Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 1913–1920 **1913**
DOI: 10.1021/ic902332q

New, Simple Synthetic Route to Functional Mono- and Biferrocenes

Abdou Khadri Diallo, Jaime Ruiz, and Didier Astruc*

Institut des Sciences Moléculaires, UMR CNRS N° 5255, Université Bordeaux 1, 33405 Talence Cedex, France

Received November 25, 2009

Visible-light photolysis using a simple 100 W lamp of the readily available precursors $[(\eta^5\text{-}C_5H_4R)Fe(\eta^6\text{-toluene})][PF_6]$ (R = H, Me, Cl, COMe, CO_2H, CO_2Me, CO_2CH_2CCH, $CONHCH_2Ph$, $NHCH_2Ph$), or the bimetallic precursor $[(\mu_2,\eta^5,\eta'_5\text{-Fv})Fe_2(\eta^6\text{-toluene})_2][PF_6]_2$ (Fv = fulvalene) in the presence of a substituted cyclopentadienyl salt $C_5H_4R'M$ (R′ = $COCH_3$, CO_2CH_3, PPh_2, $SiMe_2CH_2Cl$; M = Li or Na) or the dicyclopentadienyl salt 1,4-C_6H_4-$(CH_2C_5H_4)_2Na_2$ in dichloromethane, acetonitrile, or tetrahydrofuran under ambient conditions selectively yields 15 functional mono- and biferrocenes.

Introduction

Ferrocene syntheses have been continuously pursued since 1952, when the sandwich structure was disclosed,[1] because of the aromaticity[2] and robustness[3] of the sandwich frame and because of their numerous applications.[4] Ferrocene derivatives have indeed been used in many areas including oncology[5] and other biomedical applications,[6] electrochemistry,[7] redox biosensors,[8] reagents and standards,[9] mediators of enzyme reactions,[10] resins, fuel additives, paints,[11] ligand scaffold, catalysis,[12] liquid crystals,[13] non-linear optical materials,[14] magnetic materials,[15] self-assembled monolayers,[16] polymers,[17] and dendrimers.[18] Common syntheses[4c,19] involve the reactions of substituted cyclopentadienyl derivatives of main-group metals (such as C_5Me_5Li)[20] with $FeCl_2$ that yield symmetrically di- or polysubstituted ferrocenes and the Friedel−Crafts reactions pioneered by Woodward[2] leading to mono- and symmetrically disubstituted ferrocenes. This latter reaction is especially useful to produce mono- and 1,1′-diacylferrocenes, although further chromatographic separation is required. Finally, the third well-known type of synthesis involves metalation of ferrocene with *n*-butyl-lithium followed by electrophilic reaction that also leads to mixtures of mono- and 1,1′disubstituted ferrocenes to some extent often requiring further chromatographic separation.[19]

Here we are dealing with the successive introduction of two differently substituted cyclopentadienyl rings, a strategy

---

*To whom correspondence should be addressed. E-mail: d.astruc@ism.u-bordeaux1.fr.

(1) (a) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125–2126. (b) Fischer, E. O.; Pfab, W. *Z. Naturforsch. B* **1952**, *7*, 377–379.

(2) Woodward, R. B.; Rosemblum, M.; Whittig, M. C. *J. Am. Chem. Soc.* **1952**, *74*, 3458–3459.

(3) Cotton, F. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 5764–5766.

(4) (a) Togni, A.; Hayashi, T. *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Material Science*; VCH: Weinheim, 1995. (b) *Ferrocenes*; Petr, S., Ed.; Wiley: Weinheim, 2008. (c) Astruc, D. *Organometallic Chemistry and Catalysis*; Springer: Heidelberg, 2007; Chapter 11, pp 251−288.

(5) (a) *Bioorganometallics: Biomolecules, Labeling, Medicine*; Jaouen, G., Ed.; Weinheim: Wiley, 2006. (b) van Staveren, D. R.; Metzler-Nolte, N. *Chem. Rev.* **2004**, *104*, 5931–5985. (c) Osella, D.; Ferrali, M.; Zanello, P.; Laschi, F.; Fontani, M.; Nervi, C.; Cavigiolio, G. *Inorg. Chim. Acta* **2000**, *306*, 42–48.

(6) (a) Metzler-Nolte, N. ; Salmain, M. In *Ferrocenes;* Petr, S., Ed.; Wiley: Weinheim, 2008; Chapter 13, pp 499−639. (b) Wlassoff, W. A.; King, G. C. *Nucleic Acids Res.* **2002**, *30* (12).

(7) (a) Nishihara, H. *Adv. Inorg. Chem.* **2002**, *53*, 41–86. (b) Zatsepin, T. S.; Andreev, S. Y.; Hianik, T.; Oretskaya, T. S. *Russ. Chem. Rev.* **2003**, *72*, 537–554.

(8) (a) Bayly, S. R.; Beer, P. D.; Chen, G. Z. In *Ferrocenes*; Petr, S., Ed.; Wiley: Weinheim, 2008; Chapter 8, pp 281−318. (b) Astruc, D.; Daniel, M.-C.; Ruiz, J. *Chem. Commun* **2004**, 2637–2649.

(9) (a) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 977–910. (b) Astruc, D. *Bull. Soc. Chem. Jpn.* **2007**, *80*, 1658–1671. (c) Astruc, D. *New J. Chem.* **2009**, *33*, 1191–1206.

(10) Padeste, C.; Grubelnik, A.; Tiefenauer, L. *Biosens. Bioelectron.* **2000**, *15*, 431–438.

(11) (a) Bruce, M. I. *Organomet. Chem. Rev.* **1972**, *10*, 75–82. (b) Nesmeyanov, A. N.; Kotchekova, N. S. *Russ. Chem. Rev.* **1974**, *43*, 1513–1523.

(12) Arrayás, R. G.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7674–7715.

(13) Deschenaux, R. In *Ferrocenes*; Petr, S., Ed.; Wiley: Weinheim, 2008; Chapter 11, pp 447−463.

(14) (a) Green, M. L. H.; Marder, S. R.; Thompson, M. E. *Nature* **1987**, *330*, 360–362. (b) Heck, J.; Dede, M. In *Ferrocenes*; Petr, S., Ed.; Wiley: Weinheim, 2008; Chapter 9, pp 319−392. (c) Braga, D.; Curzi, M.; Giaffreda, S. L.; Grepioni, F.; Maini, L.; Pettersen, A.; Polito, M. In *Ferrocenes*; Petr, S., Ed.; Wiley: Weinheim, 2008; Chapter 12, pp 465−498.

(15) Dvorikova, R.; Nikitin, L.; Korshak, Y.; Shanditsev, V.; Rusanov, A.; Abramchuk, S.; Khokhlov, A. *Dokl. Chem.* **2008**, *422*, 231–235.

(16) Abbott, N. L.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1493–1497.

(17) (a) Nguyen, P.; Gomez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515–1548. (b) Nicholas, J.; Long, R. Kowalski, K. In *Ferrocenes*; Petr, S., Ed.; Wiley: Weinheim, 2008; Chapter 10, pp 393−446. (c) Boisselier, E.; Chan, A.; Ruiz, J.; Astruc, D. *New J. Chem.* **2009**, *33*, 246–253.

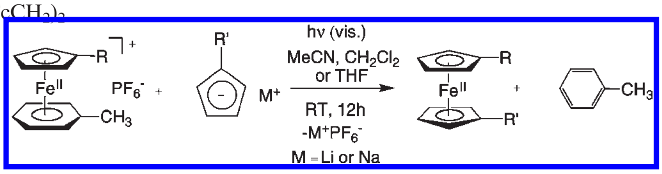
(18) (a) Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; Garcia, J. B.; Gonzales, B.; Losada, L. *Coord. Chem. Rev.* **1999**, *185−186*, 53. (b) Astruc, D.; Ornelas, C.; Ruiz, J. *J. Inorg. Organomet. Polym.* **2008**, *18*, 4–17. (c) Astruc, D.; Ornelas, C.; Ruiz, J. *Acc. Chem. Res.* **2008**, *41*, 841–856.

(19) (a) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. *4*, Chapter 31.3, pp 475−512. (b) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. *8*, Chapter 59, pp 1013−1071.

(20) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287–294. (b) Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466–470. (c) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5.

Table 1. Syntheses of Ferrocene and Biferrocene Derivatives by Visible-Light Photolysis Reactions of [CpFe(η^6-toluene)][PF$_6$] with Functional Cyclopentadienyls As Sodium Salts [except for R′ = PPh$_2$ (**7**, entry 2) and SiMe$_2$CH$_2$Cl (**8** and **10**, entries 3 and 6) with Lithium Salts]

entry	[Fe(η^5-C$_5$H$_4$R)(η^5-C$_5$H$_4$R′)]	R	R′	yield (%)
1	**6**[a]	H	CO$_2$Me	98
2	**7**[a]	H	PPh$_2$	51
3	**8**[b]	H	SiMe$_2$CH$_2$Cl	80
4	**9**[a]	COMe	CO$_2$Me	95
5	**9**[a]	CO$_2$Me	COMe	88
6	**10**[b]	COMe	SiMe$_2$CH$_2$Cl	75
7	**11**[a]	CO$_2$H	COMe	15
8	**12**[a]	CO$_2$CH$_2$C≡CH	CO$_2$Me	85
9	**13**[a]	CONHCH$_2$Ph	CO$_2$Me	70
10	**14**[a]	Cl	CO$_2$Me	90
11	**15**[a]	Me	CO$_2$Me	98
12	**16**[a]	NHCH$_2$Ph	CO$_2$Me	44
13	**17**[a] [Fe(η^5-C$_5$R$_5$)(η^5-C$_5$H$_4$R′)]	Me	CO$_2$Me	27
14	**18**[a] [Fe$_2$(η^5-C$_5$H$_4$R′)$_2$(μ_2-η^5,η'^5-Fv)]		CO$_2$Me	87
15	**19**[a] [Fe$_2$(η^5-C$_5$H$_4$R′)$_2$(μ_2-η^5, η'^5-Fv)]		COMe	86
16	**20**[c] 1,4-C$_6$H$_4$(FcCH$_2$)$_2$			18



[a] In MeCN. [b] In dichloromethane. [c] In THF, **20**, entry 16: Fv = fulvalene (C$_5$H$_4$−C$_5$H$_4$), Fc = ferrocenyl (C$_{10}$H$_9$).

that has so far not been exploited except in a few exceptional cases with C$_5$Me$_5$ (Cp*). Indeed [Cp*Fe(NCMe)$_3$][PF$_6$][21] and [Cp*Fe(acac)][22] (acac = acetylacetonate) are known stable (although air-sensitive) complexes, and they have been used to synthesize 1,2,3,4,5-pentamethylferrocene[23] and piano-stool-shape complexes.[24] The complex [Cp*Fe(NCMe)$_3$][PF$_6$] has recently been used to also further introduce C$_5$H$_4$R ligands with long functional R arms to link pentamethylferrocene moieties to gold nanoparticles and dendrimers.[25] The dimers [(η^5-C$_5$R$_5$)Fe(CO)$_2$]$_2$ (R = H or Me) have also been used in rare occasions as C$_5$R$_5$Fe sources to introduce special pentahapto ligands such as phospholes[26] and C$_{60}$ derivatives at high temperatures, but the method cannot be generalized to functional cyclopentadienyls.[27] Also note that [CpFe(NCMe)$_3$]-[PF$_6$] (Cp = η^5-C$_5$H$_5$) is not stable above −40 °C and can thus only be a short-lived intermediate under ambient conditions.[28] Likewise, [CpFe(acac)] is unknown.

Therefore, we have addressed the families of complexes [(η^5-C$_5$H$_4$R)Fe(η^6-arene)][PF$_6$] (R = functional group)[29] as precursors of the intermediate 12-electron fragments (η^5-C$_5$H$_4$R)-Fe$^+$ or their weakly solvated forms in ferrocene syntheses. These complexes are easily accessible in large scales by reactions of ferrocenes with arenes in the presence of aluminum chloride. They are are robust, being stable thermally up to above 200 °C. The parent complex [CpFe(η^6-C$_6$H$_6$)][PF$_6$] and many derivatives are stable in concentrated sulfuric acid.[30] These families have a very rich ring-functionalization chemistry for both the Cp and arene ligands,[29] and their redox chemistry is well-known with reversibility properties.[31] Despite their thermal robustness, these complexes are sensitive to visible light, and visible-light-induced exchange of the arene ligand by various other ligands is known. In dichloromethane, the arene ligand can be exchanged by a more electron-rich arene,[32] whereas in acetonitrile, piano-stool complexes can be obtained upon visible-light photolysis in the presence of potential two-electron ligands.[21,33] In a preliminary communication, we have reported visible-light-induced exchange of the toluene ligand in the complexes [(η^5-C$_5$H$_4$R)Fe(η^6-toluene)][PF$_6$] by substituted cyclopentadienyls leading to functional ferrocenes.[34] We have now extended this useful and simple visible-light photolysis reaction to new complexes of the type [(η^5-C$_5$H$_4$R)Fe(η^6-toluene)][PF$_6$] (R = benzylamino), [(η^5-Cp*)Fe(η^6-toluene)][PF$_6$], and to binuclear fulvalene complexes [(μ_2,η^5,η'^5-Fv)Fe(η^6-toluene)][PF$_6$]

---

(21) (a) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1983**, *248*, C9–C12. (b) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094–1100.

(22) (a) Bunuel, E. E.; Valle, L.; Manriquez, J.-M. *Organometallic* **1985**, *4*, 1680–1683. (b) Morrow, J.; Catheline, D.; Desbois, M.-H.; Manriquez, J.-M.; Ruiz, J.; Astruc, D. *Organometallics* **1987**, *6*, 2605–2607. (c) Bunuel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Barra, C.; Gonzales, M.; Munoz, N.; Visconti, G.; Aizman, A.; Manriquez, J.-M. *J. Am. Chem. Soc.* **1988**, *110*, 6596–6598.

(23) (a) Herberich, G. E.; Gaffke, A.; Eckenrath, H. J. *Organometallics* **1998**, *17*, 5931–5932.

(24) (a) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1984**, *266*, C11–C14. (b) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1984**, *269*, C33–C35.

(25) (a) Labande, A.; Ruiz, J.; Astruc, D. *J. Am. Chem. Soc.* **2002**, *124*, 1782–1789. (b) Ornelas, C.; Ruiz, J.; Belin, C.; Astruc, D. *J. Am. Chem. Soc.* **2009**, *131*, 590–601.

(26) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1977**, *99*, 3537–3538.

(27) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354–9355.

(28) (a) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 1986–1990. (b) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1984**, *272*, 417–426. (c) Ruiz, J.; Astruc, D. *Inorg. Chim. Acta* **2008**, *361*, 1–4.

(29) (a) Astruc, D. *Tetrahedron* **1983**, *39*, 4027–4095. (b) Abd-El-Aziz, A. *Coord. Chem. Rev.* **2000**, *203*, 219–267. (c) Trujillo, H. A.; Casado, C.; Ruiz, J.; Astruc, D. *J. Am. Chem. Soc.* **1999**, *121*, 5674–5686.

(30) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Tetrahedron Lett.* **1963**, *4*, 1725–1729. (b) Astruc, D.; Dabard, R. *Tetrahedron* **1976**, *32*, 245–249.

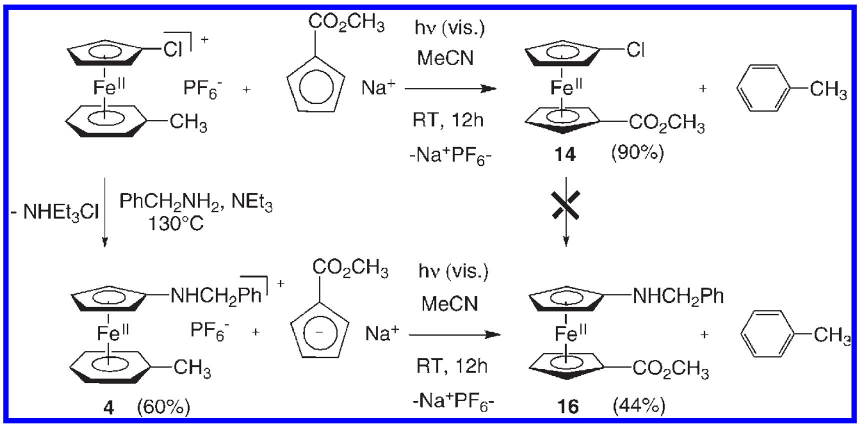
(31) (a) Green, J. C.; Kelly, M. R.; Payne, M. P.; Seddon, E. A.; Astruc, D.; Hamon, J.-R.; Michaud, P. *Organometallics* **1983**, *2*, 211–218. (b) Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504–6506. (c) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F. *J. Am. Chem. Soc.* **1989**, *111*, 5800–5809.

(32) (a) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1980**, *19*, 308–312. (b) Gill, T. P.; Mann, K. R. *J. Organomet. Chem.* **1981**, *216*, 65. (c) Hamon, J.-R.; Michaud, P.; Astruc, D. *J. Am. Chem. Soc.* **1981**, *103*, 758–766.

(33) (a) Catheline, D.; Astruc, D. J. *Organomet. Chem.* **1984**, *269*, C33–C35. (b) Ruiz, J.; Román, E.; Astruc, D. *J. Organomet. Chem.* **1987**, *322*, C13–C15. (c) Ruiz, J.; Garland, M.-T.; Román, E.; Astruc, D. *J. Organomet. Chem.* **1989**, *377*, 309–326.

(34) Diallo, A.; Ruiz, J.; Astruc, D. *Org. Lett.* **2009**, *11*, 2635–2637.

Scheme 1

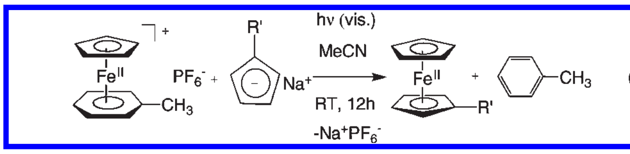


(Fv = fulvalene), and arenes containing two cyclopentadienyl rings. The overall results are reported and discussed here.

Results

All reactions were carried out overnight using a desk lamp outside an ordinary Schlenk flask, and all the results are gathered in Table 1.

1. Visible-Light Photolysis of [CpFe(η^6-toluene)][PF$_6$] with Cyclopentadienyl Salts. The reaction of [CpFe(η^6-toluene)][PF$_6$] with substituted cyclopentadienyl salts $C_5H_4R'Li$ or $C_5H_4R'Na$ in dichloromethane or acetonitrile under visible light (standard 100 W lamp) proceeds readily in a few hours to give the expected substituted ferrocene derivative quantitatively or in high yield (eq 1, Table 1, 7−9 entries 2−4) except if the cyclopentadienyl derivative bears a strong ligand such as a phosphine in $C_5H_4PPh_2Li$ (**7**, entry 2, 51% yield).

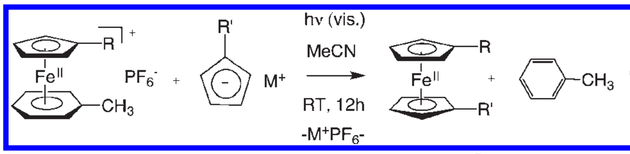


(1)

2. Optimization of the Counteranion and Arene in the [CpFe(η^6-arene)][X] Salt. The visible-light photolysis can be carried out using various arene ligands and counteranions X^- in [CpFe(η^6-arene)][X] salt. The benzene and mono- or polymethylbenzene complexes are sensitive to visible light, but the hexamethylbenzene complexes [CpFe(η^6-C_6Me_6)][X] are no longer so. The durene and pentamethylbenzene complexes are solids, and their complexes are synthesized in methylcyclohexane or decalin.[20a] They are also more expensive than toluene, xylenes, and mesitylene, and were thus not used. The benzene, toluene, xylene, and mesitylene complexes are visible-light sensitive, and their syntheses proceed in high yields without the need of an additional solvent. Thus, they are all suitable as precursors. We have carried out all the reactions using the toluene complexes, because toluene is easily removed under vacuum after photolysis.

The influence of the nature of the counteranion was examined with the counteranions PF_6^-, BF_4^-, and BPh_4^- in the series of complexes [CpFe(η^6-C_6H_6)][X] in the visible-light photolysis in the presence of $NaC_5H_4CO_2CH_3$ in acetonitrile. It was found that the yields of the syntheses of carboxymethylferrocene using this visible-light-photolysis method were 98% with PF_6^-, 82% with BF_4^-, and 80% with BPh_4^-. The yield (98%) obtained with [CpFe(η^6-C_6H_6)][PF$_6$] was the same as obtained with [CpFe(η^6-$C_6H_5CH_3$)][PF$_6$]. Accordingly, the PF_6^- anion was chosen for the overall study.

3. Selective Synthesis of Heterobifunctional Ferrocenes by Visible-Light Photolysis of [(η^5-C_5H_4R)Fe(η^6-toluene)][PF$_6$] with Functional Cyclopentadienyl Salts. The reaction of the complexes [(η^5-C_5H_4R)Fe(η^6-toluene)][PF$_6$], with substituted cyclopentadienyl salts $C_5H_4R'Li$ or $C_5H_4R'Na$ in dichloromethane or acetonitrile under visible light (standard 100 W lamp), also proceeds readily in a few hours to give the expected substituted ferrocene derivative (eq 2, Table 1). The reaction yields are fair to good (entries 3 to 6 and 8 to 11), except if the cyclopentadienyl derivative bears a strong ligand such as a carboxylic acid function in [(η^5-$C_5H_4CO_2H$)Fe(η^6-toluene)][PF$_6$] (**11**, entry 7). In these cases, the yields are lower. When the Cp ligand in the salt [(η^5-C_5H_4R)Fe(η^6-toluene)][PF$_6$] bears an amino or amido group, the yields are only modest. Conjugation of these groups with the Cp ligand provokes a hypsochromic shift rendering visible photolysis somewhat more difficult. The solvent is chosen in such a way that both the salts [CpFe(η^6-toluene)][PF$_6$] and C_5H_4RM (M = Li or Na) are soluble, otherwise the reaction does not proceed.

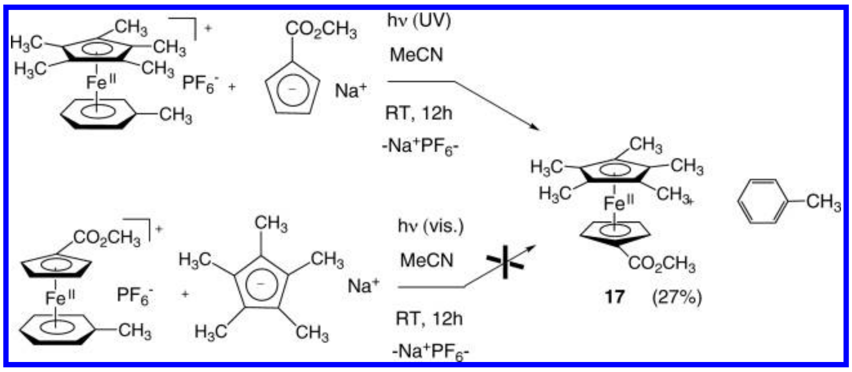


(2)

A variety of precursor complexes [(η^5-C_5H_4R)Fe(η^6-toluene)][PF$_6$] with different R groups are accessible by reaction of 1,1′-dialkylferrocenes, 1,1′-dichloroferrocene, monoacyl-ferrocenes, or ferrocenecarboxylic acid with toluene in the presence of aluminum chloride. The reactions of these complexes [(η^5-C_5H_4R)Fe(η^6-toluene)][PF$_6$] bearing a substituent on the cyclopentadienyl ring work well with the 100 W visible light if the reactants are soluble in the reaction solvent, providing good yields of the 1,1′-hetero-disubstituted ferrocene derivative (**9**−**16**, entries 5−12). The complex [(η^5-C_5H_4Cl)Fe(η^6-toluene)][PF$_6$] reacts with amines such as benzylamine at 130 °C to yield the benzylaminocyclopentadienyl mixed-sandwich salt that also undergoes the visible-light-induced arene substitution by a functional cyclopentadienyl salt (Scheme 1, **16**, entry 12).

4. Synthesis of Functional Pentamethylferrocenes. Visible-light photolysis of the complex [Cp*Fe(η^6-toluene)][PF$_6$], under these conditions, does not work, and the starting compound is quantitatively recovered. In this case

Scheme 2

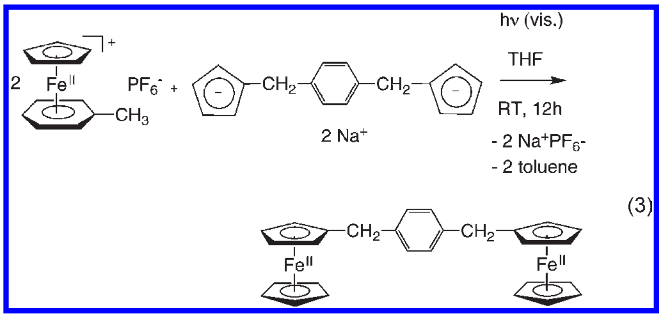


(only), photolytic synthesis requires the use of a UV lamp that provides the desired sandwich derivative [Cp*Fe(η^5-C_5H_4R)] (**17**, entry 13). The alternative synthesis of these later complexes (R = H) starting from [CpFe(η^6-toluene)-[PF_6] and Cp*Na in MeCN using visible light does not work at all, however. Only ferrocene is formed by light-induced decomposition, and the awaited 1,2,3,4,5-pentamethylferrocene derivative is not formed (Scheme 2).

5. Synthesis of Functional Biferrocenes by Visible-Light Photolysis of [(μ_2,η^5,η'_5-Fv)Fe_2(η^6-toluene)$_2$][PF_6]$_2$ (Fv = fulvalene) in the Presence of a Functional Cyclopentadienyl Salt. These reactions of functional ferrocenes have been extended to the syntheses of functional biferrocenes. The fulvalene bis (toluene) diiron salt, accessible by reaction of biferrocene with toluene (Scheme 3), is photolyzed with visible light in acetonitrile in the presence of a functional cyclopentadienyl salt to yield the biferrocene derivative bearing the functional group on both free cyclopentadienyl ligands.

This reaction was successfully carried out in high yields in both cases of acetyl-cyclopentadienylsodium and carboxymethylcyclopentadienylsodium (Scheme 3, **18** and **19**, entries 14 and 15).

6. Synthesis of Functional Biferrocenes by Visible-Light Photolysis of [CpFe(η^6-toluene)][PF_6] in the Presence of a Bis-cyclopentadienyl Dianion. The other way to synthesize biferrocene derivatives using the visible-light photolysis reaction consist in photolyzing [CpFe(η^6-toluene)][PF_6] in the presence of a bis(cyclopentadienyl) dianion. This has been achieved with the dianion (C_5H_4)$_2$-1,4-$C_6H_4Na_2$, yielding the biferrocene derivative 1,4-C_6H_4($FcCH_2$)$_2$ (eq 3, Fc = ferrocenyl, **20**, entry 16), although the yield is low for this reaction that is carried out in tetrahydrofuran (THF), a solvent compatible with the solubilization of both substrates.



(3)

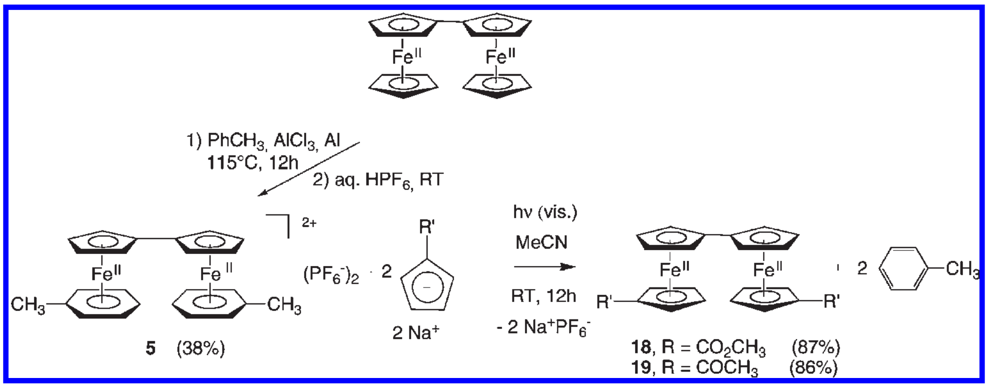
Discussion

Mechanistic studies have identified the photoexcited state as the distorted $^3E_1$ ligand field (LF) state produced by rapid decay and intersystem crossing from $^1E_2$ and $^1E_1$ LF excited states resulting from absorption.[35] The resulting destabilization can be compared to that provided by monoelectronic reduction of the d^6 cations to the d^7 $^1E_1$ state.[31] In both cases, nucleophilic attack at the iron center is fast leading to ligand substitution if the nucleophile is a ligand. It is likely that ligand substitution readily operates with solvents such as CH_3CN and THF that are relatively good ligands, and even also CH_2Cl_2 that is a very weak ligand. All these temporary ligands are displaced by stronger hydrocarbon ligands. Arene exchange only proceeds in CH_2Cl_2 that is a weak enough ligand, whereas arene exchange does not work in CH_3CN. On the other hand, the cyclopentadienyl anion is a much stronger ligand than the arenes and can displace three CH_3CN ligands even in the thermally stable complex [Cp*Fe(NCMe)$_3$][PF_6]. As a result, the thermally robust complexes [(η^5-C_5H_4R)Fe-(η^6-toluene)][PF_6] are ideal sources of the "12-electron" species (η^5-C_5H_4R)Fe^+ or weakly coordinated forms in the presence of a simple external visible-light source. The choice of toluene as the potential leaving group in the starting materials results from the high yield of synthesis of the toluene complexes by ligand exchange from ferrocenes, from its easy decomplexation using visible light, its low cost, lack of high toxicity and easy removal under vacuum from the final ferrocene derivative. When the number of methyl groups on the arene ligand is increased, the light absorption undergoes a hypsochromic shift, and the fully methylated hexamethylbenzene complex [CpFe(η^6-C_6Me_6)][PF_6], as [Cp*Fe(η^6-toluene)]-[PF_6], cannot be photolyzed by visible light. UV light is required to photolyze these complexes and obtain arene/cyclopentadienyl substitution. A strong hypsochromic shift is also found in the complexes of the type [CpFe(η^6-C_6H_5-NHR)][PF_6] because of the contribution of the mesomeric iminocyclohexadienyl structure [CpFe(η^5-C_6H_5(=N^+HR)]-[PF_6],[29c] the cyclohexadienyl complexes [CpFe(η^5-C_6H_5-(=XHR)] (X = C or N^+) being, as most ferrocene derivatives, insensitive to visible light in common organic solvents. The visible-light-induced arene/cyclopentadienyl substitution works well with fulvalene-diiron-bis(toluene) dication and less well for bis(cyclopentadienyl) derivatives for which the solvent often is a difficult problem. The failure of the reaction with Cp*Na indicated that steric bulk around the incoming cyclopentadienyl ligand is a problem. Thus, the limits of this reaction are the steric bulk of the entering Cp ligand (for

---

[35] (a) McNair, A. M.; Schrenck, J. L.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 2633–2637. (b) Schrenck, J. L.; McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501–3504.

Scheme 3



5 (38%)

18, R = CO$_2$CH$_3$ (87%)

19, R = COCH$_3$ (86%)

instance with C_5Me_5) and the solubility (in particular with entering bis(cyclopentadienyl) anions).

Concluding Remarks

The visible-light photolysis of $[(\eta^5\text{-}C_5H_4R)Fe(\eta^6\text{-toluene})][PF_6]$ in the presence of functional cyclopentadienyl salts using an ordinary 100 W lamp allows facile syntheses of 1,1′ heterobifunctional ferrocenes and biferrocenes. The simplicity of the reaction, and its extension to various ferrocenyl substituents and functional groups including syntheses of biferrocene derivatives is remarkable because various heterobifunctional ferrocenes and biferrocenes could be made in this way. The synthetic path is all the more powerful as the family of the precursors $[(\eta^5\text{-}C_5H_4R)Fe(\eta^6\text{-toluene})][PF_6]$ has a rich chemistry related to the multiple possibilities of functionalization of the Cp ligand.[29]

The limitations are the following: (i) the difficulty to extend the reaction to the permethylated complexes $[Cp^*Fe(\eta^6\text{-toluene})][PF_6]$ that require UV light instead of visible light to introduce functional cyclopentadienyl subsituents, (ii) the bulk of sterically crowded incoming cyclopentadienyls resulting in decreased reaction yields, and (iii) the poor solubility of some substituted cyclopentadienyl salts that needs to be circumvented to carry out the photolytic reactions.

In conclusion, this new, remarkably simple and selective synthetic route to functional ferrocenes and biferrocenes is very useful because it is complementary to classic synthetic routes and, in particular, it should allow the introduction of redox-robust ferrocene and biferrocene derivatives into nanoscopic devices.

Experimental Section

General Data. Acetonitrile was predried over P_2O_5 and distilled under argon immediately prior to use. THF was predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. Dichloromethane was distilled from calcium hydride just before use. The benzylamine and the triethylamine were distilled from $LiAlH_4$ just before use. All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere drylab.

^1H NMR spectra were recorded at 25 °C with a Bruker AC 300 (300 MHz) spectrometer. ^{13}C NMR spectra were obtained in the pulsed FT mode at 75 MHz, ^{31}P NMR spectra were obtained in at 81 MHz, and ^{29}Si NMR spectra were obtained in at 59.6 MHz with a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS).

Electrochemical measurement was recorded under nitrogen atmosphere. Solvent: dichloromethane; temperature: 20 °C; supporting electrolyte: $[n\text{-}Bu_4N][PF_6]$, 0.1 M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: $FeCp^*_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$); scan rate: 0.200 V s^{-1}.

Elemental analyses were performed by the Centre of Microanalysis of the CNRS at Solaize, France. The mass spectra were performed by the CESAMO (Bordeaux, France) on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source, and spectra were recorded in the positive mode. The electrospray needle was maintained at 5000 V and operated at room temperature. Samples were introduced by injection through a 10 mL sample loop into a 200 mL/min flow of methanol from the LC pump.

The complexes $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-toluene})][PF_6]$,[36] $Na[\eta^5\text{-}C_5H_4COCH_3]$,[37] $Na[\eta^5\text{-}C_5H_4CO_2CH_3]$,[38] $Na_2[1,4\text{-}C_6H_4(CH_2C_5H_4)_2]$,[38] $Li[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$,[39] $Li[\eta^5\text{-}C_5H_4Si(CH_3)_2CH_2Cl]$,[40] $[(\eta^5\text{-}C_5H_4CO_2H)Fe(\eta^6\text{-toluene})][PF_6]$,[41] $[(\eta^5\text{-}C_5H_4COCl)Fe(\eta^6\text{-toluene})][PF_6]$,[41] $[(\eta^5\text{-}C_5H_4COMe)Fe(\eta^6\text{-toluene})][PF_6]$,[42] $[(\eta^5\text{-}C_5H_4Cl)Fe(\eta^6\text{-toluene})][PF_6]$,[43] $[Fe_2Fv(\eta^5\text{-}C_5H_5)_2]$ (Fv = $\mu_2\text{-}\eta^5, \eta'^5$-fulvalenediyl),[44] $[(\eta^5\text{-}C_5H_4Me)Fe(\eta^6\text{-toluene})][PF_6]$,[36] and $[(\eta^5\text{-}Cp^*)Fe(\eta^6\text{-toluene})][PF_6]$[45] were synthesized according to the references.

Synthesis of $[(\eta^5\text{-}C_5H_4CO_2Me)Fe(\eta^6\text{-toluene})][PF_6]$, 1. Sodium methoxide (0.276 g, 5 mmol) was added to a dichloromethane/methanol (1:1) solution of $[(\eta^5\text{-}C_5H_4COCl)Fe(\eta^6\text{-toluene})][PF_6]$ (1 g, 2.47 mmol). This solution was stirred for 4 h at room temperature, then the solvent was removed under vacuum, and the residue was dissolved in dichloromethane and washed with an aqueous solution of HPF_6. The organic layer was dried with sodium sulfate, filtered, and the solvent was

---

(36) Nesmeyanov, A. N.; Vol'keneau, N. A.; Bolesova, I. N. *Doklady Akad. Nauk S.S.R* **1963**, *149*, 615–618.

(37) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196–1198.

(38) Dory, T. S.; Zuckerman, J. J. *J. Organomet. Chem.* **1984**, *264*, 295–303.

(39) Mathey, F.; Lampin, J.-P. *Tetrahedron* **1975**, *31*, 2685–2690.

(40) Ciruelo, G.; Cuenca, T.; Gómez, R.; Gómez-Sal, P.; Martin, A. *J. Chem. Soc., Dalton Trans.* **2001**, 1657–1663.

(41) Roman, E.; Dabard, R.; Moinet, C.; Astruc, D. *Tetrahedron Lett.* **1979**, *20*, 1433–1436.

(42) Astruc, D.; Dabard, R. *Bull. Soc, Chim. Fr.* **1975**, N° *11−12*, 2571−2574.

(43) Nesmeyanov, A. N.; Vol'keneau, N. A.; Bolesova, I. N. *Doklady Akad. Nauk S.S.R.* **1966**, *166*, 607–610.

(44) (a) Perevalova, E. G.; Nesmeyanova, O. A. *Doklady Akad. Nauk S.S.S.R.* **1960**, *132*, 1093–1094. (b) Nesmeyanova, O. A.; Perevalova, E. G. *Doklady Akad. Nauk S.S.S.R.* **1959**, *126*, 1007–1008. (c) Rausch, M. D. *Inorg. Chem.* **1962**, *1*, 414–417. (d) Shechter, H.; Helling, J. F. *J. Org. Chem.* **1961**, *26*, 1034–1037. (e) Rausch, M. D. *J. Org. Chem.* **1961**, *26*, 1802–1805.

(45) Astruc, D.; Hamon, J.-R. ; Lacoste, M.; Desbois, M.-H. ; Román, E. In *Organometallic Synthesis*; King, R. B., Ed.; Academic Press: New York, 1988; Vol. *IV*, pp 172−187.

removed under vacuum. Precipitation with dichloromethane/ether yielded 0.873 g of an orange powder (85% yield).

^{1}H NMR (300 MHz, CD_3COCD_3) δ_{ppm}: 2.52 (s, 3H, CH_3-C_6H_5), 3.96 (s, 3H, CH_3CO), 5.39 (s, 2H, *Cp*$COCH_3$), 5.63 (s, 2H, *Cp*$COCH_3$), 6.48 (s, 5H, $C_6H_5CH_3$).

^{13}C NMR (75 MHz, CD_3COCD_3) δ_{ppm}: 20.1 ($CH_3C_6H_5$), 53.5 (CH_3CO_2Cp), 78.2, 79.8 (CH of $CpCO_2CH_3$), 80.7 (Cq of $CpCO_2CH_3$), 88.6, 90.0, 90.7 (CH of $C_6H_5CH_3$), 106.1 (Cq of $C_6H_5CH_3$), 166.9 (CO_2Cp).

Anal. Calcd for $C_{14}H_{15}F_6FeO_2P$: C 40.41; H 3.63; found: C 40.34.56; H 3.63.

ESI mass spectrum: calcd *m*/*z* for M^+ ($C_{14}H_{15}FeO_2$) 271.113; found 271.042 (M^+).

Synthesis of [(η^5-$C_5H_4CO_2CH_2CCH$)Fe(η^6-toluene)][PF_6], 2. $HOCH_2CCH$ (0.11 mL, 1.86 mmol) was added to a dichloromethane solution of triethylamine (1 mL) and [(η^5-C_5H_4-COCl)Fe(η^6-toluene)][PF_6] (0.5 g, 1.24 mmol). This solution was stirred for 4 h at room temperature. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane and washed with an aqueous solution of K_2CO_3 and with an aqueous solution of HPF_6. The organic layer was dried with sodium sulfate, filtered, and the solvent was removed under vacuum. Precipitation with dichloromethane/ether yielded 0.464 g of an orange powder (85% yield).

[(η^5-$C_5H_4CO_2CH_2CCH$)Fe(η^6-toluene)][PF_6]: ^{1}H NMR (300 MHz, CD_3COCD_3) δ_{ppm}: 2.56 (s, 3H, $CH_3C_6H_5$), 3.28 (s, 1H, $C\equiv CH$), 5.04 (d, 2H, $CH\equiv CCH_2$), 5.43 (s, 2H, CH of $CpCO_2$-CH_3), 5.68 (s, 2H, CH of $CpCO_2CH_3$), 6.50 (s, 5H, $C_6H_5CH_3$).

^{13}C NMR (75 MHz, CD_3COCD_3) δ_{ppm}: 20.4 ($CH_3C_6CH_5$), 54.1 ($CH\equiv CCH_2$), 77.8 ($CH\equiv CCH_2$), 78.4 (CH of $CpCO_2$), 78.5 ($C\equiv CH$), 79.6 (CH of $CpCO_2$), 80.2 (Cq of $CpCO_2$), 88.8, 90.1, 90.8 (CH of $C_6H_5CH_3$), 106.4 (Cq of $C_6H_5CH_3$), 166.1 (CO_2CH_3).

ESI mass spectrum: calcd *m*/*z* for M^+ ($C_{16}H_{15}FeO_2$); found 295.043 (M^+).

Synthesis of [(η^5-$C_5H_4CONHCH_2C_6H_5$)Fe(η^6-toluene)][PF_6], 3. A 2.3 mL portion of benzylamine was added to a dichloromethane solution of [(η^5-C_5H_4COCl)Fe(η^6-toluene)][PF_6] (0.5 g, 1.24 mmol), and this solution was stirred for 4 h at room temperature. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane and washed with an aqueous solution of HPF_6. The organic layer was dried with sodium sulfate, filtrated, and the solvent was removed under vacuum. Precipitation with dichloromethane/ether yielded 0.333 g of an orange powder (60% yield).

[(η^5-$C_5H_4CONHCH_2C_6H_5$)Fe(η^6-toluene)][PF_6]: ^{1}H NMR (300 MHz, CD_3COCD_3) δ_{ppm}: 2.45 (s, 3H, $CH_3C_6H_5$), 4.57 (s, 2H, $CH_2C_6H_5$), 5.31 (s, 2H, CH of *Cp*CO), 5.65 (s, 2H, CH of *Cp*CO), 6.28 (s, 5H, $CH_3C_6H_5$), 7.27 (m, 5H, $C_6H_5CH_2$), 8.34 (s, 1H, $NHCH_2$).

^{13}C NMR (75 MHz, CD_3COCD_3) δ_{ppm}: 19.0 ($CH_3C_6H_5$), 43.3 ($NHCH_2$), 75.9, 78.0 (CH of *Cp*CO), 85.2 (Cq of *Cp*CO), 87.3, 88.7, 89.6 ($CH_3C_6H_5$), 127.2, 128.0, 128.4 ($C_6H_5CH_2$), 138.8 (*CO*NH).

Anal. Calcd for $C_{20}H_{20}F_6FeNOP$: C 48.91; H 4.10; found: C 48.46; H 4.03

ESI mass spectrum: calcd *m*/*z* for M^+ ($C_{20}H_{20}FeNO$) 346.224; found 346.089 (M^+).

Synthesis of [(η^5-$C_5H_4NHCH_2C_6H_5$)Fe(η^6-toluene)][PF_6], 4. [(η^5-C_5H_4Cl)Fe(η^6-toluene)] [PF_6] (1.170 g, 2.5 mmol) was dissolved in a solution of benzylamine (1.6 mL, 12.5 mmol) and triethylamine (0.4 mL, 2.5 mmol). This solution was stirred for 24 h at 130 °C. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane and washed with an aqueous solution of HPF_6. The organic layer was dried with sodium sulfate, filtrated, and the solvent was removed under vacuum. Precipitation with dichloromethane/ether yielded 0.678 g of an orange powder (58% yield).

[(η^5-$C_5H_4NHCH_2C_6H_5$)Fe(η^6-toluene)][PF_6]: ^{1}H NMR (300 MHz, CD_3COCD_3) δ_{ppm}: 2.40 (s, 3H, $CH_3C_6H_5$), 4.30 (d, 2H, $CH_2C_6H_5$), 4.64, 4.77 (CH of *Cp*NH), 5.71 (s, 1H, *NH*Cp), 5.99 (s, 5H, $C_6H_5CH_3$), 7.32 (m, 5H, $C_6H_5CH_3$).

^{13}C NMR (75 MHz, CD_3COCD_3) δ_{ppm}: 20.2 ($CH_3C_6H_5$), 49.2 ($NHCH_2$), 60.1, 72.2 (CH of *Cp*NH), 86.4, 87.5, 88.5 (C_6-H_5CH_3), 102.8 (Cq of *Cp*NH), 128.5, 128.8, 129.6 ($C_6H_5CH_2$).

Anal. Calcd for $C_{19}H_{20}F_6FeNP$: C 49.27; H 4.35; found: C 49.37; H 4.34

Synthesis of [Fe_2Fv(η^6-toluene)$_2$][PF_6]$_2$, 5 (Fv = μ_2-η^5, η'^5-fulvalenyl). [Fe_2Fv(η^5-C_5H_5)$_2$] (Fv = μ_2-η^5, η'^5-fulvalenyl) (2 g, 5.4 mmol), aluminum chloride (7.2 g, 54 mmol), Al powder (0.146 g, 5.4 mmol), and H_2O (0.097 mL, 5.4 mmol) are mixed under N_2 and heated at 115 °C for 12 h in 50 mL of toluene. After hydrolysis at 0 °C, aqueous NH_3 is added to the aqueous layer to remove Al^{3+}, and then aqueous HPF_6 (0.6 mL, 10.8 mmol) is added to the filtrate to precipitate the salt. Re-precipitation by addition of excess CH_2Cl_2 to an acetone solution provides 1.5 g (38% yield) of powdered salt.

[Fe_2Fv((η^6-toluene)][PF_6]: ^{1}H NMR (300 MHz, CD_3COCD_3) δ_{ppm}: 2.28 (s, 6H, $CH_3C_6H_5$), 5.42 (s, 4H, CH of Fv), 5.74 (s, 4H, CH of Fv), 6.22 (s, 10H, $C_6H_5CH_3$).

^{13}C NMR (75 MHz, CD_3COCD_3) δ_{ppm}: 20.2 ($CH_3C_6H_5$), 75.5, 78.9 (CH of Fv), 88.4, 89.8, 90.4 ($C_6H_5CH_3$), 105.5 (Cq of Fv).

Anal. Calcd for $C_{24}H_{24}F_{12}Fe_2P_2$: C 40.37; H 3.39; found: C 39.70 ; H 3.78

General Procedure for the Photochemical Reactions. In a double-wall Schlenk flash, amounts of complex [(η^5-C_5H_4R)Fe-(η^6-toluene)][PF_6] and 2 equiv of cyclopentadienyl salt MC_5H_4R' (M = Li or Na) or 4 equiv of disodium (phenylenedimethylene)-dicyclopentadienide salt 1,4-$C_6H_4(CH_2C_5H_4)_2Na_2$ were dissolved in dry acetonitrile, dichloromethane or THF. The solution was irradiated with visible light for 12 h, under magnetic stirring and water cooling on the exterior wall of the Schlenk tube. The solvent was removed under vacuum, and the crude product was dissolved in dichloromethane. The solution was washed several times with water, and the organic phase was dried over Na_2SO_4. Dichloromethane was removed under vacuum, and the crude product was then adsorbed on silica and purified by column chromatography (SiO_2) using the mixture pentane- diethyl ether (90:10) as eluent.

Synthesis of [(η^5-C_5H_5)Fe(η^5-$C_5H_4CO_2Me$)],[46] 6. The complex **6** was synthesized from [(η^5-C_5H_5)Fe(η^6-toluene)][PF_6] (0.25 g, 0.698 mmol) and Na(η^5-$C_5H_4CO_2CH_3$) (0.204 g, 1.40 mmol) following the general procedure for the photochemical reactions. A 0.167 g portion of **6** was obtained (98% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 3.80 (s, 3H, CH_3CO_2Cp), 4.20 (s, 5H, *Cp*), 4.39 (s, 2H, CH of $CpCO_2CH_3$), 4.80 (s, 2H, CH of $CpCO_2CH_3$).

^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm}: 51.5 (CH_3CO_2Cp), 69.6 (*Cp*), 70.0, 71.2 (CH of $CpCO_2CH_3$), 172.2 (CO_2).

IR (cm^{-1}): 1702.33 (γ_{CO2Me}).

Synthesis of [(η^5-C_5H_5)Fe(η^5-$C_5H_4PPh_2$)],[47] 7. The complex **7** was synthesized from [(η^5-C_5H_5)Fe(η^6-toluene)][PF_6] (0.358 g, 1 mmol) and Li[η^5-$C_5H_4P(C_6H_5)_2$] (0.512 g, 2 mmol) following the general procedure for the photochemical reactions. A 0.189 g portion of **7** was obtained (51% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 4.10 (s, 5H, *Cp*), 4.14 (m, 2H, CH of $CpP(Ph)_2$), 4.40 (m, 2H, CH of $CpP(Ph)_2$), 7.30−7.40 (m, 10H, CH of $P(Ph)_2$).

^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm}: 69.1 (*Cp*), 70.7, 72.8 (CH of $CpP(Ph)_2$), 75.8 (Cq of $CpP(Ph)_2$), 128.1, 133.3 (CH of $P(Ph)_2$), 139.0 (Cq of $P(Ph)_2$).

^{31}P NRM (81 MHz, $CDCl_3$) δ_{ppm}: −15.3.

Synthesis of [(η^5-C_5H_5)Fe(η^5-$C_5H_4SiMe_2CH_2Cl$)],[48] 8. The complex **8** was synthesized from [(η^5-C_5H_5)Fe(η^6-toluene)]-

---

(46) Barisic, L.; Rapic, V.; Pritzkow, H.; Pavlovic, G.; Nemet, I. *J. Organomet. Chem.* **2003**, *682*, 131–142.

(47) Butler, I. R.; Cullen, W. R. *Organometallics* **1986**, *5*, 2537–2542.

(48) Altmann, R.; Gausset, O.; Horn, D.; Jurkschat, K.; Schrmann, M.; Fontani, M.; Zanello, P. *Organometallics* **2000**, *19*, 430–443.

[PF$_6$] (0.358 g, 1 mmol) and Li[η^5-C$_5$H$_4$Si(CH$_3$)$_2$CH$_2$Cl] (0.357 g, 2 mmol) following the general procedure for the photochemical reactions in dichloromethane. The crude product was then adsorbed on silica and purified by column chromatography (SiO$_2$) using pentane as eluent. A 0.205 g portion of **8** was obtained (80% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 0.41 (s, 6H, Si(*CH*$_3$)$_2$), 2.91 (s, 2H, Cl*CH*$_2$Si(CH$_3$)$_2$), 4.18 (s, 7H, CH of *Cp* and *Cp*Si(CH$_3$)$_2$), 4.41 (m, 2H, CH of *Cp*Si(CH$_3$)$_2$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: −3.6 (Si(*CH*$_3$)$_2$), 31.2 (Cl*CH*$_2$), 67.3 (Cq of *Cp*Si(CH$_3$)$_2$), 68.2 (*Cp*), 71.2, 73.1 (CH of *Cp*Si(CH$_3$)$_2$).

^{29}Si NMR (59.6 MHz, CDCl$_3$) δ_{ppm}: −1.46.

Synthesis of [(η^5-C$_5$H$_4$CO$_2$Me)Fe(η^5-C$_5$H$_4$COMe)],[49] 9. The complex **9** was synthesized from [(η^5-C$_5$H$_4$CO$_2$Me)Fe(η^6-toluene)][PF$_6$], **1** (0.250 g, 0.6 mmol) and Na[η^5-C$_5$H$_4$COCH$_3$] (0.156 g, 1.2 mmol) following the general procedure for the photochemical reactions. A 0.151 g portion of **9** was obtained (88% yield).

The complex **9** was also obtained from [(η^5-C$_5$H$_4$COMe)Fe(η^6-toluene)][PF$_6$] and Na[η^5-C$_5$H$_4$CO$_2$CH$_3$] in 95% yield.

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 2.40 (s, 3H, *CH*$_3$COCp), 3.84 (s, 3H, *CH*$_3$CO$_2$Cp), 4.42 (m, 2H, CH of *Cp*COCH$_3$), 4.51 (m, 2H, CH of *Cp*CO$_2$CH$_3$), 4.78 (m, 2H, CH of *Cp*COCH$_3$), 4.82 (m, 2H, *Cp*CO$_2$CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 27.5 (*CH*$_3$COCp), 51.7 (*CH*$_3$CO$_2$Cp), 70.9, 71.5, 72.6, 73.4 (CH of *Cp*CO$_2$CH$_3$ and *Cp*COCH$_3$), 80.4 (Cq of *Cp*CO$_2$CH$_3$ and *Cp*COCH$_3$), 170.6 (*CO*$_2$CH$_3$), 201.3 (*CO*Cp).

IR (cm^{-1}): 1671.85 (γ_{CO}); 1715.73 (γ_{CO2Me}).

Synthesis of [(η^5-C$_5$H$_4$COMe)Fe(η^5-C$_5$H$_4$SiMe$_2$CH$_2$Cl)], 10. The complex **10** was synthesized from [(η^5-C$_5$H$_4$COMe)Fe(η^6-toluene)][PF$_6$] (0.384 g, 1 mmol) and Li[η^5-C$_5$H$_4$Si(CH$_3$)$_2$CH$_2$Cl] (0.357 g, 2 mmol) following the general procedure for the photochemical reactions in dichloromethane. A 0.251 g portion of **10** was obtained (75% yield).

^{1}H NMR (300 MHz, CD$_3$COCD$_3$) δ_{ppm}: 0.41 (s, 6H, Si(*CH*$_3$)$_2$), 2.40 (s, 3H, *CH*$_3$COCp), 2.91 (s, 2H, Cl*CH*$_2$Si(CH$_3$)$_2$), 4.18 (s, 2H, CH of *Cp* and *Cp*Si(CH$_3$)$_2$), 4.40 (m, 4H, CH of *Cp*COCH$_3$ and *Cp*Si(CH$_3$)$_2$), 4.65 (m, 2H, CH of CH of *Cp*COCH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: −3.6 (Si(*CH*$_3$)$_2$), 27.5 (*CH*$_3$COCp), 31.2 (Cl*CH*$_2$), 67.3 (Cq of *Cp*Si(CH$_3$)$_2$), 71.2, 71.5, 73.1, 73.4 (CH of *Cp*CO$_2$CH$_3$ and *Cp*Si(CH$_3$)$_2$), 80.4 (Cq of *Cp*COCH$_3$), 202.0 (CH$_3$*CO*).

^{29}Si NMR (59.6 MHz, CDCl$_3$) δ_{ppm}: −1.46.

IR (cm^{-1}): 1626.30 (γ_{CO}).

Synthesis of [(η^5-C$_5$H$_4$CO$_2$H)Fe(η^5-C$_5$H$_4$COMe)],[50] 11. The complex **11** was synthesized from [(η^5-C$_5$H$_4$CO$_2$H)Fe(η^6-toluene)][PF$_6$] (0.250 g, 0.6 mmol) and Na[η^5-C$_5$H$_4$COCH$_3$] (0.156 g, 1.2 mmol) following the general procedure for the photochemical reactions. The crude product was then adsorbed on silica and purified by column chromatography (SiO$_2$) using the mixture methanol-diethyl ether (1:4) as eluent. A 0.025 g portion of **11** was obtained (15% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 2.40 (s, 3H, *CH*$_3$COCp), 4.42 (m, 2H, CH of *Cp*COCH$_3$), 4.52 (m, 2H, CH of *Cp*CO$_2$H), 4.78 (m, 2H, CH of *Cp*COCH$_3$), 4.82 (m, 2H, *Cp*CO$_2$H).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 27.5 (*CH*$_3$COCp), 70.9, 71.5, 72.6, 73.4 (CH of *Cp*CO$_2$H and *Cp*COCH$_3$), 80.4 (Cq of *Cp*CO$_2$H and *Cp*COCH$_3$), 170.6 (*CO*$_2$H), 201.3 (*CO*Cp).

IR (cm^{-1}): 1637.16 (γ_{COCH3}), 1725.05 (γ_{CO2H}).

Synthesis of [(η^5-C$_5$H$_4$CO$_2$CH$_2$CCH)Fe(η^5-C$_5$H$_4$CO$_2$Me)], 12. The complex **12** was synthesized from [(η^5-C$_5$H$_4$CO$_2$CH$_2$CCH)Fe(η^6-toluene)][PF$_6$], **2** (0.361 g, 0.8 mmol) and Na[η^5-C$_5$H$_4$CO$_2$CH$_3$] (0.234 g, 1.6 mmol) following the general procedure for the photochemical reactions. A 0.227 g portion of **7** was obtained (85% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 2.53 (m, 1H, *CH*≡C), 3.85 (s, 3H, *CH*$_3$CO$_2$Cp), 4.45 (m, 4H, CH of *Cp*CO$_2$CH$_3$ and *Cp*CO$_2$CH$_2$CCH), 4.84 (m, 6H, CH of *Cp*CO$_2$CH$_3$, *Cp*CO$_2$CH$_2$CCH and CH$_2$ of *CH*$_2$CCH).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 51.7 (CH≡C*CH*$_2$), 51.8 (*CH*$_3$CO$_2$Cp), 71.5, 72.7 (CH of *Cp*CO$_2$CH$_3$ and *Cp*CO$_2$CH$_2$CCH), 74.7 (*CH*≡CCH$_2$), 78.1 (*C*≡CH), 169.7 (*CO*$_2$CH$_2$) 170.7 (*CO*$_2$CH$_3$).

IR (cm^{-1}): 1718.05 (γ_{CO2}); 2120.36 ($\gamma_{\mathrm{C{\equiv}C}}$).

Anal. Calcd for C$_{16}$H$_{14}$FeO$_4$: C 58.93; H 4.33; found: C 59.00; H 4.46

ESI mass spectrum: calc. *m*/*z* for M$^+$ (C$_{16}$H$_{14}$FeO$_4$) 326.132; found 327.034 (M$^+$), 349.014 (MNa$^+$).

Synthesis of [(η^5-C$_5$H$_4$CONHCH$_2$C$_6$H$_5$)Fe(η^5-C$_5$H$_4$CO$_2$Me)], 13. The complex **13** was synthesized from [(η^5-C$_5$H$_4$CONHCH$_2$C$_6$H$_5$)Fe(η^6-toluene)][PF$_6$], **3** (0.255 g, 0.57 mmol) and Na[η^5-C$_5$H$_4$CO$_2$CH$_3$] (0.166 g, 1.14 mmol) following the general procedure for the photochemical reactions. A 0.150 g portion of **13** was obtained (70% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 3.76 (s, 3H, *CH*$_3$CO$_2$Cp), 4.36 (d, 4H, CH of *Cp*CONH and *Cp*CO$_2$CH$_3$), 4.57 (m, 6H, CH of *Cp*CONH and *Cp*CO$_2$CH$_3$, CH$_2$ of CONH*CH*$_2$Ph), 6.65 (s, 1H, *NH*CO), 7.32 (m, 5H, *C*$_6$*H*$_5$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 43.6 (NH*CH*$_2$), 51.8 (*CH*$_3$CO$_2$Cp), 70.0, 71.6, 72.7 (CH of *Cp*CONH and *Cp*CO$_2$CH$_3$), 127.4, 127.9, 128.6 (*C*$_6$*H*$_5$CH$_2$), 138.7 (Cq of *C*$_6$*H*$_5$CH$_2$), 169.2 (*CO*NHCH$_2$), 171.6 (*CO*$_2$CH$_3$).

IR (cm^{-1}): 1716.43 (γ_{CO2}).

Anal. Calcd for C$_{20}$H$_{19}$FeNO$_3$: C 63.68; H 5.09; found: C 63.48; H 4.89.

ESI mass spectrum: calc. *m*/*z* for M$^+$ (C$_{20}$H$_{19}$FeNO$_3$) 377.223; found 378.0796 (M$^+$), 400.0617 (MNa$^+$).

Synthesis of [(η^5-C$_5$H$_4$Cl)Fe(η^5-C$_5$H$_4$CO$_2$Me)], 14. The complex **14** was synthesized from [(η^5-C$_5$H$_4$Cl)Fe(η^6-toluene)][PF$_6$] (0.422 g, 1.13 mmol) and Na[η^5-C$_5$H$_4$CO$_2$CH$_3$] (0.330 g, 2.26 mmol) following the general procedure for the photochemical reactions. A 0.283 g portion of **13** was obtained (90% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 3.83 (s, 3H, *CH*$_3$CO$_2$Cp), 4.09 (m, 2H, CH of *Cp*Cl), 4.42 (m, 4H, CH of *Cp*Cl and *Cp*CO$_2$CH$_3$), 4.87 (m, 2H, CH of *Cp*CO$_2$CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 51.6 (*CH*$_3$CO$_2$Cp), 67.6, 69.2, 71.8, 73.2 (CH of *Cp*Cl and *Cp*CO$_2$CH$_3$), 93.2 (Cq of *Cp*Cl), 170.7 (*CO*$_2$CH$_3$).

Anal. Calcd for: C$_{12}$H$_{11}$ClFeO$_2$ for calcd: C 51.75; H 3.98; found: C 52.02; H 4.48

ESI mass spectrum: calc. *m*/*z* for M$^+$ (C$_{12}$H$_{11}$ClFeO$_2$) 278.518; found 278.988 (M$^+$), 300.969 (MNa$^+$).

IR (cm^{-1}): 1712.49 (γ_{CO}).

Synthesis of [(η^5-C$_5$H$_4$Me)Fe(η^5-C$_5$H$_4$COMe)], 15. The complex **15** was synthesized from [(η^5-C$_5$H$_4$Me)Fe(η^6-toluene)][PF$_6$] (0.250 g, 0.672 mmol) and Na[η^5-C$_5$H$_4$COCH$_3$] (0.175 g, 1.35 mmol) following the general procedure for the photochemical reactions. A 0.159 g portion of **15** was obtained (98% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 1.87 (s, 3H, *CH*$_3$Cp); 2.35 (s, 3H, *CH*$_3$CO); 4.04 (s, 4H, *Cp*CH$_3$); 4.40 (m, 2H, *Cp*CO); 4.65 (m, 2H, *Cp*CO).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 13.7 (*CH*$_3$Cp), 27.5 (*CH*$_3$CO), 69.1, 70.1, 70.7, 73.1 (CH of *Cp*CH$_3$ and *Cp*COCH$_3$), 79.6 (Cq of *Cp*CH$_3$), 85.6 (Cq. of *Cp*CO), 202.0 (CH$_3$*CO*).

IR (cm^{-1}): 1660 (γ_{CO}).

Anal. Calcd for C$_{13}$H$_{14}$FeO: C 64.50; H 5.83; found: C 64.56; H 5.74.

ESI mass spectrum: calc. *m*/*z* for M$^+$ (C$_{13}$H$_{14}$FeO) 242.101; found 243.0473 (M$^+$), 265.0289 (MNa$^+$).

Synthesis of [(η^5-C$_5$H$_4$NHCH$_2$C$_6$H$_5$)Fe(η^5-C$_5$H$_4$CO$_2$Me)], 16. The complex **16** was synthesized from [(η^5-C$_5$H$_4$NHCH$_2$C$_6$H$_5$)Fe(η^6-toluene)][PF$_6$], **4** (0.287 g, 0.6 mmol) and Na[η^5-C$_5$H$_4$CO$_2$CH$_3$] (0.175 g, 1.2 mmol) following the general procedure for the

---

(49) Cakić Semenčić, M.; Dropučić, M.; BarišićL; Rapić, V. *Croat. Chem. Acta* **2006**, *79*, 599–612.

(50) Little, W. F.; Eisenthal, R. *J. Am. Chem. Soc.* **1960**, *82*, 1577–1580.

photochemical reactions. The crude product was then adsorbed on silica and purified by column chromatography (SiO$_2$) using dichloromethane as eluent. A 0.096 g portion of **16** was obtained (44% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 2.83 (s, 1H, *NH*CH$_2$), 3.78 (s, 3H, *CH*$_3$CO$_2$Cp), 3.94 (s, 4H, CH of *Cp*NH and CH$_2$ of *CH*$_2$C$_6$H$_5$), 4.16 (s, 2H, CH of *Cp*NH), 4.40 (m, 2H, CH of *Cp*CO$_2$CH$_3$), 4.83 (m, 2H, CH of *Cp*CO$_2$CH$_3$), 7.29 (m, 5H, C$_6$H$_5$CH$_2$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 51.0 (*CH*$_3$CO$_2$Cp), 56.7 (*CH*$_2$C$_6$CH$_5$), 64.7, 70.2, 71.2 (CH of *Cp*CO$_2$CH$_3$ and CH of *Cp*NHCH$_2$), 112.3 (Cq of *Cp*NHCH$_2$), 139.2 (Cq of *Cp*CO$_2$CH$_3$), 172.4 (CO$_2$CH$_3$).

ESI mass spectrum: calc. *m*/*z* for M$^+$ (C$_{19}$H$_{19}$FeNO$_2$) 349.212; found 350.0838 (M$^+$), 372.0650 (MNa$^+$).

Synthesis of [(η^5-C$_5$Me$_5$)Fe(η^5-C$_5$H$_4$CO$_2$Me)],[25] 17. Solid [(η^5-C$_5$Me$_6$)Fe(η^6-toluene)][PF$_6$] (0.619 g, 1.4 mmol) was added with stirring to a suspension of Na[η^5-C$_5$H$_4$CO$_2$CH$_3$] (0.409 g, 2.8 mmol) in acetonitrile. The solution was irradiated with a Hanovia lamp (250 nm, 450 W) at −30 °C for 1 h. The temperature was allowed to rise to ambient temperature. The solvent was removed under vacuum, and the crude product was dissolved in dichloromethane. The solution was washed several times with water, and the organic phase was dried over Na$_2$SO$_4$. Dichloromethane was removed under vacuum, and the crude product was then adsorbed on silica and purified by column chromatography (SiO$_2$) using the mixture pentane-diethyl ether (95:5) as eluent. A 0.121 g portion of **17** was obtained (27% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 1.77 (s, 15H, *Me*$_5$C$_5$), 3.80 (s, 3H, *CH*$_3$CO$_2$Cp), 3.98 (s, 2H, CH of *Cp*CO$_2$), 4.30 (s, 2H, CH of *Cp*CO$_2$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 10.6 (*Me*$_5$C$_5$), 51.1 (*CH*$_3$CO$_2$Cp), 73.1 (CH of *Cp*CO$_2$CH$_3$), 76.3 (CH of *Cp*CO$_2$CH$_3$), 81.9 (Cq of C$_5$Me$_5$), 171.2 (*CO*$_2$CH$_3$).

Synthesis of [(η^5-C$_5$H$_4$CO$_2$Me)$_2$ Fe$_2$Fv] (Fv = μ_2-η^5, η'^5-fulvalenyl),[51] 18. The complex **18** was synthesized from [Fe$_2$Fv((η^6-toluene)$_2$][PF$_6$]$_2$, **5** (0.306 g, 0.4 mmol) and Na[η^5-C$_5$H$_4$CO$_2$CH$_3$] (0.467 g, 3.2 mmol) following the general procedure for the photochemical reactions. The crude product was washed several times with diethyl ether. A 0.179 g portion of **18** was obtained (87%).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 3.62 (s, 6H, CH$_3$CO$_2$Cp), 4.19 (m, 8H, CH of Fv), 4.36 (m, 4H, CH of *Cp*CO$_2$CH$_3$), 4.59 (m, 4H, CH of *Cp*CO$_2$CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 51.5 (*CH*$_3$CO$_2$Cp), 67.5, 69.5, 71.1, 72.2 (CH of Fv and *Cp*CO$_2$CH$_3$), 83.9 (Cq of Fv), 171.2 (*CO*$_2$CH$_3$).

Synthesis of [(η^5-C$_5$H$_4$COMe)$_2$ Fe$_2$Fv] (Fv = μ_2-η^5, η'^5-fulvalenyl),[51,52] 19. The complex **19** was synthesized from [Fe$_2$Fv((η^6-toluene)$_2$][PF$_6$]$_2$, **5** (0.250 g, 0.3 mmol) and Na[η^5-C$_5$H$_4$COCH$_3$] (0.302 g, 2.4 mmol) following the general procedure for the photochemical reactions. The crude product was then adsorbed on silica and purified by column chromatography (SiO$_2$) using ethyl acetate as eluent. A 0.136 g portion of **19** was obtained (87% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 2.07 (s, 6H, *CH*$_3$COCp), 4.19 (m, 12H, CH of *Cp*COCH$_3$ and Fv), 4.49 (m, 4H, CH of *Cp*COCH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 27.6 (*CH*$_3$CO$_2$Cp), 67.6, 69.8, 70.7, 73.4 (CH of *Cp*COCH$_3$ and Fv), 84.0 (Cq of Fv), 201.9 (*CO*CH$_3$).

Synthesis of [1,4-C$_6$H$_4$(CH$_2$Fc)$_2$] (Fc = C$_{10}$H$_9$), 20. The complex **20** was synthesized from [(η^5-C$_5$H$_5$)Fe(η^6-toluene)]-[PF$_6$] (1.6 g, 4.5 mmol) and Na$_2$[1,4-C$_6$H$_4$(CH$_2$C$_5$H$_4$)$_2$] (0.625 g, 2.25 mmol) in THF following the general procedure for the photochemical reactions. The crude product was then adsorbed on silica and purified by column chromatography (SiO$_2$) using the mixture pentane- diethyl ether (80:20) as eluent. A 0.384 g portion of **20** was obtained (18% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ_{ppm}: 3.56 (s, 4H, *CH*$_2$Cp), 3.98 (m, 18H, CH of Cp and *Cp*CH$_2$), 6.99 (s, 4H, C$_6$*H*$_4$CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_{ppm}: 35.6 (*CH*$_2$Cp), 67.5, 68.6 (CH of Cp and *Cp*CH$_2$), 88.2 (Cq of *Cp*CH$_2$), 128.2 (CH of C$_6$H$_4$CH$_3$), 139.2 (Cq of C$_6$H$_4$CH$_3$).

Anal. Calcd for: C$_{28}$H$_{26}$Fe$_2$: C 70.92; H 5.53; found: C 70.77; H 5.50.

ESI mass spectrum: calc. *m*/*z* for M$^+$ (C$_{28}$H$_{26}$Fe$_2$) 474.208; found 474.3 (M$^+$).

Cyclic voltammetry (CH$_2$Cl$_2$; supporting electrolyte [*n*-Bu$_4$N]PF$_6$; 293 K): only one reversible wave is observed because of the equivalence of the two sufficiently separated ferrocenyl groups,[53] $E_{1/2} = 0.525$ V versus decamethylferrocene.[54]

Acknowledgment. Financial support from the Université Bordeaux 1, the Centre National de la Recherche Scientifique (CNRS), and the Agence Nationale pour la Recherche (ANR-06-NANO-026-02) is gratefully acknowledged.

Supporting Information Available: ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR and electrospray mass spectra of the ferrocenyl derivatives, and cyclic voltammogram of the functional biferrocene derivative **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(51) Kovar, R. F.; Rausch, M. D. *J. Organomet. Chem.* **1972**, *35*, 351–366.

(52) Rausch, M. D. *J. Org. Chem.* **1964**, *29*, 1257–1259.

(53) Diallo, A. K.; Daran, J.-C.; Varret, F.; Ruiz, J.; Astruc, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 3141–3145.

(54) (a) Ruiz, J.; Astruc, D. *C. R. Acad. Sci. Paris, t. 1, Série II c* **1998**, 21–27. (b) Ruiz, J.; Daniel, M.-C.; Astruc, D. *Can. J. Chem.* **2006**, *84*, 288–299.