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(η^5-C_5H_5)-Ring alkylation reaction with the C_5H_5 anion: towards the construction of tri-Fe complex Fe{[$\mu,\eta^5:\eta^4$-5-*exo*-(1′-C_5H_4)C_5H_5]Fe$(CO)_2(PPh_3)$}$_2$

Lung-Shiang Luh [a], Ling-Kang Liu [a,b,*]

[a] *Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan*
[b] *Department of Chemistry, National Taiwan University, Taipei 10607, Taiwan*

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Abstract

The reaction of (η^5-C_5H_5)Fe$(CO)_2$I with C_5H_5M (M = Na, Li) in the presence of PPh_3 gives the Cp-ring alkylation η^4-Fe products **10a**,**b**. The compounds **10a**,**b** could be deprotonated with *n*-BuLi to generate **12**. When **12** reacts with $FeCl_3$, the reaction produces the tri-Fe complex **6**, Fe{[$\mu,\eta^5:\eta^4$-5-*exo*-(1′-C_5H_4)C_5H_5]Fe$(CO)_2(PPh_3)$}$_2$, whose hydride abstraction with Ph_3CPF_6 results in **13**, [Fe{[$\mu,\eta^5:\eta^5$-1-(1′-C_5H_4)C_5H_4]Fe$(CO)_2(PPh_3)$}$_2$][PF_6]$_2$. A similar strategy was applied in the preparation of penta-Fe complex **15**, Fe[μ-η^5-C_5H_3-1,3-{(C_5H_5-5′-*exo*-η^4)Fe$(CO)_2(PPh_3)$}$_2$]$_2$, which has four η^4-Fe arms attached to a ferrocene core. The compound **12**, upon treatment with the $W(CO)_3(EtCN)_3$ then MeI sequence, gives the dimetallic η^4-Fe, η^5-W complex **17**. The *endo*-hydride of **17** could be abstracted with Ph_3CPF_6 to result in **18** whose reaction with C_5H_5Na proceeds smoothly with the Cp-ring alkylation and gives η^4-Fe products **19a**,**b**. Treatment of **19a**,**b** with *n*-BuLi, followed by the $W(CO)_3(EtCN)_3$ then MeI sequence yields the trimetallic η^5-W, η^4-Fe, η^5-W complex **20**. © 2001 Elsevier Science B.V. All rights reserved.

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

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1. Introduction

At −78 °C, the reaction of RLi (R = *n*-Bu, *s*-Bu, Me, Ph) and half-sandwich halide complex (η^5-C_5H_5)Fe$(CO)_2$X (X = Cl, Br, and I) in the presence of phosphine PR'_3 ($R'_3 = Ph_3$, Ph_2Me, $PhMe_2$, Me_3) produces (η^4-*exo*-RC_5H_5)Fe$(CO)_2PR'_3$ (**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 (η^5-C_5H_5) to (η^4-*exo*-RC_5H_5), 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 (η^5-C_5H_5)Fe(CO)(PR'_3)C(O)R (**2**) as a by-product.

As one example, the reaction of (η^5-C_5H_5)Fe$(CO)_2$I with BuLi in the presence of $Ph_2PCH_2CH_2PPh_2$ (= dppe) results in products of both Cp-ring butylation and CO butylation [3]. There are two PPh_2 groups in dppe to serve as the phosphine ingredient in three-component reaction. The isolated dppe-bridging products are as follows: (η^4-*exo*-BuC_5H_5)Fe$(CO)_2$($\mu,\eta^1:\eta^1$-dppe)(η^4-*exo*-BuC_5H_5)Fe$(CO)_2$ (**3**, 55%), (η^4-*exo*-BuC_5H_5)Fe$(CO)_2$($\mu,\eta^1:\eta^1$-dppe)(η^5-C_5H_5)Fe(CO)C(O)Bu (**4**, 18%), and (η^5-C_5H_5)Fe(CO)C(O)Bu($\mu,\eta^1:\eta^1$-dppe)(η^5-C_5H_5)Fe(CO)C(O)Bu (**5**, 1%). The two PPh_2 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

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* Corresponding author. Tel.: +886-2-2789-8532; fax: +886-2-2783-1237.

E-mail address: liuu@chem.sinica.edu.tw (L.-K. Liu).

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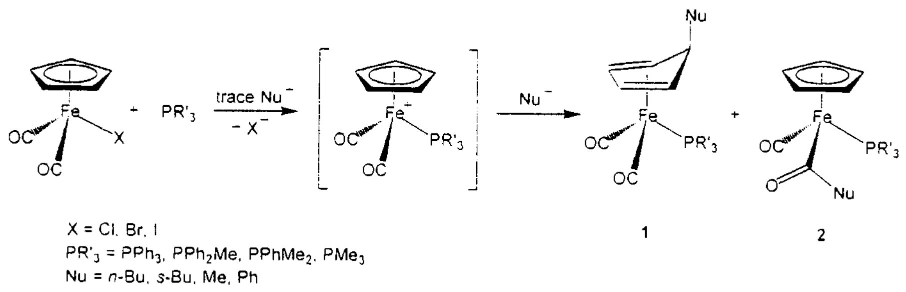
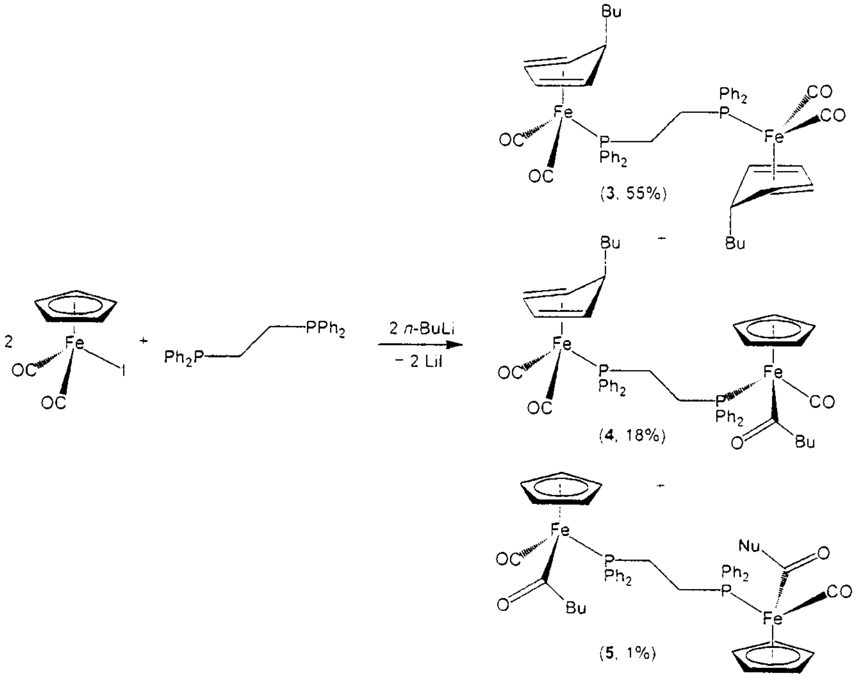


Scheme 1.

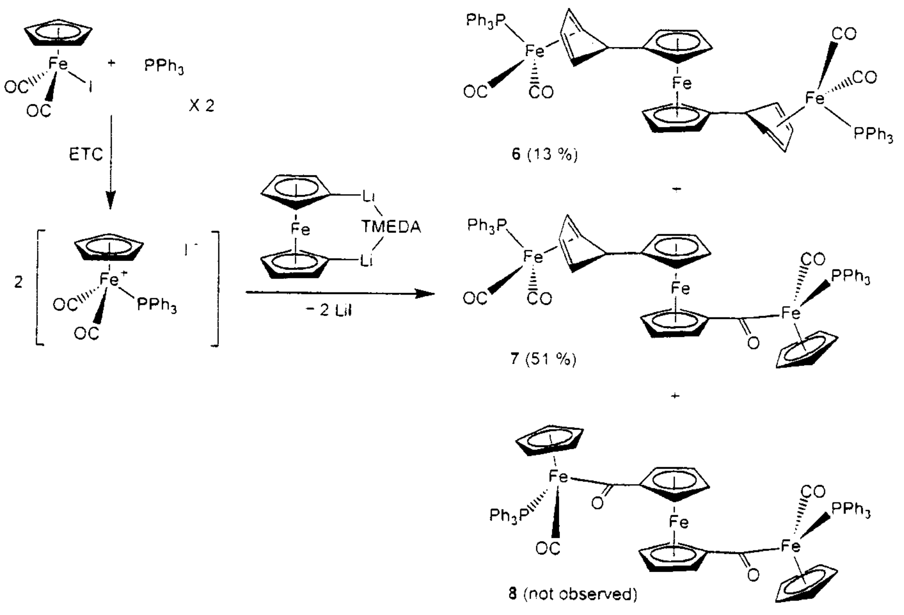
are known, among which lithioferrocenes provide key intermediates for further elaboration [5]. The reaction between metal halides and FcLi [6], the ferrocenyl transfer from Fc_2Hg [7], and the thermal or photo-induced decarbonylation of ferrocenoyl complexes [8] are inter alia useful methods for the preparation of ferrocenyl derivatives.

The above three-component reaction has been extended to that of two equivalents of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, 1,1′-dilithioferrocene, and two equivalents of PPh_3 (see Scheme 3) [9]. It has been found that under this condition, the substitution of the iodide on $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ by PPh_3 is much faster than nucleophilic Fc-addition at the Fe-center or at a CO ligand of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. The reaction thus proceeds through the intermediate $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+]$ and results in the interesting ferrocenediyl-bridged tri-Fe complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)[\mu,\mathit{C}{:}\eta^5\text{-}C(O)C_5H_4]Fe[\mu,\eta^5{:}\eta^4\text{-}5\text{-}\mathit{exo}\text{-}(1'\text{-}C_5H_4)C_5H_5]Fe(CO)_2(PPh_3)$ (**7**, 51%), with the 1,1′-dilithioferrocene participating twice in the nucleophilic Fc-additions: at the Cp-ring and at a CO ligand of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+]$. This reaction, however, results in only a smaller amount of double-end η^4-Fe tri-Fe complex $Fe\{[\mu,\eta^5{:}\eta^4\text{-}5\text{-}\mathit{exo}\text{-}(1'\text{-}C_5H_4)C_5H_5]Fe(CO)_2(PPh_3)\}_2$ (**6**, 13%) and no double-end CO-alkylation product $Fe[(\mu,\eta^5{:}\mathit{C}\text{-}C_5H_4)C(O)\text{-}Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)]_2$ (**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 η^4-Fe tri-Fe complex **6** that, a minor by-product with the 1,1′-dilithioferrocene reaction, could seemingly be prepared by constructing the η^4-Fe arms first and the ferrocene core second.



Scheme 2.



Scheme 3.

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 CH_2Cl_2 using CaF_2 optics on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. The ^{1}H- and ^{13}C-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 $CDCl_3$ (^{1}H δ 7.24, ^{13}C δ 77.0). The ^{31}P-NMR spectra were obtained on Bruker AC200/AC300 spectrometers using 85% H_3PO_4 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. (η^5-C_5H_5)$Fe(CO)_2I$ 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 C_5H_5Na with 1:1 (η^5-C_5H_5)$Fe(CO)_2I$/PPh_3

Three equivalents of C_5H_5Na (2 M, 15 ml) were added dropwise into a solution of (η^5-C_5H_5)$Fe(CO)_2I$ (3.04 g, 10 mmol) and PPh_3 (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 H_2O (200 ml) and extracted with Et_2O (100 ml × 2). The organic layer, combined with the ethereal extracts, was dried over $MgSO_4$ and then evaporated to dryness under vacuum. The oily residue was purified by chromatography using a SiO_2 column with EtOAc/hexane = 1:7 as an eluent. The following three bands separated in the order of appearance: unreacted PPh_3, yellow [η^4-5-*exo*-(1′-C_5H_5)C_5H_5]$Fe(CO)_2$(PPh_3), and [η^4-5-*exo*-(2′-C_5H_5)C_5H_5]$Fe(CO)_2(PPh_3)$ (**10a,b**; 2.95 g, 60%), and yellow 1′,3′-C_5H_4[(C_5H_5-5-*exo*-η^4)$Fe(CO)_2PPh_3$]$_2$ and 1′,4′-C_5H_4[(C_5H_5-5-*exo*-η^4)$Fe(CO)_2PPh_3$] (**11a,b**; 0.75 g, 16%). In the process of purification, two sets of ^{1}H-NMR data were differentiated when one component was more concentrated than the second.

10a: IR (CH_2Cl_2, cm^{-1}) 1969 (s), 1913 (s); ^{1}H-NMR (C_6D_6) δ 2.62 (b, 2H, $-CH{=}C\mathit{H}CH(C_5H_5)-$), 2.56 (b, 2H, $C_5\mathit{H}_5$), 3.87 (b, 1H, $-CH{=}CHC\mathit{H}(C_5H_5)-$), 4.92 (b, 2H, $-C\mathit{H}{=}CHCH(C_5H_5)-$), 5.81 (b, 1H, $C_5\mathit{H}_5$), 6.02 (d, 1H, J_{HH} = 1.3 Hz, $C_5\mathit{H}_5$), 6.27 (d, 1H, J_{HH} = 1.9 Hz, $C_5\mathit{H}_5$), 6.97–7.50 (m, 15H, *Ph*); ^{31}P-NMR (C_6D_6) δ 73.8 (s). **10b**: ^{1}H-NMR (C_6D_6) δ 2.43 (b, 2H, $-CH{=}C\mathit{H}CH(C_5H_5)-$), 2.56 (b, 2H, $C_5\mathit{H}_5$), 3.92 (b, 1H, $-CH{=}CHC\mathit{H}(C_5H_5)-$), 5.00 (b, 2H, $-C\mathit{H}{=}CHCH(C_5H_5)-$), 5.57 (b, 1H, $C_5\mathit{H}_5$), 6.04 (d, 1H, J_{HH} = 1.2 Hz, $C_5\mathit{H}_5$), 6.29 (d, 1H, J_{HH} = 1.8 Hz, $C_5\mathit{H}_5$), 6.97–7.50 (m, 15H, *Ph*). Anal. Calc. for $C_{30}H_{25}FeO_2P$ (mixture of **10a,b**): C, 71.44; H, 5.00. Found: C, 71.76; H, 5.08%.

11a: IR (CH_2Cl_2, cm^{-1}) 1971 (s), 1911 (s); ^{1}H-NMR (C_6D_6) δ 2.29 (b, 2H, $C_5\mathit{H}_4$), 2.52 (b, 4H, $-CH{=}C\mathit{H}CH(C_5H_5)-$), 3.80 (b, 2H, $-CH{=}CHC\mathit{H}(C_5$-

H_5)–), 4.90 (b, 4H, –C*H*=CHCH(C_5H_5)–), 5.57 (b, 2H, C_5*H_4*), 6.95–7.52 (m, 15H, *Ph*); ^{31}P-NMR (C_6D_6) δ 73.8 (s). **11b**: ^{1}H-NMR (C_6D_6) δ 2.16 (b, 2H, C_5*H_4*), 2.58 (b, 4H, –CH=C*H*CH(C_5H_5)–), 3.76 (b, 2H, –CH=CHC*H*(C_5H_5)–), 5.00 (b, 4H, –C*H*=CHCH-(C_5H_5)–), 5.31 (b, 1H, C_5*H_4*), 5.60 (b, 1H, C_5*H_4*), 6.95–7.52 (m, 15H, *Ph*). Anal. Calc. for $C_{55}H_{44}Fe_2O_4P_2$ (mixture of **11a**,**b**): C, 70.08; H, 4.71. Found: C, 70.65; H, 5.07%.

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 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+][I^-]$ 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 H_2O (200 ml) and extracted with Et_2O (100 ml × 2). The organic layer, combined with the ethereal extracts, was dried over $MgSO_4$ and then evaporated to dryness under vacuum. The oily residue was purified by chromatography using a SiO_2 column with CH_2Cl_2/hexane = 1:2.5 as an eluent. The following three bands separated in the order of appearance: PPh_3, 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 solution was stirred for 1 h, anhydrous $FeCl_3$ (0.146 g, 0.90 mmol) was added in one portion via a curved tube. The mixture was then refluxed for 15 h. The solvent was removed under vacuum to give a black residue, which was purified by SiO_2 column chromatography with 1:2 CH_2Cl_2/hexane as an eluent to give yellow **6** (0.31 g, 39%) and some unidentified compounds.

6: IR (CH_2Cl_2, cm^{-1}) 1967 (s), 1908 (s); ^{1}H-NMR ($CDCl_3$) δ 2.43 (b, 2H, –CH=C*H*CHC$_5$H$_4$–), 3.36 (b, 1H, –CH=CHC*H*C$_5$H$_4$–), 3.61, 3.72 (b, 2H × 2, C_5H_4), 5.05 (b, 2H, –C*H*=CHCHC$_5$H$_4$–), 7.36–7.41 (m, 15H, Ph); ^{13}C-NMR ($CDCl_3$) δ 54.5 (s, –CH=CH*C*HC$_5$H$_4$–), 55.9 (s, –CH=*C*HCHC$_5$H$_4$–), 66.3, 67.3 (s, C_5H_4), 82.0 (s, –C*H*=CHCHC$_5$H$_4$–), 95.1 (s, C_5H_{4ipso}), 128.1, 128.3, 129.6, 132.9, 133.1, 135.9, 136.6 (m, Ph), 219.5 (d, $^2J_{PC} = 14$ Hz, CO); ^{31}P-NMR ($CDCl_3$) δ 74.1 (s); MS (*m*/*z*) [M$^+$] 1062 (parent ion). Anal. Calc. for $C_{60}H_{48}Fe_3O_4P_2$: C, 67.82; H, 4.55. Found: C, 67.57; H, 4.70%.

2.5. Reaction between **6** and Ph_3CPF_6

A mixture of **6** (0.136 g, 0.13 mmol) and Ph_3CPF_6 (0.12 g, 0.31 mmol) was dissolved in 10 ml of CH_2Cl_2. The solution gradually became purple. After being stirred for 30 min, the mixture was added with H_2O. The CH_2Cl_2 layer was collected. The H_2O layer was extracted with CH_2Cl_2 for several times. The organic layers were combined and dried over $MgSO_4$. The by-product Ph_3CH was removed during recrystalization/filtration procedure from CH_2Cl_2 and *n*-hexane. The precipitate was washed with Et_2O (20 ml × 2) and dried under vacuum to result in a red complex $[Fe\{[\mu,\eta^5{:}\eta^5\text{-}1\text{-}(1'\text{-}C_5H_4)C_5H_4]Fe(CO)_2(PPh_3)\}_2][PF_6]_2$ (**13**, 0.15 g, 86%).

13: IR (CH_2Cl_2, cm^{-1}) 2047 (vs), 2008 (s), 1996(s); ^{1}H-NMR (acetone-d_6) δ 4.58, 4.93 (b, 2H × 2, C_5*H_4*Fe), 5.37, 5.74 (b, 2H × 2, C_5*H_4*FePPh$_3$), 7.26–7.61 (m, Ph); ^{31}P-NMR (acetone-d_6) δ 67.3 (s), −144.1 (sept). Anal. Calc. for $C_{60}H_{66}F_{12}Fe_3O_4P_4$: C, 52.55; H, 4.85. Found: C, 52.14; H, 4.69%.

2.6. Preparation of $Fe[\mu\text{-}\eta^5\text{-}C_5H_3\text{-}1,3\text{-}\{(C_5H_5\text{-}5'\text{-}exo\text{-}\eta^4)Fe(CO)_2(PPh_3)\}_2]_2$ (**15**) and attempted reaction between **15** and Ph_3CPF_6

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 $FeCl_3$ (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 SiO_2 column chromatography with CH_2Cl_2/*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 (CH_2Cl_2, cm^{-1}) 1966 (s), 1906 (s); ^{1}H-NMR (C_6D_6) δ 2.65 (m, 4H, –CH=C*H*CHC$_5$H$_3$), 3.21 (s, 1H, C_5*H_3*Fe), 3.35 (s, 1H, C_5*H_3*Fe), 3.60 (b, 2H, –CH=CHC*H*C$_5$H$_3$), 5.04 (m, 4H, –C*H*=CHCHC$_5$H$_3$), 7.00–7.06, 7.51–7.61 (m, 30H, Ph); ^{13}C-NMR (C_6D_6) δ 55.6 (s, –CH=CH*C*HC$_5$H$_3$), 56.2 (s, –CH=*C*HCHC$_5$H$_4$), 57.6, 66.0 (s, *C*$_5$H$_3$), 82.4 (s, –*C*H=CHCHC$_5$H$_3$), 94.6 (s, C_{ipso}), 128.4, 128.5, 129.7, 133.3, 133.4, 136.8, 137.1 (Ph), 220.2 (d, $J_{PC} = 11$ Hz, CO), 220.3 (d, $J_{PC} = 11$ Hz, CO); ^{31}P-NMR (C_6D_6) δ 73.1 (s). Anal. Calc. for $C_{110}H_{86}Fe_5O_8P_4$: C, 68.14; H, 4.47. Found: C, 68.47; H, 4.71%.

The reaction of **15** and four equivalents of Ph_3CPF_6 gave a number of cationic species on the basis of IR (2050 and 2010 cm^{-1}) and ^{31}P-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. $Fe(CO)_2(PPh_3)[\mu$-(η^4-C_5H_5)-5-*exo*-(1′-C_5H_4-η^5)]-$M(CO)_3Me$, 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_2Cl_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_2Cl_2, cm^{-1}) 2011 (s), 1974 (s), 1916 (vs); ^{1}H-NMR (C_6D_6) δ 0.46 (s, 3H, *Me*), 2.36 (b, 2H, –CH=C*H*CHC$_5$H$_4$), 3.34 (b, 1H, –CH=CHC*H*C$_5$H$_4$), 4.27 (s, 4H, C$_5$*H*$_4$), 4.81 (b, 2H, –C*H*=CHCHC$_5$H$_4$), 7.00–7.05, 7.44–7.49 (m, 15H, Ph); ^{13}C-NMR (C_6D_6) δ –33.5 (s, *Me*), 52.6 (s, –CH=CHCHC$_5$H$_4$), 54.8 (s, –CH=*C*HCHC$_5$H$_4$), 82.1 (s, –*C*H=CHCHC$_5$H$_4$), 89.3, 89.8 (s, *C*$_5$H$_4$), 119.4 (d, J_{PC} = 5.0 Hz, C_{ipso}), 128.5, 128.7, 130.0, 133.1, 133.3, 135.8, 136.6 (Ph), 217.7 (s, J_{WC} = 30 Hz, CO_{trans}), 219.2 (d, J_{PC} = 14 Hz, CO), 230.7 (s, CO); ^{31}P-NMR (C_6D_6) δ 73.6 (s); MS (*m*/*z*) [M$^+$] 786 (parent ion). Anal. Calc. for $C_{34}H_{27}FeO_5PW$: 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_2Cl_2/*n*-hexane = 1/3 as an eluent afforded yellow **17′** (0.5 g, 72%).

17′: IR (CH_2Cl_2, cm^{-1}) 2015 (s), 1973 (s), 1918 (vs); ^{1}H-NMR (C_6D_6) δ 0.38 (s, 3H, *Me*), 2.40 (b, 2H, –CH=C*H*CHC$_5$H$_4$), 3.34 (b, 1H, –CH=CHC*H*C$_5$H$_4$), 4.29 (s, 4H, C$_5$*H*$_4$), 4.83 (b, 2H, –C*H*=CHCHC$_5$H$_4$), 7.01–7.03, 7.44–7.49 (m, 15H, Ph); ^{13}C-NMR (C_6D_6) δ –21.0 (s, *Me*), 52.8 (s, –CH=CH*C*HC$_5$H$_4$), 55.0 (s, –CH=*C*HCHC$_5$H$_4$), 82.1 (s, –*C*H=CHCHC$_5$H$_4$), 90.6, 91.0 (s, *C*$_5$H$_4$), 121.3 (s, C_{ipso}), 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_{trans}), 241.1 (s, CO); ^{31}P-NMR (C_6D_6) δ 73.7 (s); MS (*m*/*z*) [M$^+$] 698 (parent ion). Anal. Calc. for $C_{34}H_{27}FeO_5PMo$: C, 58.48; H, 3.90. Found: C, 58.19; H, 3.82%.

2.8. {$Fe(CO)_2(PPh_3)[\mu,\eta^5{:}\eta^5$-1-(1′-$C_5H_4$)$C_5H_4$]$W(CO)_3$-Me}$PF_6$ (**18**)

A mixture of **17** (0.91 g, 1.16 mmol) and Ph_3CPF_6 (0.49 g, 1.26 mmol) was dissolved in 20 ml of CH_2Cl_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_2O (30 ml) was then added. The precipitate was filtered and washed with Et_2O until the washings were colorless, resulting in a yellow–orange powder **18** (1.01 g, 94%).

18: IR (CH_2Cl_2, cm^{-1}) 2055 (m), 2021 (s), 1932 (vs); ^{1}H-NMR (acetone-d$_6$) δ 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*$_6$) δ –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_{ipso}), 130.5, 130.7, 133.2, 133.8, 133.9, 136.1, 136.5 (Ph); ^{31}P-NMR (acetone-d$_6$) δ 67.0 (s), –138.3 (sept); MS (*m*/*z*) [M$^+$] 698 (parent ion). Anal. Calc. for $C_{34}H_{26}F_6FeO_5P_2W$: C, 43.87; H, 2.82. Found: C, 44.10; H, 2.85%.

2.9. Reaction of C_5H_5Na with **18**

A suspension of **18** (1.01 g, 1.09 mmol) in 30 ml of THF was treated with C_5H_5Na (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_2Cl_2/*n*-hexane = 1/1 as an eluent afforded yellow $Fe(CO)_2(PPh_3)[\mu$-(η^4-C_5H_4)-5-*exo*-(1′-C_5H_5)-2-(C_5H_4-η^5)]$W(CO)_3Me$ and $Fe(CO)_2(PPh_3)[\mu$-(η^4-C_5H_4)-5-*exo*-(2′-C_5H_5)-2-(C_5H_4-η^5)]$W(CO)_3Me$, **19a**,**b** (0.636 g, 69%). A second yellow band showed similar IR pattern and ^{31}P-NMR spectroscopic data to that of the first band (0.15 g), presumably the bis(η^4-Fe) products that were not analyzed. The first band exhibited two unseparated isomers, each with very complicated ^{1}H-NMR spectrum, corresponding to 1′- or 2′-substitution on the cyclopentadiene without metal.

19a,**b**: IR (CH_2Cl_2, cm^{-1}) 2008 (s), 1971 (s), 1918 (vs); ^{31}P-NMR (C_6D_6) δ 73.6 (s). MS (*m*/*z*) [M$^+$] 850 (parent ion). Anal. Calc. for $C_{39}H_{31}FeO_5PW$: C, 55.09; H, 3.67. Found: C, 55.40; H, 3.87%.

2.10. $Fe(CO)_2(PPh_3)[\mu$-(η^4-C_5H_4)-2-{(η^5-C_5H_4)W-$(CO)_3Me$}-5-*exo*-{(η^5-C_5H_4)$W(CO)_3Me$}] (**20**)

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_2Cl_2/*n*-hexane = 1/3 as an eluent to afford unreacted starting materials (0.2 g) and yellow **20** (0.3 g, 57%).

20: IR (CH_2Cl_2, cm^{-1}) 2010 (s), 1974 (m), 1918 (vs); ^{1}H-NMR (C_6D_6) δ 0.43, 0.45 (s, 3H × 2, *Me*), 1.85 (m, 1H, H_b), 3.40 (m, 1H, H_{endo}), 4.27, 4.34, 4.37, 4.50, 4.55, 4.63, 4.78, 4.80 (m, 1H × 8, C_5H_4W), 4.76 (m, 1H, H_a), 5.10 (m, 1H, H_c), 7.04–7.08, 7.34–7.40 (m, 15H, Ph); ^{31}P-NMR (C_6D_6) δ 73.6 (s). Anal. Calc. for $C_{43}H_{33}FeO_8PW_2$: C, 45.61; H, 2.94. Found: C, 45.80; H, 3.09%.

3. Results and discussion

3.1. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+][I^-]$ as the intermediate for Cp-ring and/or CO alkylation

The preparation of the η^4-Fe compounds in three-component reaction is actually a two-stage transformation (Schemes 1–3), in which the ionic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+][I^-]$ 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 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+][I^-]$ from $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and PPh_3 is an electron-transfer chain catalytic replacement of iodide on $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ by PPh_3, 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 initiator 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 $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}C(O)R$ is generally minor, i.e. the carbon nucleophiles (alkyl and aryl) favor addition onto the Cp-ring [1,2]. Yet for the ferrocenyl 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 $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)[\mu,C{:}\eta^5\text{-}C(O)C_5H_4]Fe(C_5H_4Li)$ (**9**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+][I^-]$ 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 η^4-Fe tri-Fe **6** using an alternative method is very challenging to organometallic chemists. Retrochemically, if one wants to build the η^4-Fe arm on Cp-ring first and make the ferrocene core second, one must employ the Cp anion in the three-component reaction. While C_5H_5Na is available from commercial sources, the reactivity of C_5H_5Li in three-component reaction is the same as that of C_5H_5Na and is readily generated by deprotonation of C_5H_6 using *n*-BuLi.

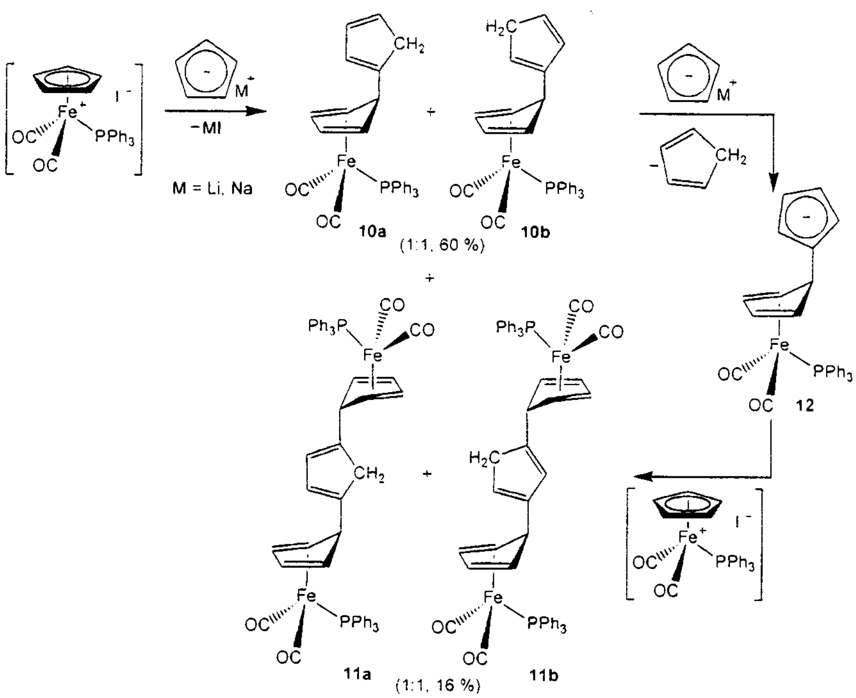
The reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with C_5H_5M (M = Na, Li) in the presence of PPh_3 gives two unseparated, isomeric η^4-Fe products (in about 1:1 ratio, total yield 60%, see Scheme 4). One is **10a** and the other **10b**. The difference is only at the site of substitution on the cyclopentadiene that is not attached to Fe. There was no spectroscopic evidence for the third possible isomer $[\eta^4\text{-}5\text{-}exo\text{-}(5'\text{-}C_5H_5)C_5H_5]Fe(CO)_2PPh_3$ (**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 $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)(C_5H_5)$. Thus the Cp anion is different from Fc 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 C_5H_5M reaction yielded the interesting extra bis(η^4-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 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+]$ 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 $[\eta^4\text{-}5\text{-}exo\text{-}(C_5H_4^-)C_5H_5]Fe(CO)_2PPh_3$ (**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 C_5H_5M was increased to three equivalents in order to maximize the yield of **10a**,**b**.

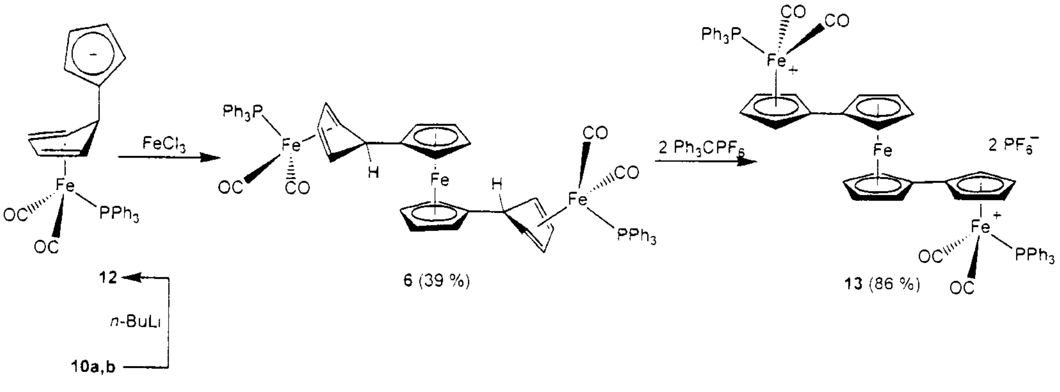
3.3. Preparation of **6** from **12** and its hydride abstraction reaction

Treatment of pure **10a**,**b** with *n*-BuLi generated **12**. When **12** reacted with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+][I^-]$, the products were **11a**,**b** (44%). When **12** reacted with $FeCl_3$ following a literature procedure [15] the product was mainly **6** (39%, Scheme 5) plus some unidentified by-products. The 5-*endo*-H on a $(\eta^4\text{-}5\text{-}exo\text{-}RC_5H_5)Fe(CO)_2PPh_3$ moiety has been shown to be a hydride that could be abstracted with a strong Lewis acid, e.g. $[PPh_3C^+]$ [16]. Accordingly, treatment of **6** with Ph_3CPF_6, produces the double-end, cationic tri-Fe complex **13** (86%, Scheme 5). The characteristic IR ν_{CO} 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 ^{1}H-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 $CDCl_3$). The hydride abstraction removes the 2H:1H:2H pattern completely. In **13**, the ^{1}H-NMR spectrum shows only the 2H:2H pattern at δ 5.37, 5.74 (in acetone-d^6), characteristic for a Cp-ring attached to Fe. The electrophilic abstraction of the *endo*-hydride shifts the bonding mode of metal to ring from (η^4-5-*exo*-RC_5H_5) to (η^5-RC_5H_4), the metal center being oxidized from Fe(0) to Fe(II).

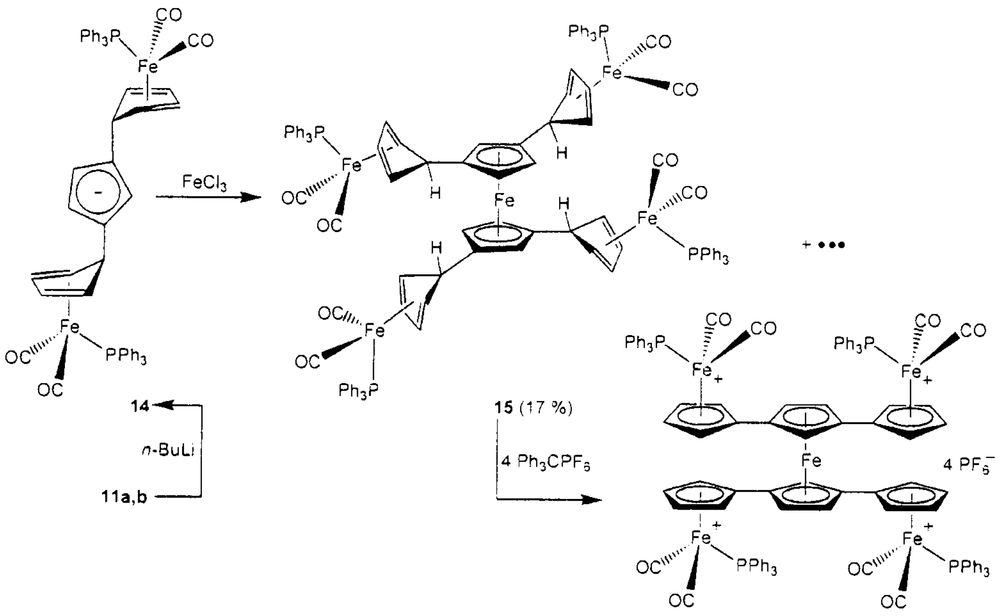
Similar strategy has been applied to the preparation of penta-Fe complex **15** that has four η^4-Fe arms attached to a ferrocene core. As shown in Scheme 6, treatment of **11a**,**b** with *n*-BuLi produced *in-situ* the anion $(1,3\text{-}C_5H_3^-)[(C_5H_5\text{-}5'\text{-}exo\text{-}\eta^4)Fe(CO)_2PPh_3]_2$ (**14**) that, when reacted with $FeCl_3$, resulted in 15 (17%) and some unidentified compounds which were cationic in nature. The hydride abstraction on **15** with excess Ph_3CPF_6 was attempted, giving seemingly **16** on the basis of IR and ^{31}P-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 η^4-Fe, 0 η^5-Fe) arms attached to



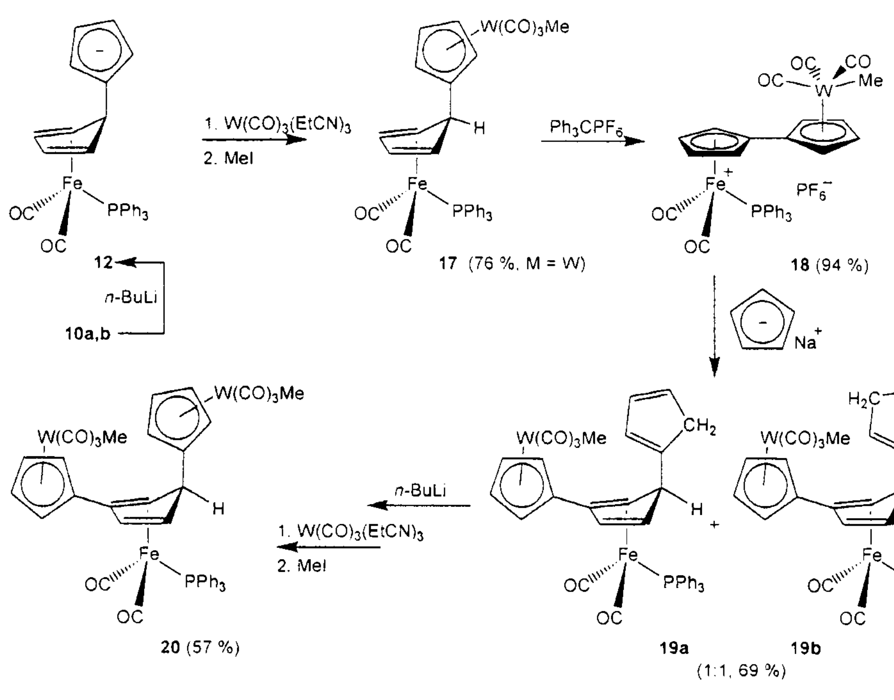
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

ferrocene core to a complex with (0 η^4-Fe, 4 η^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-(η^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 η^4-Fe, η^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_3CPF_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 ν_{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 (η^4-5-*exo*-RC_5H_5)Fe to (η^5-RC_5H_4)Fe.

Complex **18** is a derivative of [(η^5-C_5H_4R)Fe-$(CO)_2PPh_3^+$] with R = –(η^5-C_5H_4)$W(CO)_3Me$ and is thus a substrate for C_5H_5Na. The reaction between **18** and C_5H_5Na 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 cyclopentadiene that is not attached to Fe. There was no spectroscopic evidence for the third possible isomer $Fe(CO)_2(PPh_3)$[μ-(η^4-C_5H_4)-5-*exo*-(5′-C_5H_5)-2-(C_5H_4-η^5)]$W(CO)_3Me$ (**19c**), believed to be the immediate product rearranging to **19a**,**b** by proton shifts on the cyclopentadiene. Similar to Scheme 4, there were also the bis(η^4-Fe) by-products (not shown in Scheme 7) that were nonetheless not studied presently. Treatment of pure **19a**,**b** with *n*-BuLi, followed by the $W(CO)_3$-$(EtCN)_3$ then MeI sequence yielded the trimetallic η^5-W, η^4-Fe, η^5-W complex **20** (57%). For **20**, the –(η^5-C_5H_4)$W(CO)_3Me$ substituents on the cyclopentadiene 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_3CPF_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 –(η^5-C_5H_4)$W(CO)_3Me$ in **20** and [Ph_3C^+] is a bulky reagent.

4. Conclusion

The reaction of (η^5-C_5H_5)$Fe(CO)_2I$ 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.

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