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Transition Metal Complexes in Organic Synthesis. Part 46 [1]

Synthesis of 5-Arylmethyl-substituted Tricarbonyl(1-4-η-cyclohexa-1,3-diene)iron Complexes

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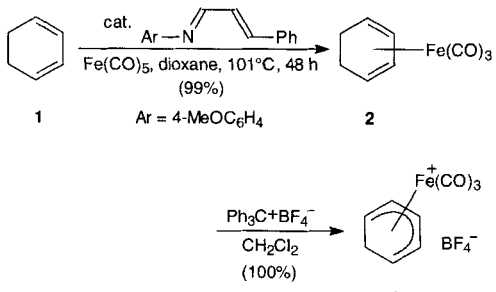
Abstract. The reaction of tricarbonyl(η^5-cyclohexadienylium) iron tetrafluoroborate **3** with the methyl arylacetate **6**, the dimethyl arylmalonate **12**, and the di-*tert*-butyl arylmalonate **14** provides regio- and stereoselectively the tricarbonyliron-complexed 5-arylmethylcyclohexa-1,3-dienes **7**, **13**, and **15**.

The addition of nucleophiles to tricarbonyliron-complexed cyclohexadienyl cations is a useful method for regio- and stereoselective C–C bond formation at six-membered ring systems, which has found many applications to organic synthesis [2]. The regioselectivity of these reactions, addition of the nucleophile at one of the termini of the coordinated π system, is rationalized by the Davies-Green-Mingos rules [3]. The stereoselectivity, attack from the diene face opposite to the iron atom (*anti* selectivity), is a consequence of the steric demand of the bulky tricarbonyliron moiety. In connection with our studies directed towards the application of transition metal complexes to the synthesis of heterocyclic compounds we were searching for an access to tricarbonyliron-complexed 5-(nitroarylmethyl)cyclohexa-1,3-dienes. In the present paper we describe the regioselective synthesis of arylmalonic acid esters by nucleophilic aromatic *ipso*-substitution of a chloroarene and their subsequent regio- and stereoselective addition to tricarbonyl(η^5-cyclohexadienylium)iron tetrafluoroborate. Arylmalonic acid esters represent useful precursors for the synthesis of nonsteroidal antiinflammatory agents and barbiturates, and their preparation by reaction of 2-substituted malonates with (η^6-arene)tricarbonylchromium complexes was recently reported in this journal [4].

Results and Discussion

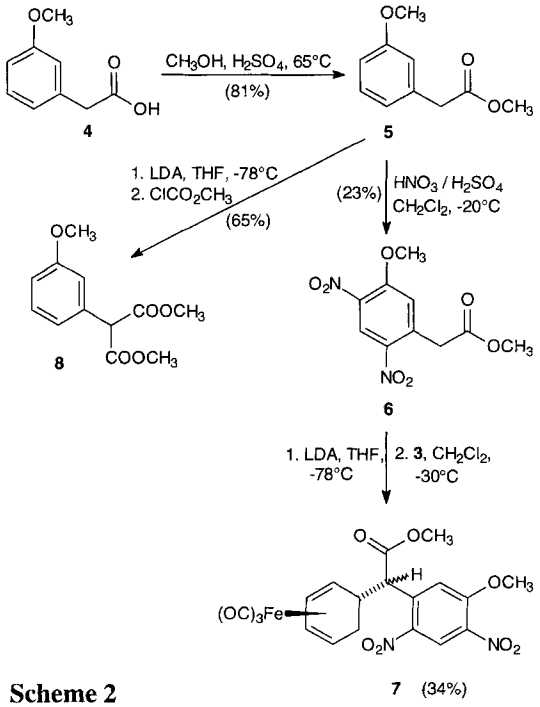
The 1-azabuta-1,3-diene-catalyzed complexation of cyclohexa-1,3-diene **1** with pentacarbonyliron to tricarbonyl(η^4-cyclohexa-1,3-diene)iron **2** [1, 5] and subsequent hydride abstraction using triphenylmethyl tetrafluoroborate provide tricarbonyl(η^5-cyclohexadienylium)iron tetrafluoroborate **3** in virtually quantitative overall yield [6] (Scheme 1).



Scheme 1

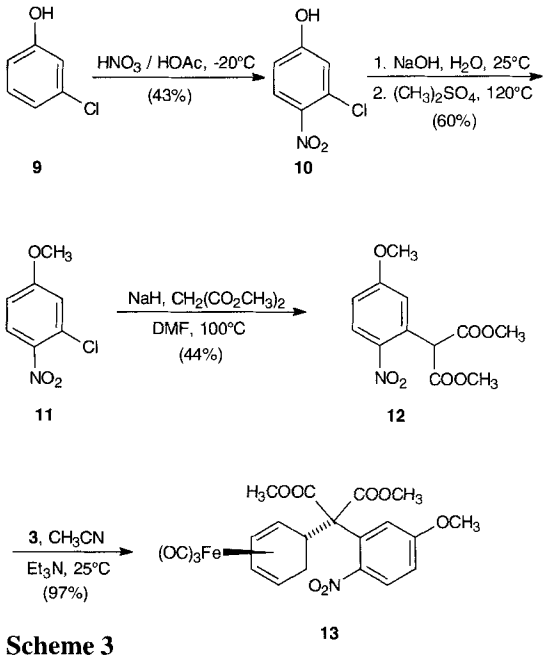
In our first approach to substituted tricarbonyliron-complexed 5-arylmethylcyclohexa-1,3-dienes we started from phenylacetic acid derivatives. Methyl 3-methoxyphenylacetate **5** was prepared from commercial 3-methoxyphenylacetic acid **4** (Scheme 2). Nitration of

5 with fuming nitric acid/conc. sulfuric acid in dichloromethane at −20 °C provided methyl 5-methoxy-2,4-dinitrophenylacetate **6** in only 23% yield along with methyl 3-methoxy-4-nitrophenylacetate (16% yield) and methyl 3-methoxy-2,6-dinitrophenylacetate (4% yield). Structural assignments are based on ^{1}H NMR and ^{13}C NMR spectral data and are supported by NOE experiments (see experimental section).



Scheme 2

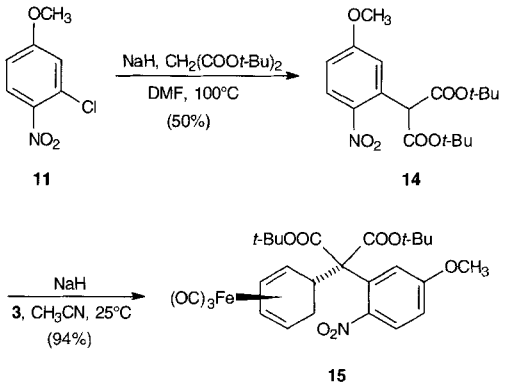
The formation of carbon–carbon bonds by nucleophilic additions to tricarbonyliron-complexed cyclohexadienyl cations were generally achieved by using soft nucleophiles [2]. However, reactions with alkyllithium reagents in dichloromethane at −78 °C [7] or with lithium ester enolates in tetrahydrofuran at −78 °C [8] provide the corresponding 5-substituted cyclohexadiene-tricarbonyliron complexes in high yields. Deprotonation of the dinitro derivative **6** using lithium diisopropylamide in tetrahydrofuran at −78 °C followed by addition of a suspension of the complex salt **3** in dichloromethane at −30 °C afforded the tricarbonyliron complex **7** in 34% yield as a 3:2 mixture of two diastereoisomers. Much better results for nucleophilic additions to tricarbonyliron-complexed cyclohexadienyl cations were achieved by using stabilized carbanions resulting from deprotonation of β-diketones, β-ketoesters, and dialkyl malonates [9]. Therefore, we decided to transform the methyl arylacetate **5** into the dimethyl arylmalonate **8**. Deprotonation of **5** with lithium diisopropylamide at −78 °C and subsequent addition of methyl chloroformate afforded dimethyl 3-methoxyphenylmalonate **8** in a yield of 65%. However, the projected nitration of the aromatic ring to the dimethyl 5-methoxy-2-nitrophenylmalonate **12** was not successful and resulted in an inseparable mixture of isomers.



Scheme 3

Finally, compound **12** was prepared by a variation of the reaction sequence in which first the nitro group and then the dialkyl malonate substituent were introduced to the aryl ring (Scheme 3). Nitration of 3-chlorophenol **9** following a literature procedure [10] with nitric acid/glacial acetic acid at −30 °C afforded the desired 3-chloro-4-nitrophenol **10** in 43% yield along with 5-chloro-2-nitrophenol (20% yield) and 25% of the starting material **9**. Subsequent *O*-methylation of the 3-chloro-4-nitrophenol **10** gave 3-chloro-4-nitroanisole **11** in 60% yield (38% of the starting material **10** were recovered). The nucleophilic aromatic *ipso*-substitution at the regioisomeric 4-chloro-3-nitroanisole by replacement of the chloro substituent with dimethyl malonate was previously reported (70% yield) [11]. Treatment of 3-chloro-4-nitroanisole **11** with sodium dimethyl malonate in *N*,*N*-dimethylformamide at 100 °C provided by *ipso*-substitution of the chloroatom dimethyl 5-methoxy-2-nitrophenylmalonate **12** in 44% yield. The reaction of the dimethyl arylmalonate **12** with the complex salt **3** in the presence of triethylamine at room temperature afforded almost quantitatively the tricarbonyliron complex **13**. Surprisingly, the attempt to reduce the ester functions of complex **13** with diisobutylaluminum hydride (DIBAL) resulted in cleavage of the carbon–carbon bond and regenerated the arylmalonate **12** (62% yield) along with the tricarbonyl(η^4-cyclohexa-1,3-diene)iron **2** (36% yield). In contrast to this observation,

the 5-dimethylmalonyl-substituted tricarbonyl(η^4-cyclohexa-1,3-diene)iron complex was successfully reduced by DIBAL to the corresponding diol as described by Pearson [12].



Scheme 4

The bulky di-*tert*-butyl malonyl group could also be introduced by the sequence described above. Thus, *ipso*-substitution of 3-chloro-4-nitroanisole **11** by sodium di-*tert*-butyl malonate in *N,N*-dimethylformamide at 100 °C afforded di-*tert*-butyl 5-methoxy-2-nitrophenylmalonate **14** in 50% yield. Deprotonation of the di-*tert*-butyl arylmalonate **14** by using sodium hydride followed by alkylation with the complex salt **3** provided the tricarbonyliron complex **15** in 94% yield.

A tricarbonyliron-complexed 5-substituted η^4-cyclohexa-1,3-diene ring can be easily converted to a phenyl ring by demetalation and subsequent dehydrogenation [2]. Therefore, the tricarbonyliron complexes **13** and **15** are precursors for dialkyl arylphenylmalonates.

Conclusion

Ipso-substitution of 3-chloro-4-nitroanisole by dialkyl malonates provides an easy access to dialkyl arylmalonates which represent potential synthons for the synthesis of biologically active compounds. Deprotonation of the dialkyl arylmalonates and subsequent alkylation with the tricarbonyliron-complexed cyclohexadienylium cation afford in high yields the tricarbonyliron-complexed 5-arylmethylcyclohexa-1,3-dienes.

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Experimental

All reactions were carried out using anhydrous solvents under an argon atmosphere. Flash chromatography: Baker or Merck silica gel (0.03–0.06 mm). Melting points: Büchi 535. IR spectra: Perkin-Elmer 882 and IFS 88 (FT-IR); $\tilde{\nu}$ in cm^{-1}. ^1H NMR and ^{13}C NMR spectra: Bruker AC-250, AM-400, and DRX-500; internal standard: tetramethylsilane or the signal of the deuterated solvent; δ in ppm, coupling constants J in Hz. Mass spectra: Finnigan MAT-90; ionization potential: 70 eV. Elemental analysis: Heraeus CHN-Rapid.

Methyl 3-methoxyphenylacetate (**5**)

Methanol (4.81 g, 6.1 ml, 150 mmol) and a catalytic amount of conc. sulfuric acid (628 mg, 0.34 ml, 6.4 mmol) were added to 3-methoxyphenylacetic acid (**4**) (4.99 g, 30 mmol). The reaction mixture was stirred for 5 h at reflux, methanol was evaporated *in vacuo*, and ice-water was added to the residue. The mixture was extracted three times with ether, the combined organic layers were washed twice with a saturated aqueous solution of sodium bicarbonate, and then with water. The organic layer was dried over magnesium sulfate and the solvent was removed to provide the acetate **5** as a yellow liquid. Yield 4.40 g (81%). — IR (film): $\tilde{\nu}$ /cm^{-1} = 3001, 2953, 2837, 1735, 1598, 1583, 1488, 1452, 1434, 1260, 1149, 1090, 1048, 1012, 949, 877, 843, 771, 717, 691. – ^1H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.58 (s, 2H), 3.67 (s, 3H), 3.77 (s, 3H), 6.77–6.86 (m, 3H), 7.22 (t, J = 7.7 Hz, 1H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ/ppm = 41.21 (CH_2), 52.03 (CH_3), 55.16 (CH_3), 112.63 (CH), 114.92 (CH), 121.59 (CH), 129.55 (CH), 135.41 (C), 159.73 (C), 171.88 (C=O). – MS (35 °C): *m/z* (%) = 180 (81, M^+), 121 (100), 102 (6), 91 (11), 78 (4). – HRMS: Calcd. for $C_{10}H_{12}O_3$ (M^+): 180.0786, found: 180.0793.

Methyl 5-methoxy-2,4-dinitrophenylacetate (**6**)

A solution of fuming nitric acid (3.15 g, 2.0 ml, 50 mmol) and conc. sulfuric acid (6.28 g, 3.4 ml, 64 mmol) in dichloromethane (10 ml) was added slowly to a solution of methyl 3-methoxyphenylacetate (**5**) (5.00 g, 27.7 mmol) at –20 °C and stirred for 30 min at this temperature. The reaction mixture was washed twice with a diluted solution of sodium bicarbonate and then with water. The organic layer was dried over magnesium sulfate, the solvent was evaporated *in vacuo*, and the residue was subjected to flash chromatography (hexane/EtOAc 1:2) on silica gel to provide as the less polar fraction methyl 3-methoxy-4-nitrophenylacetate, then methyl 3-methoxy-2,6-dinitrophenylacetate, and methyl 5-methoxy-2,4-dinitrophenylacetate (**6**) as the most polar fraction.

Methyl 3-methoxy-4-nitrophenylacetate

Yield 995 mg (16%), colorless crystals. – *m.p.* 63–65 °C. – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3116, 3083, 3009, 2985, 2954, 2847, 1737, 1609, 1588, 1511, 1492, 1461, 1437, 1334, 1260, 1201, 1072, 1024, 1002, 934, 901, 870, 830, 747, 711. – ^1H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.72 (s, 3H), 3.90 (s, 3H), 4.01 (s, 2H), 6.80 (d, J = 2.7 Hz, 1H), 6.92 (dd, J = 9.1, 2.7 Hz, 1H), 8.20 (d, J = 9.1 Hz, 1H). – ^1H NMR NOE experiments (400 MHz, $CDCl_3$), δ/ppm: 1. Irradiation at 3.90, observed NOE 6.80, 2. irradiation at 4.01, observed NOE's 6.80, 6.92, 3. irradiation at 6.80, observed NOE's 3.90, 4.01, 4. irradiation at 6.92, observed NOE's 4.01, 8.20, 5. irradiation at 8.20, observed NOE 6.92. – ^{13}C NMR and DEPT (100 MHz,

$CDCl_3$): δ/ppm = 40.44 (CH_2), 52.23 (CH_3), 55.93 (CH_3), 113.01 (CH), 118.62 (CH), 128.10 (CH), 132.74 (C), 141.59 (C), 163.43 (C), 170.43 (C=O). – MS (40 °C): *m/z* (%) = 225 (13, M^+), 194 (12), 179 (100), 151 (10), 136 (8), 122 (5), 106 (10). – HRMS: Calcd. for $C_{10}H_{11}NO_5$ (M^+): 225.0637, found: 225.0641.

Methyl 3-methoxy-2,6-dinitrophenylacetate

Yield 293 mg (4%), colorless crystals. – *m.p.* 115–118 °C. – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3095, 2955, 1737, 1611, 1584, 1523, 1476, 1432, 1348, 1294, 1211, 1071, 997, 933, 906, 866, 828, 751, 727, 667. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.73 (s, 3H), 3.96 (s, 2H), 4.02 (s, 3H), 7.15 (d, *J* = 9.3 Hz, 1H), 8.33 (d, *J* = 9.3 Hz, 1H). – ^{1}H NMR NOE experiments (400 MHz, $CDCl_3$), δ/ppm: 1. Irradiation at 3.96, observed NOE none, 2. irradiation at 4.02, observed NOE 7.15, 3. irradiation at 7.15, observed NOE's 4.02, 8.33. – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ/ppm = 34.03 (CH_2), 52.68 (CH_3), 57.23 (CH_3), 111.53 (CH), 124.58 (C), 128.78 (CH), 141.38 (C), 142.68 (C), 154.54 (C), 168.36 (C=O). – MS (75 °C): *m/z* (%) = 270 (1, M^+), 239 (15), 224 (100), 207 (27), 179 (40), 59 (13). – HRMS: Calcd. for $C_{10}H_{10}N_2O_7$ (M^+): 270.0488, found: 270.0452.

Methyl 5-methoxy-2,4-dinitrophenylacetate (**6**)

Yield 1.75 g (23%), light yellow crystals. – *m.p.* 95–98 °C. – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3131, 3073, 2980, 2965, 2945, 2849, 1727, 1616, 1594, 1521, 1437, 1353, 1290, 1214, 1167, 1053, 996, 903, 863, 833, 760, 742, 710, 679. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.74 (s, 3H), 4.10 (s, 3H), 4.13 (s, 2H), 7.05 (s, 1H), 8.77 (s, 1H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ/ppm = 40.26 (CH_2), 52.61 (CH_3), 57.45 (CH_3), 117.85 (CH), 124.12 (CH), 137.25 (C), 137.61 (C), 140.27 (C), 156.01 (C), 169.26 (C=O). – MS (75°C): *m/z* (%) = 270 (2, M^+), 239 (9), 224 (100), 177 (4), 135 (7), 59 (13). – HRMS: Calcd. for $C_{10}H_{10}N_2O_7$ (M^+): 270.0488, found: 270.0470.

Tricarbonyl[methyl (2-5-η)cyclohexa-2,4-dienyl(5-methoxy-2,4-dinitrophenyl)acetate]iron (**7**)

A 1.6M solution of *n*-butyllithium in hexane (2.9 ml, 4.64 mmol) was added slowly to a stirred solution of diisopropylamine (564 mg, 0.73 ml, 5.57 mmol) in tetrahydrofuran (10 ml) at –6 °C. After stirring for 15 min the mixture was cooled to –78 °C and a solution of compound **6** (500 mg, 1.85 mmol) in tetrahydrofuran (3 ml) was added over a period of 10 min. The resulting brown suspension was stirred for 1.5 h, warmed to –30 °C, and a suspension of the complex salt **3** (470 mg, 1.54 mmol) in dichloromethane (16 ml) was added slowly. After a reaction time of 19 h at –30 °C hydrochloric acid (10%, 10 ml) was added. The mixture was stirred at 25 °C for further 10 min, ether (30 ml) was added, and the layers were separated. The organic layer was washed twice with water, dried over magnesium sulfate, and the solvent was evaporated *in vacuo*. The residue was subjected to flash chromatography (hexane/EtOAc 2:1) on silica gel to afford two diastereoisomers of the iron complex **7**. The major diastereoisomer was isolated as the less polar fraction (yield 154 mg, 20%, colorless crystals) and the minor diastereoisomer was eluted as the more polar fraction (yield 104 mg, 14%, brown oil). Yield of **7**: 258 mg (34%) as diastereoisomers in a ratio of 3:2. – Major diastereoisomer: *m.p.* 170–172 °C. IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3074, 3001, 2954, 2859, 2040, 1950, 1731, 1608, 1587, 1521, 1457, 1336, 1279, 1159, 1054, 984, 871, 831, 740, 707, 618, 532, 503. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 1.40 (br d, *J* = 15.0 Hz, 1H), 2.20 (ddd, *J* = 15.0, 11.3, 4.0 Hz, 1H), 2.36 (m, 1H), 2.71 (m, 1H), 3.06 (m, 1H), 3.64 (s, 3H), 4.08 (s, 3H), 4.18 (d, *J* = 10.6 Hz, 1H), 5.18 (br t, *J* = 5 Hz, 1H), 5.41 (br t, *J* = 5 Hz, 1H), 7.36 (s, 1H), 8.54 (s, 1H). – MS (125 °C): *m/z* (%) = 488 (2, M^+), 460 (3), 432 (100), 404 (80), 374 (67), 345 (15), 316 (12), 280 (16), 232 (17), 219 (26), 165 (28), 135 (33), 78 (31), 56 (33). – HRMS: Calcd. for $C_{19}H_{16}FeN_2O_{10}$ (M^+): 488.0154, found: 488.0132. – Minor diastereoisomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 1.13 (br d, *J* = 15.0 Hz, 1H), 1.74 (ddd, *J* = 15.0, 10.9, 4.0 Hz, 1H), 2.81 (m, 1H), 2.99 (m, 1H), 3.06 (m, 1H), 3.71 (s, 3H), 4.05 (s, 3H), 4.12 (d, *J* = 10.7 Hz, 1H), 5.41 (br t, *J* = 5 Hz, 1H), 5.47 (br t, *J* = 5 Hz, 1H), 7.30 (s, 1H), 8.47 (s, 1H).

Dimethyl 3-methoxyphenylmalonate (**8**)

A 1.6M solution of *n*-butyllithium in hexane (43.4 ml, 69.4 mmol) was added slowly to a stirred solution of diisopropylamine (8.57 g, 11.1 ml, 84.7 mmol) in tetrahydrofuran (160 ml) at –6 °C. After 15 min the mixture was cooled to –78 °C, methyl 3-methoxyphenylacetate (**5**) (5.00 g, 27.7 mmol) was added over a period of 10 min, and the reaction mixture was stirred for 2 h at –78 °C. After addition of methyl chloroformate (3.95 g, 3.23 ml, 41.8 mmol) the mixture was stirred for further 2 h at –78 °C, then warmed to 25 °C, and quenched with ice-water (50 ml). The layers were separated, the organic layer was washed twice with a saturated aqueous solution of ammonium chloride, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with water and dried over magnesium sulfate. The solvent was evaporated and the residue was distilled (176 °C/0.1 mbar) to afford the malonate **8** as a light yellow oil. Yield 4.30 g (65%). – IR (film): $\tilde{\nu}$ /cm^{-1} = 3003, 2956, 2839, 1734, 1598, 1584, 1490, 1432, 1309, 1258, 1148, 1091, 1025, 939, 914, 882, 855, 783, 747, 692. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.75 (s, 6H), 3.80 (s, 3H), 4.63 (s, 1H), 6.86–6.89 (m, 1H), 6.95–6.97 (m, 2H), 7.28 (m, 1H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ/ppm = 52.84 ($2CH_3$), 55.23 (CH_3), 57.48 (CH), 113.92 (CH), 114.86 (CH), 121.55 (CH), 129.62 (CH), 133.85 (C), 159.71 (C), 168.44 (2C=O). – MS (20 °C): *m/z* (%) = 238 (57, M^+), 180 (85), 179 (21), 151 (26), 135 (7), 121 (100), 91 (17), 78 (7), 59 (5). – HRMS: Calcd. for $C_{12}H_{14}O_5$ (M^+): 238.0841, found: 238.0819.

3-Chloro-4-nitrophenol (**10**)

A mixture of nitric acid (65%, 9.1 ml, 0.13 mol) and glacial acetic acid (25.5 ml) was added slowly to a cold solution (–20 °C) of 3-chlorophenol (**9**) (8.53 g, 7.00 ml, 66.4 mmol) in glacial acetic acid (8.5 ml). The reaction mixture was stirred for 2.5 h at –20 °C, diluted with water (75 ml), and subjected to a steam distillation. On cooling of the aqueous distillate to 0 °C the by-product, 5-chloro-2-nitrophenol, was obtained by crystallization (yield 2.3 g, 20%, light yellow crystals). The residue of the distillation was neutralized by addition of sodium bicarbonate and extracted with ether. The combined organic

layers were washed with water and dried over magnesium sulfate. Removal of the solvent and flash chromatography (hexane/EtOAc 4:1) of the residue on silica gel afforded as the less polar fraction the starting material **9** (2.1 g, 25%) and as the more polar fraction the 4-nitrophenol **10** (yield 5.0 g, 43%, yellow crystals).

5-Chloro-2-nitrophenol

m.p. 39–40 °C (ref. [10]: *m.p.* 39.5–40 °C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 6.98 (dd, J = 9.0, 2.2 Hz, 1H), 7.19 (d, J = 2.2 Hz, 1H), 8.07 (d, J = 9.0 Hz, 1H), 10.66 (s, 1H).

3-Chloro-4-nitrophenol (**10**)

m.p. 121–122 °C (ref. [10]: *m.p.* 120–120.5 °C). – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3380 (br), 3098, 1594, 1578, 1504, 1477, 1426, 1327, 1298, 1241, 1192, 1119, 1037, 923, 853, 837, 821, 746, 681, 626. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 5.66 (s, 1H), 6.84 (dd, J = 8.9, 2.7 Hz, 1H), 7.02 (d, J = 2.7 Hz, 1H), 7.98 (d, J = 8.9 Hz, 1H). – MS (20°C): *m/z* (%) = 175 (29, M$^+$ + 2), 173 (100, M$^+$), 157 (5), 145 (14), 143 (47), 127 (8), 117 (4), 115 (15), 101 (9), 99 (34), 75 (5), 73 (16), 63 (22). – HRMS: Calcd. for $C_6H_4ClNO_3$ (M$^+$): 172.9880, found: 172.9884.

3-Chloro-4-nitroanisole (**11**)

A solution of sodium hydroxide (2.95 g, 73.8 mmol) in water (14 ml) was added to 3-chloro-4-nitrophenol (**10**) (6.4 g, 36.9 mmol) and stirred for 30 min at room temperature. After addition of dimethyl sulfate (14.1 g, 10.6 ml, 112 mmol) the reaction mixture was heated at 120 °C for 4 h. The cold mixture was washed with an aqueous solution of sodium hydroxide (10%) and the aqueous layer was extracted with ether. The combined organic layers were washed with water and dried over magnesium sulfate. The solvent was evaporated, and the residue was subjected to flash chromatography (hexane/EtOAc 3:1) on silica gel. As the less polar fraction the starting material (2.47 g, 38%) was eluted, and as the more polar fraction the nitroanisole **11** was isolated as light yellow crystals. Yield 4.18 g (60%). – *m.p.* 53–55 °C (ref. [10]: 53–55°C). – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3104, 3024, 2988, 2946, 2843, 1589, 1511, 1470, 1340, 1281, 1225, 1036, 867, 815, 742, 680, 612, 552. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.88 (s, 3H), 6.87 (dd, J = 9.1, 2.7 Hz, 1H), 7.01 (d, J = 2.7 Hz, 1H), 8.00 (d, J = 9.1 Hz, 1H). – MS (20 °C): *m/z* (%) = 189 (32, M$^+$ + 2), 187 (100, M$^+$), 159 (21), 157 (66), 141 (5), 129 (13), 128 (14), 126 (43), 113 (4), 111 (11), 98 (10), 77 (16), 75 (12), 63 (33). – HRMS: Calcd. for $C_7H_6ClNO_3$ (M$^+$): 187.0036, found: 187.0055.

Dimethyl 5-methoxy-2-nitrophenylmalonate (**12**)

Dimethyl malonate (856 mg, 0.74 ml, 6.48 mmol) was added slowly to a suspension of sodium hydride (156 mg, 6.48 mmol) in *N,N*-dimethylformamide (2 ml) at room temperature, heated at 50 °C for 30 min, and then diluted with *N,N*-dimethylformamide (3 ml). A solution of the anisole **11** (500 mg, 2.67 mmol) in *N,N*-dimethylformamide (2 ml) was added over a period of 10 min, and the reaction mixture was heated to 100 °C (the color of the mixture turned to dark red). After a reaction time of 50 h at this temperature ether was added, and the mixture was washed with water. The organic layer was dried over magnesium sulfate, the solvent was evaporated *in vacuo*, and the residue was subjected to flash chromatography (hexane/EtOAc 3:1) on silica gel to provide a yellow oil. Crystallization from ether at –10 °C afforded **12** as colorless crystals. Yield 336 mg (44%). – *m.p.* 86–88 °C. – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 2979, 2951, 2846, 1748, 1729, 1613, 1582, 1512, 1457, 1437, 1345, 1308, 1251, 1220, 1154, 1084, 1035, 1019, 998, 868, 854, 825, 746, 634, 541. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.81 (s, 6H), 3.90 (s, 3H), 5.45 (s, 1H), 6.93 (d, J = 2.7 Hz, 1H), 6.96 (dd, J = 9.0, 2.7 Hz, 1H), 8.17 (d, J = 9.0 Hz, 1H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ/ppm = 53.17 ($2CH_3$), 54.54 (CH), 56.01 (CH_3), 113.43 (CH), 116.91 (CH), 128.18 (CH), 130.76 (C), 141.51 (C), 163.47 (C), 167.71 (2C=O). – MS (55°C): *m/z* (%) = 283 (12, M$^+$), 237 (100), 178 (8), 163 (8), 106 (17), 59 (14). – HRMS: Calcd. for $C_{12}H_{13}NO_7$ (M$^+$): 283.0692, found: 283.0680.

Tricarbonyl[dimethyl (2-5-η)-cyclohexa-2,4-dienyl(5-methoxy-2-nitrophenyl)malonate]iron (**13**)

The complex salt **3** (365 mg, 1.19 mmol) was dissolved in acetonitrile (10 ml), a solution of the anisole derivative **12** (500 mg, 1.77 mmol) in acetonitrile (5 ml) and then triethylamine (145 mg, 0.2 ml, 1.43 mmol) was added, and the reaction mixture was stirred for 4 h at 25 °C. The solvent was evaporated *in vacuo* and the residue was subjected to flash chromatography (hexane/EtOAc 2:1) on silica gel to afford a brown oil. Crystallization from ether (4 ml) at –10 °C provided the complex **13** as light yellow crystals. Yield 580 mg (97%). – *m.p.* 147–149 °C. – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3103, 3008, 2978, 2953, 2842, 2050, 1960, 1749, 1697, 1607, 1581, 1517, 1341, 1247, 1199, 1059, 1003, 946, 914, 869, 852, 823, 740, 625, 608, 557, 528. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 1.70 (br d, J = 15.2 Hz, 1H), 1.88 (ddd, J = 15.2, 10.8, 4.1 Hz, 1H), 3.00 (m, 1H), 3.21 (ddd, J = 6.2, 2.9, 1.1 Hz, 1H), 3.47 (m, 1H), 3.70 (s, 3H), 3.72 (s, 3H), 3.90 (s, 3H), 5.27 (m, 1H), 5.34 (m, 1H), 6.88 (dd, J = 9.0, 2.6 Hz, 1H), 6.97 (d, J = 2.6 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ/ppm = 27.10 (CH_2), 44.20 (CH), 52.55 (CH_3), 52.77 (CH_3), 55.84 (CH_3), 58.57 (CH), 59.69 (CH), 65.66 (C), 85.16 (CH), 85.58 (CH), 111.54 (CH), 116.90 (CH), 128.27 (CH), 134.84 (C), 142.29 (C), 162.66 (C), 168.12 (C=O), 168.43 (C=O), 211.40 (3CO). – MS (140 °C): *m/z* (%) = 501 (0.1, M$^+$), 473 (1), 445 (33), 417 (48), 339 (15), 308 (22), 277 (11), 263 (24), 219 (23), 205 (71), 191 (26), 177 (38), 176 (100), 165 (12), 164 (23), 163 (36), 134 (32), 122 (23), 121 (10), 120 (24), 78 (28), 77 (25), 56 (29). – HRMS: Calcd. for $C_{21}H_{19}FeNO_{10}$ (M$^+$): 501.0358, found: 501.0397.

Reduction of Complex 13 with DIBAL

A 1M solution of diisobutylaluminum hydride (0.9 ml, 0.9 mmol) in heptane was added slowly to a solution of the tricarbonyliron complex **13** (100 mg, 0.2 mmol) in ether (3 ml) and tetrahydrofuran (4 ml) at –20 °C. After 3 h at –20 °C the reaction mixture was warmed to 25 °C over a period of 15 h and quenched with methanol (10 ml) and water (10 ml) at 0 °C. The mixture was extracted with ether, the organic layer was dried over magnesium sulfate, and the solvent was evaporated *in vacuo*. Flash chromatography (hexane/

EtOAc 5:1) of the residue on silica gel afforded as the less polar fraction tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**2**) (yield 16 mg, 36%; spectral data, see ref. [5b]) and as the more polar fraction the anisole **12** (yield 35 mg, 62%; spectral data, see above).

Di-tert-butyl 5-methoxy-2-nitrophenylmalonate (**14**)

Di-*tert*-butyl malonate (2.30 g, 2.38 ml, 10.6 mmol) was added slowly to a suspension of sodium hydride (310 mg, 12.9 mmol) in *N,N*-dimethylformamide (15 ml) at room temperature and heated for 30 min at 50 °C. A solution of the anisole **11** (800 mg, 4.26 mmol) in *N,N*-dimethylformamide (5 ml) was added slowly and the reaction mixture was heated to 100 °C for 50 h. The cold mixture was extracted three times with ether, and the combined organic layers were dried over magnesium sulfate. The solvent was evaporated *in vacuo*, and the residue was subjected to flash chromatography (hexane/EtOAc 3:1) on silica gel to provide a yellow oil. The malonate **14** was crystallized from ether at −15 °C. – Yield 781 mg (50%), bright yellow crystals. – *m.p.* 88 °C. – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 2982, 1740, 1725, 1582, 1517, 1369, 1341, 1319, 1299, 1258, 1231, 1162, 1141, 1073, 877, 870, 852, 838, 830, 754. – ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 1.50 (s, 18H), 3.88 (s, 3H), 5.23 (s, 1H), 6.92 (dd, J = 9.1, 2.7 Hz, 1H), 6.98 (d, J = 2.7 Hz, 1H), 8.14 (d, J = 9.1 Hz, 1H). – ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ/ppm = 27.90 ($6CH_3$), 55.88 (CH_3), 57.01 (CH), 82.78 (2C), 113.45 (CH), 115.91 (CH), 127.94 (CH), 132.09 (C), 141.84 (C), 163.30 (C), 166.63 (2C=O). – MS (65 °C): *m/z* (%) = 367 (0.2, M$^+$), 294 (2), 265 (6), 238 (9), 209 (18), 194 (12), 57 (100). – HRMS: Calcd. for $C_{18}H_{25}NO_7$ (M$^+$): 367.1631, found: 367.1644. – Anal. calcd. for $C_{18}H_{25}NO_7$: C 58.85, H 6.86, N 3.81; found: C 58.78, H 7.18, N 4.20.

Tricarbonyl[di-tert-butyl (2-5-η)-cyclohexa-2,4-dienyl(5-methoxy-2-nitrophenyl)malonate]iron (**15**)

A solution of di-*tert*-butyl 5-methoxy-2-nitrophenylmalonate (**14**) (200 mg, 0.54 mmol) in acetonitrile (5 ml) was added slowly to a suspension of sodium hydride (18 mg, 0.75 mmol) in acetonitrile (15 ml) at room temperature. Then a solution of the complex salt **3** (172 mg, 0.56 mmol) in acetonitrile (5 ml) was added, and the reaction mixture was stirred for 4 h at 25 °C. The solvent was evaporated *in vacuo*, and the residue was subjected to flash chromatography (hexane/EtOAc 3:1) on silica gel to afford **15** as brown crystals. Yield 298 mg (94%). – *m.p.* 54 °C. – IR (KBr): $\tilde{\nu}$ /cm^{-1} = 2982, 2938, 2045, 1964, 1721, 1604, 1578, 1518, 1367, 1345, 1312, 1252, 1143, 839, 731, 622. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 1.44 (s, 9H), 1.45 (s, 9H), 1.80 (dd, J = 14.8, 4.4 Hz, 1H), 1.95 (ddd, J = 14.8, 10.7, 4.2 Hz, 1H), 3.06 (m, 1H), 3.13 (br dd, J = 6.1, 1.5 Hz, 1H), 3.50 (ddd, J = 10.7, 4.9, 2.9 Hz, 1H), 3.89 (s, 3H), 5.32 (m, 1H), 5.37 (m, 1H), 6.85 (dd, J = 9.0, 2.6 Hz, 1H), 7.00 (d, J = 2.6 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ/ppm = 26.86 (CH_2), 27.86 ($3CH_3$), 27.88 ($3CH_3$), 44.01 (CH), 55.74 (CH_3), 58.75 (CH), 60.71 (CH), 67.09 (C), 82.88 (C), 83.02 (C), 84.56 (CH), 86.92 (CH), 111.36 (CH), 116.88 (CH), 128.13 (CH), 136.25 (C), 142.55 (C), 162.46 (C), 167.03 (C=O), 167.07 (C=O), 211.69 (3CO). – MS (105 °C): *m/z* (%) = 585 (0.01, M$^+$), 557 (0.2), 553 (0.5), 529 (34), 501 (51), 445 (6), 327 (16), 267 (42), 250 (33), 221 (52), 219 (48), 205 (100), 177 (41), 86 (61), 84 (53), 57 (84). – HRMS: Calcd. for $C_{27}H_{31}FeNO_{10}$ (M$^+$): 585.1297, found: 585.1266. – Anal. calcd. for $C_{27}H_{31}FeNO_{10}$: C 55.40, H 5.34, N 2.39; found: C 55.30, H 5.70, N 2.66.

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