Convenient Synthesis of Mixed Ferrocenes

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Received June 27, 1996[⊗]

Summary: The deprotonated form of [(fluorene)FeCp]PF$_6$ functions as an efficient cyclopentadienyliron (CpFe) transfer reagent to other cyclopentadienyls (Cp′) to give mixed ferrocenes (CpFeCp′). By using this method, many new mixed ferrocenes have been prepared, and one of the mixed ferrocenes has been used to make bi- and trimetallic compounds.

Due to its high stability and its versatility as starting material in the synthesis of useful compounds, ferrocene plays a key role in many areas of research, and extensive chemistry associated with ferrocene has been published.[1] An important advantage of the ferrocene-containing complexes is that their electron-donor ability may be fine-tuned by the choice of number and nature of the substituents.[2] Thus, the synthesis of ferrocenes with tailor-made properties has been a goal for many synthetic chemists. Many useful synthetic methods have been published.[3] However, most of the published methods are applicable only in special cases.[4] In fact, there seems to be a dearth of systematic investigations into the complexation behavior of substituted cyclopentadienyl ligands because there are no general routes to synthesize unsymmetrically substituted ferrocenes.

Several years ago, Manriquez *et al.*[5] reported the use of Cp*Fe(acac) as a Cp*Fe transfer reagent. However, attempted use of CpFe(acac) as a CpFe transfer reagent was not successful. The use of [CpFe(*p*-xylene)]PF$_6$ in ligand exchange reactions to prepare substituted metallocenes has been reported,[6] but in this reaction, the cyclopentadiene derivatives are limited only to 6-(dimethylamino)pentafulvenes. We have screened several Fe(I) and Fe(II) complexes as CpFe transfer reagents. Among the compounds which we have screened, CpFe(η^5-oxocyclohexadienyl) and CpFe(naphthalene)$^+$ have some marginal utility. Only sometimes are they successful in transferring the CpFe moiety. However, the deprotonated form of [CpFe(fluorene)] PF$_6$ can be applied very successfully to transfer of the CpFe moiety in most cases. Several years ago, the thermal and electron-transfer-induced isomerization of Fe(η^6-fluorenyl)(η^5-C$_5$H$_5$) were reported.[7] In this communication, we demonstrate the usefulness and the scope of the CpFe transfer reaction using the deprotonated form of [CpFe(fluorene)]PF$_6$.

[CpFe(fluorene)]PF$_6$ (**1**) was synthesized by a known route.[8] Treatment of **1** with *t*-BuOK in THF generated the deprotonated fluorene iron complex **2**, which has been reported earlier by Treichel and Johnson.[9] When **2** was treated with hydrocarbon-substituted cyclopentadienides, mixed ferrocenes were obtained in reasonable to high yield (eq 1).[10] The scope of the substituted cyclopentadienides can be seen in Table 1.[11]

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.

(1) (a) Togni, A., Hayashi, T., Eds. *Ferrocenes: homogeneous catalysis, organic synthesis, and material science*; VCH: Weinheim, Germany, 1995. (b) Oriol, L.; Serrano, J. L. *Adv. Mater.* **1995**, *7*, 348. (c) Coville, N. J.; du Plooy, K. E.; Pickl, W. *Coord.Chem. Rev.* **1992**, *116*, 1.

(2) (a) Dong, T.-Y.; Chang, C.-K.; Huang, C.-H.; Wen, Y. S.;Lee, S. L.; Chen, J. A.; Yeh, W. Y.; Yeh, A. *J. Chem. Soc., Chem. Commun.* **1992**, 526. (b) Dong, T.-Y.; Chang, C.-K.; Huang, C.-H.; Wen, Y. S.; Lee, S. L.; Chen, J. A.; Yeh, W. Y.; Yeh, A. *J. Am. Chem. Soc.* **1993**, *115*, 6357. (c) Geiger, W. E. J. *Organomet. Chem. Libr.* **1990**, *22*, 142. (d) Zanello, P.; Opromolla, G.; Giorgi, G.; Sasso, G.; Togni, A. *J. Organomet. Chem.* **1996**, *506*, 61.

(3) (a) Rockett, B. W.; Marr, G. *J. Organomet. Chem.* **1991**, *416*, 327−398. (b) Dong, T.-Y.; Lai, L.-L. *J. Organomet. Chem.* **1996**, *509*, 131.

(4) (a) Oberhoff, M.; Duda, L.; Karl, J.; Mohr, R.; Erker, G.; Fröhlich, R.; Grehl, M. *Organometallics* **1996**, *15*, 4005. (b) Dong, T.-Y.; Lai, L.-L. *J. Organomet. Chem.* **1996**, *509*, 131. (c) Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502. (d) Buchmeiser, M.; Schottenberger, H. *Organometallics* **1993**, *12*, 2472. (e) Clark, T. J.; Killian, C. M.; Nile, T. A. *J. Organomet. Chem.* **1993**, *462*, 247. (f) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6942. (g) Plenio, H. *Organometallics* **1992**, *11*, 1856. (h) Bunel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Gonzalez, M.; Munoz, N.; Manriquez, J. M. *Organometallics* **1988**, *7*, 789.

(5) (a) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680. (b) Bunel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Barra, C.; Gonzalez, M.; Munoz, N.; Visconti, G.; Aizman, A.; Manriquez, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 6596.

(6) (a) Bickert, P.; Hildebrandt, B.; Hefner, K. *Organometallics* **1984**, *3*, 653. (b) Paquette, L. A.; Schirch, P. F. T.; Hathaway, S. J.; Hsu, L.-Y.; Gallucci, J. C. *Organometallics* **1986**, *5*, 490.

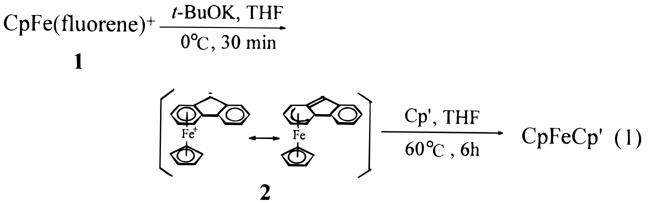
(7) (a) Pomazanova, N. A.; Novikova, L. N.; Ustnyuk, N. A.; Kravtsov, D. N. *Metalloorg. Khim.* **1989**, *2*, 422 (*Chem. Abstr.* **1990**, *112*, 139384c). (b) Kukharenko, S. V.; Strelets, V. V.; Ustynyuk, N. A.; Novikova, L. N.; Denisovitch, L. I.; Peterleitner, M. G. *Metalloorg. Khim.* **1991**, *4*, 299 (*Chem. Abstr.* **1991**, *115*, 29560m).

(8) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Dokl. Akad. Nauk SSSR* **1966**, *166*, 607. (b) Helling, J. F.; Hendrickson, W. A. *J. Organomet. Chem.* **1977**, *141*, 99.

(9) (a) Treichel, P. M.; Johnson, J. W. *J. Organomet. Chem.* **1975**, *88*, 207. (b) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749. (c) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 688. Johnson, J. W.; Treichel, P. M. *J. Am. Chem. Soc.* **1977**, *99*, 1427.

(10) The cyclopentadiene derivatives used in this study were prepared by the reported methods. For the entries 1−3, see: Lee, B. Y.; Moon, H.; Chung, Y. K.; Jeong, N. *J. Am. Chem. Soc.* **1994**, *116*, 2163. For entry 4, see: Rausch, M. D.; wang, Y.-P. *Organometallics* **1991**, *10*, 1438. For entry 5, see: Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1. For entries 7 and 8, see: Leblanc, J. C.; Moise, C. *J. Organomet. Chem.* **1976**, *120*, 65. For entry 10, see: Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 547. Typical procedure for thepreparation of mixed ferrocenes: The substituted cyclopentadiene (0.173 g, 0.87 mmol) (entry 1 in Table 1) was dissolved in 10 mL of THF at −78 °C. To the resulting solution, *n*-BuLi (1.3 mmol, 0.52 mL of a 2.5 M solution in *n*-hexane) was added dropwise during 1 h. The resulting solution was transferred by cannula to another flask containing **2** (generated *in situ* by the reaction of **1** (0.188 g, 0.44 mmol) with *t*-BuOK (0.08 g, 0.7 mmol) for 30 min) in 10 mL of THF at 0 °C. The reaction mixture was heated at 60 °C for 6 h. After cooling to room temperature, water (30 mL) and hexane (30 mL) were added to the reaction mixture and a few drops of 1 N HCl solution were added. The organic layer was separated, dried over anhydrous MgSO$_4$, filtered, and concentrated. Purification was effected by column chromatography on silica gel eluting with hexane. Compound **3** was obtained in 75% yield (0.10 g, 0.33 mmol). ^{1}H NMR (CDCl$_3$) δ 7.55−7.21 (m, 5 H, Ph), 4.36−4.13 (m, 3 H), 4.04 (s, 5 H, Cp), 2.59−2.48 (m, 2 H, CH$_2$), 1.55−1.27 (m, 4 H, CH$_2$), 0.88 (t, 3 H, CH$_3$) ppm; HRMS (*m/z*) M$^+$ calcd 318.1071, obsd 318.1053. Anal. Calcd for C$_{20}$H$_{22}$Fe: C, 75.48; H, 6.97. Found: C, 75.55; H, 7.38. **7**: Mp 158−160 °C; ^{1}H NMR(CDCl$_3$) δ 5.42 (s, 2 H), 4.62 (t, 1.95 Hz, 4 H), 4.27 (t, 1.95 Hz, 4 H), 4.15 (s, 10 H) ppm; HRMS (*m/z*) M$^+$ calcd 396.0264, obsd 396.0586. Anal. Calcd for C$_{22}$H$_{20}$Fe$_2$: C, 66.71; H, 5.09. Found: C, 66.47; H, 5.04. **8**: ^{1}H NMR (CDCl$_3$) δ 7.55−7.445 (m, 2 H, Ph), 7.38−7.21 (m, 3 H, Ph), 3.81 (s, 5 H, Cp), 2.01 (s, 6 H, CH$_3$), 1.95 (s, 6 H, CH$_3$) ppm; HRMS (*m/z*) M$^+$ calcd 318.1071, obsd 318.1273. Anal. Calcd for C$_{20}$H$_{22}$Fe: C, 75.48; H, 6.97. Found: C, 75.39; H, 7.48.

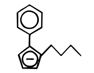
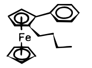
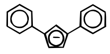
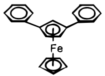
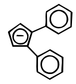
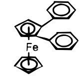
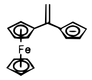
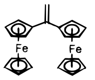
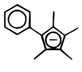
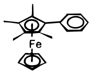
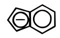
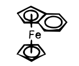
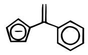
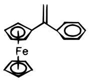
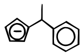
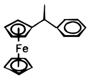
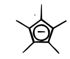
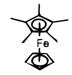
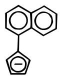
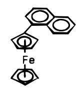
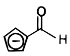
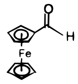
S0276-7333(96)00517-1 CCC: $14.00



Several results presented in Table 1 are worthy of comment. (1) This synthetic route is quite generally applicable to the synthesis of mixed ferrocenes bearing hydrocarbon substituent(s). (2) This route is quite efficient and produces moderate to high yields. Moise and Leblanc[11] reported the formation of **11** by refluxing a solution of $FeCl_2$ with NaCp and the anion from 6-methyl-6-phenylfulvene in THF for 2 days. However, they obtained **11** in only 11% yield. By using the CpFe transfer reaction, **11** was obtained in 81% yield. (3) The reaction is quite straightforward, and therefore, the products are easily separated in pure form. In most cases, byproducts were ferrocene and fluorene. (4) The successful conversion of **6** to **7** demonstrates the utility of this new synthetic route for the preparation of bimetallic 1,1-diferrocenylethylene. The low yield of **7** was due to its partial decomposition during column chromatography on silica gel. After isolation, **7** can be stored in the freezer for several days. Compound **7** cannot be obtained by other routes. (5) Substituted cyclopentadiene derivatives used in this study were easily obtained from readily available organic compounds. Most of the cyclopentadiene derivatives used in this study were known or could be easily synthesized. (6) Multigram quantities of mixed ferrocenes can be obtained.[12] Thus, the route described in this report is quite useful from a synthetic point of view.

At present we have no conclusive mechanism to explain the formation of mixed ferrocenes. However, it is well-known that arene ligands in (arene)$FeCp^+$ cations are readily displaced by other ligands[6,13,14] due to their stability in the free state and the longer bond length[15] of Fe to the arenes compared to the cyclopentadienyl ligands. Thus, we expected that for **2** a ring slippage and ring displacement by a 2e or 6e nucleophile may be possible without difficulty. As we expected, treatment of **2** with $P(OMe)_3$ in THF led to a ligand exchange to yield $CpFe\{P(OMe)_3\}_3^+$.[13] The reaction may involve the nucleophilic substitution by Cp′ anion with a concomitant ring slippage and, finally, ring displacement and the liberation of fluorene and formation of CpFeCp′. A similar interpretation has been presented to explain the formation of $[(arene)M(CO)_3]^{n+}$ (M = Cr, n = 0; M = Mn, n = 1) in the reaction of $[(naphthalene)M(CO)_3]^{n+}$ or (N-methylpyrrole)$Cr(CO)_3$ with arenes.[16]

Table 1. Yields of Mixed Ferrocenes

entry	Cp anions	product		isolated yield(%)
1			3[a]	75
2			4	64
3			5	64
4	 6		7	23
5			8	56
6			9	81
7			10	61
8			11	81
9			12	48
10			13	90
11			14	56

[a] An isomeric mixture.

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(11) Compounds **4**, **5**, and **9**−**14** are known compounds. The formation of **4**, **5**, **9**, and **12**−**14** were confirmed by checking ^1H NMR spectra. Compounds **10** and **11** were confirmed by ^1H NMR spectra, elemental analysis, and high-resolution mass. See the following papers. **4**: Rosenblum, M.; Howells, W. G.; Banerjee, A. K.; Bennet, C. *J. Am. Chem. Soc.* **1962**, *84*, 2726. Kamezawa, N. *J. Magn. Reson.* **1973**, *11*, 88. **5**: Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1956**, 3030. **9**: King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 796. Treichel, P. M.; Johnson, J. W. *J. Organomet. Chem.* **1975**, *88*, 207. **10**: Horspool, W. M.; Sutherland, R. G.; Thomson, B. J. *J. Chem. Soc. C* **1971**, 1550. Cardin, C. J.; Crawford, W.; Watts, W. E.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1979**, 970. **11**: Leblanc, J. C.; Moise, C. *J. Organomet. Chem.* **1976**, *120*, 65. **12**: Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680. **13**: Nesmeyanov, A. N.; Sazonova, V. A.; Drozd, V. N. *Dokl. Akad. Nauk SSSR* **1965**, *165*, 575. Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 547. **14**: Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^1H FT-NMR Spectra*; Aldrich Chemical: Milwaukee, WI, 1992; Vol. 1(3), 771A.

(12) The cyclopentadiene ligand (6.60 g, 39 mmol, 1.5 equiv) (entry 8 in Table 1) in 30 mL of THF was treated with n-BuLi (5 mL of 10 M solution in hexanes, 50 mmol) at −78 °C. The resulting solution was transferred by cannula to another flask containing **2** (generated *in situ* by the reaction of **1** (11.24 g, 26 mmol) and t-BuOK (39 mmol, 4.38 g in 120 mL of THF) at 0 °C). The reaction mixture was heated at 60 °C for 6 h. After cooling of the mixture to room temperature, water (100 mL) and hexane (300 mL) were added to the reaction mixture and, subsequently, 50 mL of saturated NH_4Cl solution. The organic layer was separated and purified. The yield based on **2** was 81% (6.10 g).

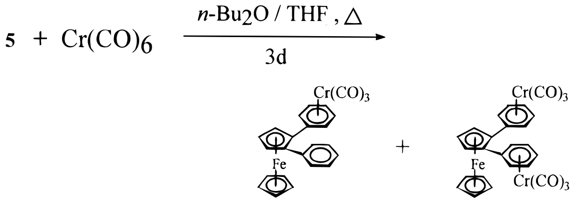
(13) (a) Gill, T. P.; Mann, K. R. *J. Organomet. Chem.* **1981**, *216*, 65. (b) Lee, C. C.; Gill, U. S.; Iqbal, M.; Azogu, C. I.; Sutherland, R. G. *J. Organomet. Chem.* **1982**, *231*, 151. Compounds **2** (generated *in situ* by the reaction of 0.86 g (2 mmol) of **1** and t-BuOK (0.38 g, 3.4 mmol) in 10 mL of THF at 0 °C) and $P(OMe)_3$ (0.94 mL, 8 mmol) were dissolved in 20 mL of THF. The solution was heated at reflux for 5 h and cooled to room temperature. A solution of $HBF_4 \cdot OEt_2$ (4 mmol) was added to the reaction mixture to provide a suitable counteranion. The resulting solution was concentrated and the product precipitated by adding an excess of Et_2O. The precipitates was filtered, recrystallized from CH_2Cl_2/Et_2O, and dried. The product was obtained in 71% (0.82 g) yield. The ^1H NMR spectrum of the product was the same as that reported by Gill and Mann.[13a] FAB mass (M^+): m/z 493.

(14) (a) Roberts, R. M. G.; Wells, A. S. *Inorg. Chim. Acta* **1986**, *112*, 171. (b) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 534. (c) Darchen, A. *J. Chem. Soc., Chem. Commun.* **1983**, 768.

(15) Houlton, A.; Roberts, R. M. G.; Silver, J.; Wells, A. S.; Frampton, C. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 1018.

(16) (a) Sun, S.; Yeung, L. K.; Sweigart, D. A.; Lee, T.-Y.; Lee, S. S.; Chung, Y. K.; Switzer, S. R.; Pike, R. D. *Organometallics* **1995**, *14*, 2613. (b) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183. Goti, A.; Semmelhack, M. F. *J. Organomet. Chem.* **1994**, *470*, C4.

One of the ways to prepare bi- and polymetallic compounds is through the utilization of a compound having cyclopentadienyl or phenyl rings.[17] Thus, we expected that **5** could be used to make bi- or trimetallic compounds. Reaction of **5** with $Cr(CO)_6$ gave **15** and **16** in 18% and 62% yields, respectively (eq 2).[18]



15 **16** (2)

The molecular structure of **16** was studied by X-ray crystallography (Figure 1).[19] At first, we expected that the two $Cr(CO)_3$ moieties would be in syn arrangement. However, the two $Cr(CO)_3$ moieties are in anti conformation presumably due to steric congestion. To reduce the steric congestion between the two $Cr(CO)_3$ moieties, the two phenyl groups are not in the same plane as the cyclopentadienyl ring. Recently, we and our collaborator[20] reported the control of ligand substitution and addition to (arene)$Cr(CO)_3$ complexes by attachment of a self-closing redox-switch ferrocenyl group. We expect that **15** and **16** will show similar chemical behavior.

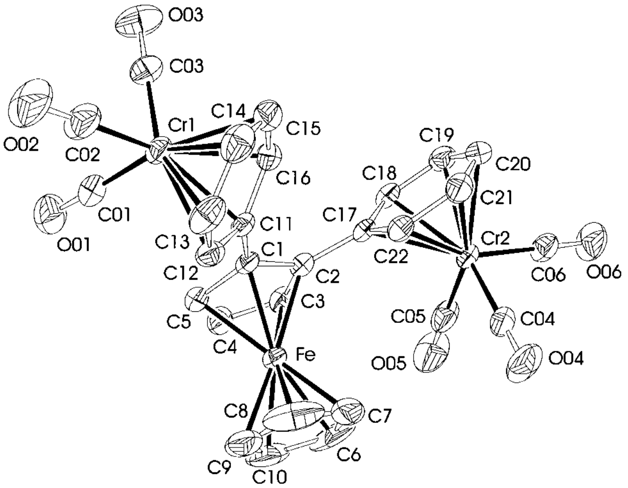


Figure 1. ORTEP drawing of **16** with the atomic numbering. Selected bond distances (Å): Fe−C(1), 2.049(4); Fe−C(3), 2.042(4); Fe−C(4), 2.024(4); C(1)−C(2), 1.445(5); C(2)−C(3), 1.419(6); C(3)−C(4), 1.414(6); C(1)−C(11), 1.476(5). Selected bond angles (deg): C(1)−C(2)−C(3), 107.1(3); C(1)−C(5)−C(4), 108.9(4); C(2)−C(1)−C(5), 106.9(3); C(1)−C(2)−C(17), 125.7(3); Cr(1)−C(03)−O(03), 179.5(3).

The synthetic method described in this communication is generally applicable to the synthesis of mixed ferrocenes. In particular, it will be very useful for the construction of mixed ferrocenes suitable for the syntheses of charge-transfer complexes and thermotropic liquid crystals.[21] The physical studies of the biferrocene compound **7** and the heterobimetallic compounds **15** and **16** are in progress.

Acknowledgment. The authors are grateful for the financial support from the SNU DaeWoo Research Fund and the Center for Molecular Catalysis.

Supporting Information Available: Tables giving crystal data and refinement details, atomic coordinates, thermal parameters, and bond distances and angles for **16** (7 pages). Ordering information is given on any current masthead page.

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[17] (a) Chung, T.-M.; Chung, Y. K. *Organometallics* **1992**, *11*, 2822. (b) Lee, B. Y.; Moon, H.; Chung, Y. K.; Jeong, N.; Carpenter, G. *Organometallics* **1993**, *12*, 2973. (c) Kim, J.-A.; Chung, T.-M.; Chung, Y. K.; Jung, J.-H.; Lee, S. W. *J. Organomet. Chem.* **1995**, *486*, 211. (d) Kang, Y. K.; Chung, Y. K.; Lee, S. W. *Organometallics* **1995**, *14*, 4905.

[18] Preparation of compounds **15** and **16**: Compound **4** (0.12 g, 0.35 mmol) and $Cr(CO)_6$ (0.31 g, 1.4 mmol) were dissolved in a mixture of n-Bu_2O (50 mL) and THF (5 mL). The resulting solution was heated at reflux for 3 d. The reaction mixture was filtered, concentrated, and column chromatographed on silica gel eluting with a mixture of hexane and ethyl acetate (v/v, 10:1) and then with CH_2Cl_2. The first eluted compound was **15**, and the next was **16**. Compounds **15** and **16** were obtained in 18% (0.03 g, 0.06 mmol) and 62% yield (0.13 g, 0.22 mmol), respectively. **15**: Mp 53−56 °C; IR ν(CO) 1950, 1864 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4−7.2 (m, 5 H, Ph), 5.8−5.2 (m, 5 H, Ph), 4.71 (dd, 1.46, 2.44 Hz, 1 H), 4.51 (dd, 1.46, 2.44 Hz, 1 H), 4.44 (t, 2.44 Hz, 1 H), 4.19 (s, 5 H, Cp) ppm; HRMS (m/z) M^+ calcd 474.0010, obsd 474.0014. Anal. Calcd for $C_{25}H_{18}FeCrO_3$: C, 63.31; H, 3.82. Found: C, 63.50; H, 3.99. **16**: Mp 194−196 °C; IR ν(CO) 1946, 1859 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.8−5.2 (m, 10 H, Ph), 4.86 (d, 2.68 Hz, 2 H), 4.52 (t, 2.68 Hz, 1 H), 4.33 (s, 5 H, Cp) ppm. Anal. Calcd for $C_{28}H_{18}Cr_2FeO_6$: C, 55.11; H, 2.97. Found: C, 55.06; H, 2.91.

[19] Single crystals suitable for X-ray analysis were obtained by CH_2Cl_2 and hexane: monoclinic; $a = 13.749(2)$, $b = 9.841(3)$, $c = 18.711(5)$ Å; $\beta = 106.92(2)°$; space group $P2_1/a$; $Z = 4$; $D_{calcd} = 1.673$ g cm^{-3}; 3017 independent reflections ($2.28° < \theta < 24.96°$); solution of the structure by the conventional heavy-atom method (SHELXS-86); hydrogen positions calculated according to ideal geometry with a C−H bond length 1.08 Å. Refinement by use of SHELXL-93 with anisotropic temperature factors for all non-hydrogen atoms gave $R = 0.0387$ and $wR^2 = 0.0925$ for 3017 unique reflections with $I > 2\sigma(I)$.

[20] Yeung, L. K.; Kim, J. E.; Chung, Y. K.; Sweigart, D. A. *Organometallics* **1996**, *15*, 3891.

[21] (a) Deschenaux, R.; Izvolenski, V.; Turpin, F.; Guillon, D.; Heinrich, B. *J. Chem. Soc., Chem. Commun.* **1996**, 439. (b) Deschenaux, R.; Kosztics, U.; Scholten, U.; Guillon, D.; Ibn-Elhaj, M. *J. Mater. Chem.* **1994**, *4*, 1351. (c) Constable, E. C.; Edwards, A. J.; Manez, R. M.; Raithby, P. R.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1994**, 645. (d) Bosque, R.; Lopez, C.; Sales, J.; Solans, X.; Bardia, M. F. *J. Chem. Soc., Dalton Trans.* **1994**, 735. (e) Bosque, R.; Bardia, M. F.; Lopez, C.; Sales, J.; Silver, J.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1994**, 747. (f) Bhadhabe, M. M.; Das, A.; Jeffery, J. C.; McCleverty, J. A.; Novas Badiola, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2769.