Consecutive Butylations on the Cyclopentadienyl Ring of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3]^+$ Cation

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Received September 25, 1996⊗

Summary: The replacement of acidic hydrogen atoms in cyclopentadiene by alkyl groups would normally involve a repetitive deprotonation and then electrophilic alkylation. By means of η^4-Fe complexation, one can reverse the polarity of cyclopentadiene and utilize multiple hydride abstraction/nucleophilic alkylation cycles in the preparation of the polybutylcyclopentadienes in the neutral η^4-Fe form and the corresponding cyclopentadienyl complexes in the cationic η^5-Fe form.

The cyclopentadienyl group, C_5H_5, is one of the most important ligands in organometallic chemistry.[1] Highly substituted cyclopentadienyls have also been attracting much attention because of the effects of their increased steric bulk and modified electronic properties.[2] The replacement of acidic hydrogen atoms in a cyclopentadiene by alkyl groups involves multiple deprotonation/electrophilic alkylation cycles, e.g., in the synthesis of tri-, tetra-, and penta(ethyl or isopropyl)cyclopentadienes *via* repetitive treatments with $NaNH_2$ and then EtBr or *i*-PrBr.[3] For metal-bound cyclopentadienyl rings, most functionalization reactions involve either Friedel−Crafts electrophilic acylation or alkylation or proton abstraction by base, followed by reaction of the resulting anion with an alkyl halide.[4,5] By means of η^4-Fe complexation, cyclopentadiene can be reversed in its polarity so that hydride abstraction is applicable instead. The resulting cationic cyclopentadienyl−Fe species can undergo nucleophilic butylation as demonstrated here by application of the novel repetitive hydride abstraction/nucleophilic butylation in the sequential preparations of di-, tri-, tetra-, and pentabutylcyclopentadienes in the neutral η^4-Fe form and the corresponding cyclopentadienyl complexes in the cationic η^5-Fe form.

The complete synthesis is depicted in Scheme 1. Compound **1H**, $(\eta^4\text{-}exo\text{-}BuC_5H_5)Fe(CO)_2PPh_3$, was prepared in a ring alkylation reaction in which 1:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and PPh_3 were treated at −78 °C with equimolar *n*-BuLi[6] or by treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3]I$ with *n*-BuLi following an early literature procedure.[7] The *endo*-H atom of the $(\eta^4\text{-}BuC_5H_5)$ ring is hydridic and could be abstracted with protic of Lewis acids,[8] e.g., $HBF_4{\cdot}OEt_2$ or $Ph_3C^+PF_6^-$, resulting in $\mathbf{[1]^+X^-}$, $(\eta^5\text{-}BuC_5H_4)Fe(CO)_2PPh_3{}^+X^-$ ($X = BF_4$, PF_6),[9] which could in turn be treated with *n*-BuLi at −78 °C to give again the ring alkylation product **2H**, $(\eta^4\text{-}exo\text{-}Bu_2C_5H_4)Fe(CO)_2PPh_3$. $HBF_4{\cdot}OEt_2$ worked better than $Ph_3C^+PF_6^-$ because H_2 is volatile but Ph_3CH remains in solution. The second hydride abstraction/butylation yielded $\mathbf{[2]^+}$ and **3H**, the third $\mathbf{[3]^+}$ and **4H**, and the fourth $\mathbf{[4]^+}$ and **5H**. Further hydride abstraction of **5H** with $HBF_4{\cdot}OEt_2$ afforded $\mathbf{[5]^+}$.[10]

The hydride abstraction of the neutral series by $HBF_4{\cdot}OEt_2$ was followed spectroscopically. The monitoring of IR ν_{CO} absorption bands during the treatment of **3H** with $HBF_4{\cdot}OEt_2$ revealed only decreasing concentrations of **3H** [1953 (s), 1892 (s) cm^{-1}] along with increasing concentrations of cation $\mathbf{[3]^+}$ [2042 (s), 1998 (s) cm^{-1}]. Yet after seemingly complete disappearance of **3H** to the cation by IR, the $^{31}P\{^1H\}$ NMR spectra of the reaction mixture showed the disappearance of resonances at δ 73.8, 72.2, 70.5, and 68.1 (corresponding to the four isomers of **3H**) and formation of new resonances at δ 53.3 and 52.6 that later were replaced by resonances at δ 62.5 and 61.7 (corresponding to the two isomers of $\mathbf{[3]^+}$). In the ^1H NMR spectrum of the reaction mixture there were broad peaks at δ −2.8 and −8.0 which could not be assigned to either the neutral η^4-Fe or the cationic η^5-Fe species. Overall, the spec-

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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[5] One of the alternative ways is the Stille coupling reaction using a Pd catalyst: (a) Lo Sterzo, C.; Stille, J. K. *Organometallics* **1990**, *9*, 687 and references cited therein. (b) Bunz, U. H. F.; Enkelman, V.; Raeder, J. *Organometallics* **1993**, *12*, 4745.

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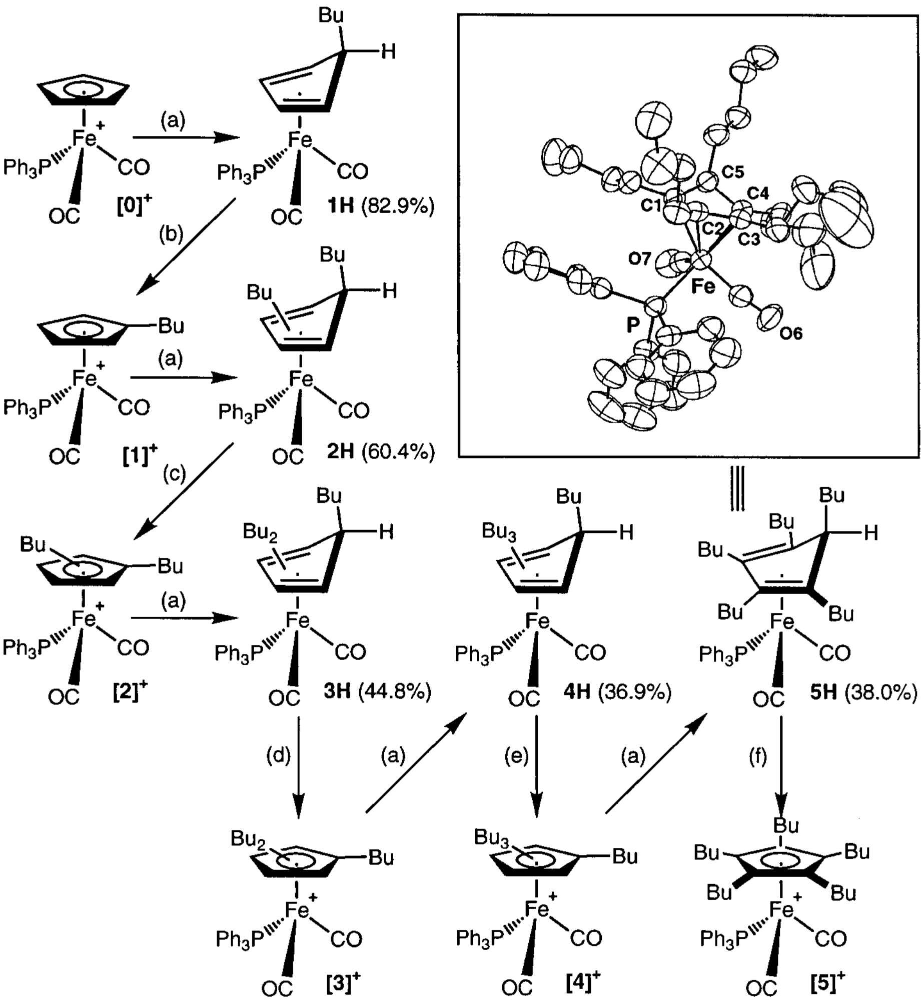
[9] For example, $(\eta^4\text{-}BuC_5H_5)Fe(CO)_2PPh_3$ (2.48 g, 5.0 mmol), dissolved in THF (100 mL), was stirred at 0 °C while $Ph_3C^+PF_6^-$ (1.91 g, 5.0 mmol) in CH_2Cl_2 (30 mL) was added dropwise. The yellow precipitate was collected, dried under vacuum, and then recrystallized from CH_2Cl_2/*n*-hexane to yield $(\eta^5\text{-}BuC_5H_4)Fe(CO)_2(PPh_3)^+PF_6^-$ in quantitative yield. $(\eta^5\text{-}BuC_5H_4)Fe(CO)_2(PPh_3)^+PF_6^-$: Mp 172−174 °C; IR ($CH_2Cl_2$) ν_{CO}: 2052 s, 2010 s cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 62.08 (s), −143.01 (sept, $^1J_{PF}$ = 711 Hz); ^1H NMR ($CDCl_3$) δ 7.10−7.55 (m, 15H, Ph), 5.18 (s, 2H, Cp′-β), 4.98 (s, 2H, Cp′-α), 2.33, 1.48, 1.35 (b, 6H, $CH_2CH_2CH_2Me$), 0.87 (s, 3H, $CH_2CH_2CH_2Me$). Anal. Calcd for $C_{29}H_{28}F_6FeO_2P_2$: C, 54.40; H, 4.41. Found: C, 54.01; H, 4.38.

[10] Satisfactory spectroscopic data and elemental analyses were obtained as described in the Supporting Information.

Scheme 1



Reaction conditions: (a) *n*-BuLi, -78°C, THF; (b) $HBF_4{\cdot}OEt_2$, THF, 3h; (c) $HBF_4{\cdot}OEt_2$, CH_2Cl_2, 2h; (d) $2HBF_4{\cdot}OEt_2$, CH_2Cl_2, reflux, 14h; (e) $4HBF_4{\cdot}OEt_2$, CH_2Cl_2, reflux, 14h; (f) $xsHBF_4{\cdot}OEt_2$, CH_2Cl_2, reflux, 14h. Isomers: **2H**: 1,5- or 2,5-dibutyl; **3H**: 1,2,5-, 1,3,5-, 1,4,5-, or 2,3,5-tributyl; **4H**: 1,2,3,5- or 1,2,4,5-tetrabutyl; **[2]⁺**: 1,2- or 1,3-dibutyl; **[3]⁺**: 1,2,3- or 1,2,4-tributyl.

troscopic data were suggestive of an unisolated, cationic transient species, likely involving an Fe−hydrogen interaction in nature.[11] Similar intermediates could also be seen during the conversions of **4H** to **[4]**$^+$ (an extra resonance at δ 53.0 in the $^{31}P\{^1H\}$ NMR spectrum and an extra broad signal at δ −11.3 in the ^1H NMR spectrum). Experimentally, the hydride abstraction steps in Scheme 1 required increasingly more forcing conditions. The optimum condition generally was decided by constant monitoring by $^{31}P\{^1H\}$ NMR spectroscopy.

Table 1. Spectroscopic Data

compd	IR ν_{CO} (CH_2Cl_2), cm^{-1}	$^{31}P\{^1H\}$ NMR ($CDCl_3$), δ
1H	1962 (s), 1902 (s)	73.32 (s)
2H	1958 (s), 1897 (s)	74.70 (s), 72.91 (s)
3H	1953 (s), 1892 (s)	73.84 (s), 72.19 (s), 70.54 (s), 68.11 (s)
4H	1949 (s), 1889 (s)	71.76 (s), 67.96 (s)
5H	1945 (s), 1887 (s)	66.75 (s)
[1]$^+BF_4^-$	2052 (s), 2010 (s)	62.14 (s)
[2]$^+BF_4^-$	2047 (s), 2004 (s)	62.90 (s), 61.93 (s)
[3]$^+BF_4^-$	2042 (s), 1998 (s)	62.50 (s), 61.71 (s)
[4]$^+BF_4^-$	2040 (s), 1994 (s)	62.45 (s)
[5]$^+BF_4^-$	2039 (s), 1997 (s)	61.09 (s)

The two series, neutral η^4-Fe complexes (**1H**−**5H**) and cationic η^5-Fe complexes (**[1]**$^+$−**[5]**$^+$), have been characterized. The number of butyl groups on the ring increases from **1H** to **5H**. Hence, the donor capability of cyclopentadiene increases from **1H** to **5H**, red-shifting the IR ν_{CO} aborption bands by 4−5 cm^{-1} per butyl group, as shown in Table 1. For the cationic series **[1]**$^+$−**[5]**$^+$, a similar trend, but with less regular differences in ν_{CO}, also could be observed. The cationic series in the IR spectra exhibits higher ν_{CO} aborption frequencies than the neutral series by 90−110 cm^{-1} for the symmetric and asymmetric bands, respectively. With the exception of **1H**, the ^{31}P NMR data of **2H**−**5H** suggest that the PPh_3 phosphorus nucleus in the neutral series becomes

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[11] Although not fully characterized, the intermediate could likely be an Fe−(hydride) or an Fe−(molecular hydrogen) species or a mixture of both. For the nature and stabilization of the transition metal−molecular hydrogen bond see: (a) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (d) Jessop, P. G.; Morris, R. H. *Coord Chem. Rev.* **1992**, *121*, 155. (e) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (f) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913. (g) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375. (h) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686.

more shielded as butyl groups accumulate on the ring. But, the ^{31}P NMR resonances of **[1]**$^+$–**[5]**$^+$ are found in a range of less than 2 ppm, indicating that there is little differentiation of the PPh_3 phosphorus nuclei in the cationic series.

The nucleophilic addition of butyl groups to the ring of **[0]**$^+$–**[4]**$^+$ is from an *exo* position to Fe, and thus at the unique carbon of the cyclopentadiene there is one *endo*-H that is available to undergo the next hydride abstraction step. Following a progressive increase in the number of butyl groups and hence a progressive increase of charge density on the ring, the nucleophilic butylation would be expected to be increasingly difficult. In the butylation of [**n**]$^+$ (n = 0–4) the yield of acyl product (η^5-$Bu_nC_5H_{5-n}$)Fe(PPh_3)(CO)C(O)Bu by way of CO alkylation[6] indeed increases at the expense of the ring alkylation product **(*n* + 1)H**. The branching ratios of CO alkylation *vs* ring alkylation increase with the number of butyl groups, 0.01, 0.06, 0.11, 0.22, and 0.35. No *gem*-dibutylcyclopentadiene–metal has been observed in this study employing the reversed-polarity, nucleophilic alkylation strategy. On the other hand, in the normal electrophilic alkylation of a cyclopentadiene, *gem*-dialkylcyclopentadienes have been formed in significant quantity. Unable to be aromatized with base, the *gem*-dialkylcyclopentadienes must be removed before the next deprotonation/alkylation step.[3]

The X-ray structure of **5H** reveals a square-pyramidal Fe(0) core with one CO apical and the rest of ligands basal, one olefin of the basal diene being *trans* to PPh_3 and the second olefin *trans* to the second CO ligand.[12] The diene plane C1–C4 (within 0.005 Å) separates Fe and C5, C5 being displaced at 0.55 Å from the plane and the connected *exo*-butyl group being further away. The four remaining butyl α-carbon atoms are almost coplanar with the diene plane. The two butyl β-carbon atoms extending from C2 and C3 are at 1.44 and 1.53 Å to the plane, opposing Fe, whereas the other two butyl β-carbon atoms are on the same side of Fe at 0.19 and 0.55 Å to the plane, respectively. The Fe–P length of **5H** is 0.025 Å longer than the corresponding length in **1H**,[6] attributed to the steric hindrance. The Fe–C(CO) lengths of **5H** are shorter by 0.015–0.024 Å than those of **1H**, parallel to the red shift of IR ν_{CO} bands.

Acknowledgment. The authors thank Academia Sinica and the National Science Council, ROC, for the kind financial support. We are indebted to Mr. Y.-S. Wen for collection of X-ray intensity data.

Supporting Information Available: For complexes **[1]**$^+$–**[5]**$^+$ and **2H**–**5H**, text describing the experimental procedures and, for **5H**, listings of crystallographic data and refinement details, positional and anisotropic thermal parameters, bond distances and angles, and structural parameters (17 pages). Ordering information is given on any current masthead page.

OM960819E

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[12] None of reported (η^4-cyclopentadiene)Fe$(CO)_2$(PPh_3) structures have substituents at the diene positions. The reported structures are as follows. (a) (η^4-*exo*-$PhCH_2C_5H_5$)Fe$(CO)_2$(PPh_3): Sim, G. A.; Woodhouse, D. I.; Knox, G. R. *J. Chem. Soc., Dalton Trans.* **1979**, 629. (b) (η^4-*exo*-BuC_5H_5)Fe$(CO)_2$(PPh_3): Reference 6. (c) (η4-*exo*-PhC_5H_5)Fe$(CO)_2$(PPh_3), Luh, L.-S.; Liu, L.-K. *Bull. Inst. Chem. Acad. Sin.* **1994**, *41*, 39. (d) (η^4-*exo*-MeC_5H_5)Fe$(CO)_2$($PMePh_2$) and [(η^4-*exo*-MeC_5H_5)Fe$(CO)_2$]$_2$(μ-dppe): Liu, L.-K.; Luh, L.-S.; Eke, U. B. *Organometallics* **1995**, *14*, 440. (e) [(η^4-*exo*-MeC_5H_5)Fe$(CO)_2$](μ-dppe)[(η^5-C_5H_5)Fe(CO)C(O)Me], Luh, L.-S.; Liu, L.-K. *Organometallics* **1995**, *14*, 1514. (f) (η^4-*exo*-MeC_5H_5)Fe$(CO)_2$(PPh_3), Liu, L.-K.; Luh, L.-S.; Chao, P.-C.; Fu, Y.-T. *Bull. Inst. Chem. Acad. Sin.* **1995**, *42*, 1.