of iodide on (η⁵-C₅H₅)Fe(CO)₂I by PPh₃, with chemical initiation by the first drops of anionic carbon nucleophile [12,13]. As an initiator at the beginning of the reaction and a normal nucleophile later, the carbanion nucleophiles have dual functions. The initiation function is a perfect match with their properties because the concerned electron-transfer chain catalysis is reductive in nature: a carbanion is known to function as a reductant, a base, and a nucleophile [14].

For a range of lithiated alkyl and aryl nucleophiles, the CO alkylation product (η⁵-C₅H₅)Fe(CO)₂PPh₃-C(O)R is generally minor, i.e. the carbon nucleophiles (alkyl and aryl) favor addition onto the Cp-ring [1,2]. Yet for the ferrocenyln anions, the pattern doesn’t conform to the general carbon nucleophiles, attributed to an interaction between the cyclopentadienyl carbons and Fe-center in ferrocene with the nature of such interaction not yet fully understood. The absence of double-end CO-alkylation product 8 has been demonstrated experimentally that the pathway from (η⁵-C₅H₅)Fe(CO)₂PPh₃[µ-C₅H₅-C(Ο)C₅H₅Fe(C₅H₅)Li] (9) and [(η⁵-C₅H₅)Fe(CO)₂PPh₃][I⁻] to 8 is not available because of a localization of the Li cation [9].

3.2. Cp anion as the carbon nucleophile in three-component reaction

Since the 1,1’-dilithioferrocene route produces 51% 7, leaving the isomeric 6 only a minor by-product, an attempt to specifically prepare the double-end η⁴-Fe tri-Fe 6 using an alternative method is very challenging to organometallic chemists. Retrosynthetically, if one wants to build the η⁴-Fe arm on Cp-ring first and make the ferrocene core second, one must employ the Cp anion in the three-component reaction. While C₅H₅Na is available from commercial sources, the reactivity of C₅H₅Li in three-component reaction is the same as that of C₅H₅Na and is readily generated by deprotonation of C₅H₅ using n-BuLi.

The reaction of (η⁴-C₅H₅)Fe(CO)₂I with C₅H₅M (M = Na, Li) in the presence of PPh₃ gives two unseparated, isomeric η⁴-Fe products (in about 1:1 ratio, total yield 60%, see Scheme 4). One is 10a and the other 10b. The difference is only at the site of substitution on the cyclopentadiene that is not attached to Fe. There was no spectroscopic evidence for the third possible isomer [η⁴-5-exo-(5’-C₅H₅)C₅H₅Fe(CO)₂PPh₃] (10c). Compound 10c is believed to be the immediate product that rearranges to 10a,b by proton shifts on the cyclopentadiene. There was no observation of the CO alkylation product (η⁴-C₅H₅)Fe(CO)₂PPh₃(C₅H₅)(C₅H₅). Thus the Cp anion is different from Fe anions and acts as a normal carbon nucleophile, preferring the Cp-ring alkylation in the three-component reaction.

The 5-membered Cp anion is an aromatic reagent during the three-component reaction. After addition, however, the cyclopentadiene skeleton in products is no more aromatic in bonding. The C₅H₅M reaction yielded the interesting extra bis(η⁴-Fe) products 11a and 11b in about 1:1 ratio (total yield 16%). The 1’,2’-isomer was not observed, attributed to over crowding. The reaction mechanism producing 11a,b involves the addition of the Cp anion which adds to the Cp-ring of [(η⁵-C₅H₅)Fe(CO)₂PPh₃][I⁻] to yield 10a,b. These compounds are deprotonated on the cyclopentadiene that is not attached to Fe by free Cp anion to form the conjugate base [η⁴-5-exo-(5’-C₅H₅)C₅H₅Fe(CO)₂PPh₃] (12). The acid–base equilibrium is very quickly established. Thus, also as a carbon nucleophile, 12 produces 11a,b when the Cp anion produces 10a,b during later stages of the reaction. In order to compensate for this problem, the quantity of C₅H₅M was increased to three equivalents in order to maximize the yield of 10a,b.

3.3. Preparation of 6 from 12 and its hydride abstraction reaction

Treatment of pure 10a,b with n-BuLi generated 12. When 12 reacted with [(η⁵-C₅H₅)Fe(CO)₂PPh₃][I⁻], the products were 11a,b (44%). When 12 reacted with FeCl₃ following a literature procedure [15] the product was mainly 6 (39%, Scheme 5) plus some unidentified by-products. The 5-endο-H on a (η⁵-5-exo-RC₅H₅Fe(CO)₂PPh₃ moiety has been shown to be a hydride that could be abstracted with a strong Lewis acid, e.g. [PPh₃C⁺] [16]. Accordingly, treatment of 6
with Ph₃CPF₆, produces the double-end, cationic tri-Fe complex 13 (86%, Scheme 5). The characteristic IR νCO stretching bands of the neutral 6 are at 1967, 1908 cm⁻¹ whereas those of the cationic 13 are at 2047, 2008 cm⁻¹, the shift being 80–100 cm⁻¹ to higher wave numbers that are consistent to the fact that the Fe-center in 13 has a higher oxidation state. The ¹H-NMR spectrum of 6 reveals a 2H:1H:2H pattern assigned to the 5 H-atoms of the cyclopentadiene ring attached to Fe at δ 2.43, 3.36, 5.05 (in CDCl₃). The hydride abstraction removes the 2H:1H:2H pattern completely. In 13, the ¹H-NMR spectrum shows only the 2H:2H pattern at δ 5.37, 5.74 (in acetone-d₆), characteristic for a Cp-ring attached to Fe. The electrophilic abstraction of the endo-hydride shifts the bonding mode of metal to ring from (η⁴-exo-RC₅H₄) to (η⁴-RC₅H₄), the metal center being oxidized from Fe(0) to Fe(II).

Similar strategy has been applied to the preparation of penta-Fe complex 15 that has four η⁴-Fe arms attached to a ferrocene core. As shown in Scheme 6, treatment of 11a,b with n-BuLi produced in-situ the anion [(1,3-C₅H₃−(1,3-C₅H₃−η⁴-Fe(CO)₂PPh₃)] (14) that, when reacted with FeCl₃, resulted in 15 (17%) and some unidentified compounds which were cationic in nature. The hydride abstraction on 15 with excess Ph₃CPF₆ was attempted, giving seemingly 16 on the basis of IR and ³¹P-NMR spectra. However, it was also noticed that in the mixture an array of compounds from 15 to 16 were likely present, ranging from a complex with (4 η⁴-Fe, 0 η⁵-Fe) arms attached to...
ferrocene core to a complex with (0 \(\eta^1\)-Fe, 4 \(\eta^5\)-Fe) arms. The yield of 15 in its preparation was low, attributed to the presence of Lewis acid FeCl\(_3\) (or ferrocenium) which presumably abstracted the endo-hydrides to produce mono- to tetra-(\(\eta^5\)-Fe) by-products.

3.4. Preparation of CpW(CO)\(_3\)Me derivatives from 12 and their hydride abstraction reaction

As shown in Scheme 7, the anionic 12 could be treated with the W(CO)\(_3\)(EtCN)\(_3\) followed by MeI sequence [15] to give a dimetallic \(\eta^4\)-Fe, \(\eta^5\)-W complex 17 (76\%) which has two directly connected five-membered rings in different bonding environments. The Mo analog 17 could also be obtained in 72\% isolated yields without any difficulty. The endo-hydride of 17 could be abstracted in the same manner with Ph\(_3\)CPF\(_6\) to result in 18 (94\%). The change of spectroscopic property from 17 to 18 is similar to the change from 6 to 13. In both cases, there is a shift of \(\nu_{CO}\) stretching bands towards...
higher frequencies by 80–100 cm$^{-1}$ in IR. There is also a change from the 2H:1H:2H pattern to the 2H:2H pattern in $^1$H-NMR corresponding, respectively, to the bonding of metal to ring from ($\eta^5$-5-exo-RC$_5$H$_5$)Fe to ($\eta^5$-RC$_5$H$_5$)Fe.

Complex 18 is a derivative of [(($\eta^5$-C$_5$H$_4$R)Fe-(CO)$_3$P(C$_6$H$_5$)$_2$] with R = ($\eta^5$-C$_5$H$_4$H)W(CO)$_3$Me and is thus a substrate for C$_5$H$_5$Na. The reaction between 18 and C$_5$H$_5$Na proceeded smoothly with the Cp-ring alkylation to give unseparated, isomeric 19a,b, in about 1:1 ratio (total yield 69%). The difference between 19a and 19b is the site of substitution on the bicyclopentadiene that is not attached to Fe. There was no spectroscopic evidence for the third possible isomer Fe(CO)$_3$(P(C$_6$H$_5$)$_3$)+($\eta^5$-C$_5$H$_4$H)-5-exo($\eta^5$-C$_5$H$_4$)-2-($\eta^5$-C$_5$H$_5$)FeW(CO)$_3$Me (19c), believed to be the immediate product rearranging to 19a,b by proton shifts on the bicyclopentadiene. Similar to Scheme 4, there were also the bis($\eta^5$-Fe) by-products (not shown in Scheme 7) that were nonetheless not studied previously. Treatment of pure 19a,b with n-BuLi, followed by the W(CO)$_3$- (EtCN)$_3$, then MeI sequence yielded the trimetallic W, $\eta^5$-Fe, $\eta^5$-W complex 20 (57%). For 20, the ($\eta^5$-C$_5$H$_5$)W(CO)$_3$Me substituents on the bicyclopentadiene ring are at the two- and five-position. The 1,5-isomers were not observed due to steric reasons.

The hydride abstraction on 20 with Ph$_3$CPF$_6$ was difficult. When abstraction was carried out at room temperature for hours, very little cationic species could be observed, likely due to steric reasons: there are two bulky groups of $\eta^5$-C$_5$H$_5$W(CO)$_3$Me in 20 and [Ph$_3$C$^+$] is a bulky reagent.

4. Conclusion

The reaction of ($\eta^5$-C$_5$H$_4$)Fe(CO)$_3$I with Cp anion in the presence of PPh$_3$ gives 10a,b. Treatment of 10a,b with n-BuLi generates 12 that can react with FeCl$_3$ to produce 6 whose hydride abstraction results in 13. The transformation from 10a,b to 17 could be repeated similarly from 19a,b to 20, the cycle to bring 17 to 19a,b being realized with an electrophilic hydride abstraction then a Cp anion addition on the Cp-ring.

Acknowledgements

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