

## Di- and Trinuclear $\sigma$ -Aryl Iron and Manganese Complexes

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**Abstract**—Reactions of *p*- and *m*-diiodobenzenes, *p,p'*-diiodobiphenyl, and 1,3,5-triiodobenzene with anions derived from dicarbonyl(cyclopentadienyl)iron and pentacarbonylmanganese, catalyzed by palladium complexes, provide a successful route to mono-, di-, and trinuclear  $\sigma$ -aryl iron and manganese complexes.

The simplest procedure for the synthesis of  $\sigma$ -aryl and  $\sigma$ -vinyl carbonyl transition metal complexes is based on the reaction of aryl and vinyl halides with anions derived from the corresponding carbonyl complexes (carbonylates). Polynuclear transition metal complexes in which the metal anions are linked through hydrocarbon bridges attract a considerable interest due to their valuable physical and chemical properties. Polymeric complexes with aryl and acetylene ligands are used as a basis for creation of new materials possessing unique properties, e.g., liquid crystals or materials for nonlinear optics. Complexes with alkyl and olefin ligands are studied as models of homogeneous catalysts in such reactions as alkene polymerization, Fischer–Tropsch synthesis, etc. [1–8].

However, transition metal carbonylates do not react with nonactivated vinyl and aryl halides [9–12], following the nucleophilic substitution pattern. Thus, the yield of  $\sigma$ -aryl iron complex in the reaction of iodobenzene with supernucleophilic  $[\text{FeCp}(\text{CO})_2]^-$  ion ( $\text{Cp} = \text{C}_5\text{H}_5$ ) is 2% [11], and in the reaction with *p*-diiodobenzene, only traces of the corresponding dinuclear complex were isolated [12]. In such cases, polynuclear complexes with arene bridges are often obtained in two steps via preparation and decarbonylation of acyl metal complexes [12–20] (Scheme 1).

In this way, a number of di- and trinuclear manganese, rhenium, and iron complexes with arene bridges

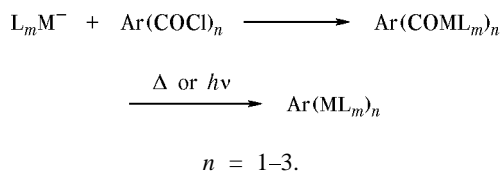
were synthesized. Their overall yields ranged from 26 to 62%. It should be noted that the decarbonylation is not always successful and that initial acyl metal complexes are also difficult to obtain [12, 16, 17].

We previously showed that mononuclear aryl and vinyl transition metal complexes can be prepared via cross coupling of aryl and vinyl halides with transition metal carbonylates in the presence of palladium or nickel complexes [21, 22]. In the present work we made an attempt to extend this approach to the synthesis of di- and trinuclear arene iron and manganese complexes.

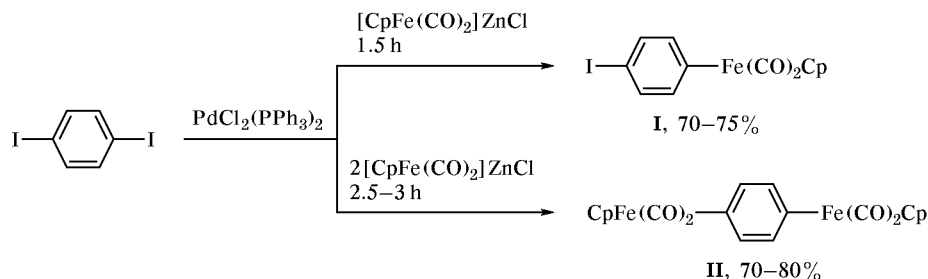
Dicarbonyl(cyclopentadienyl)iron anion is the most reactive among transition metal carbonylates. According to [23], its nucleophilicity toward alkyl halides exceeds that of manganese carbonylate by six orders of magnitude:  $\text{CpFe}(\text{CO})_2^-$  ( $7.0 \times 10^7$ ) >  $\text{Mn}(\text{CO})_5^-$  (77) >  $\text{Co}(\text{CO})_4^-$  (1). On the other hand, dicarbonyl(cyclopentadienyl)iron anion is a good reducing agent. To avoid side processes, it is advisable to use the corresponding zinc salt which is formed *in situ* [21].

Depending on the reactant ratio and reaction time, the reaction of  $[\text{CpFe}(\text{CO})_2]\text{ZnCl}$  with *p*-diiodobenzene in THF in the presence of bis(triphenylphosphine)palladium dichloride at room temperature could afford both mono- and disubstituted  $\sigma$ -aryl iron complexes in high yield (Scheme 2). Obviously, the process occurs in two steps due to strong donor effect of the  $\text{CpFe}(\text{CO})_2$  group. The formation of mononuclear carbonyl iron complex takes a relatively short time (~1.5 h), while the rate of formation of dinuclear complex **II** is considerably lower (~2.5–3 h). In the reaction of *p,p'*-diiodobiphenyl even with 2 equiv of iron carbonylate, only monosubstituted product **III** was obtained in 66% yield (Scheme 3). No formation

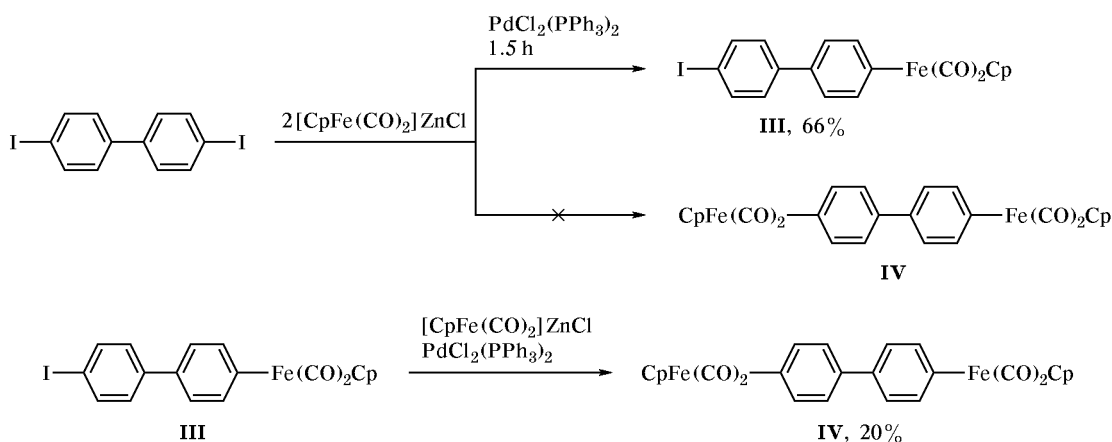
**Scheme 1.**



Scheme 2.



Scheme 3.



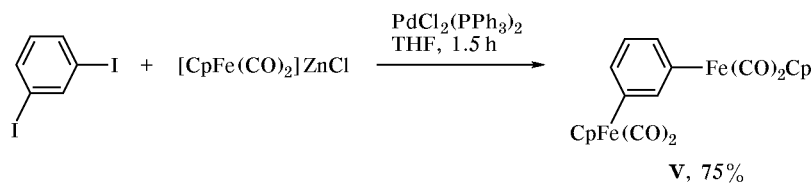
of dinuclear complex **IV** was observed in the presence of a palladium(0) complex,  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (dba is dibenzylideneacetone), and trifurylphosphine, while the yield of complex **III** considerably decreased (36%). Increase of the reaction time to 5 h also led to reduction of the yield of **III** (to 18%). Complex **IV** was synthesized in a poor yield from mononuclear complex **III**.

By contrast, the reaction of iron carbonylate with *m*-diiodobenzene afforded exclusively dinuclear complex **V**, regardless of the reactant ratio (Scheme 4). This result may be explained by the absence of conjugation between the iodine atom and  $\text{CpFe}(\text{CO})_2$  group in the monosubstitution product.

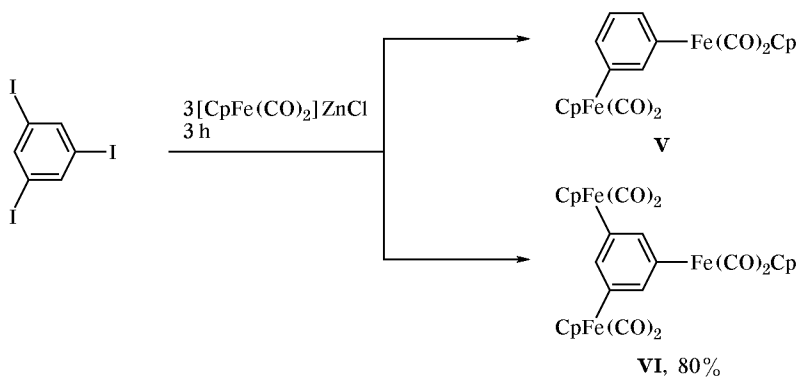
Taking into account that dinuclear complexes are readily obtained by reaction of iron carbonylate with *p*- and *m*-diiodobenzene, it was interesting to

synthesize the corresponding trinuclear complex by cross coupling with 1,3,5-triiodobenzene. According to the  $^1\text{H}$  NMR data, the reaction of 1,3,5-triiodobenzene with 3 equiv of  $[\text{CpFe}(\text{CO})_2]\text{ZnCl}$  gave trinuclear complex **VI** in quantitative yield. The  $^1\text{H}$  NMR spectrum contained two singlets at  $\delta$  6.99 (1H) and 4.85 ppm (5H), while no signal from initial triiodobenzene was present. However, after chromatographic purification on silica gel (following a standard procedure used for isolation of  $\sigma$ -aryl complexes; see Experimental), we isolated only 1,3-dinuclear complex **V** (40–60%) which was identical to a sample obtained from *m*-diiodobenzene, i.e., one  $\text{CpFe}(\text{CO})_2$  group was lost during chromatography. We succeeded in avoiding this process by passing the reaction mixture through a layer of aluminum oxide before column chromatography on silica gel. In such a way

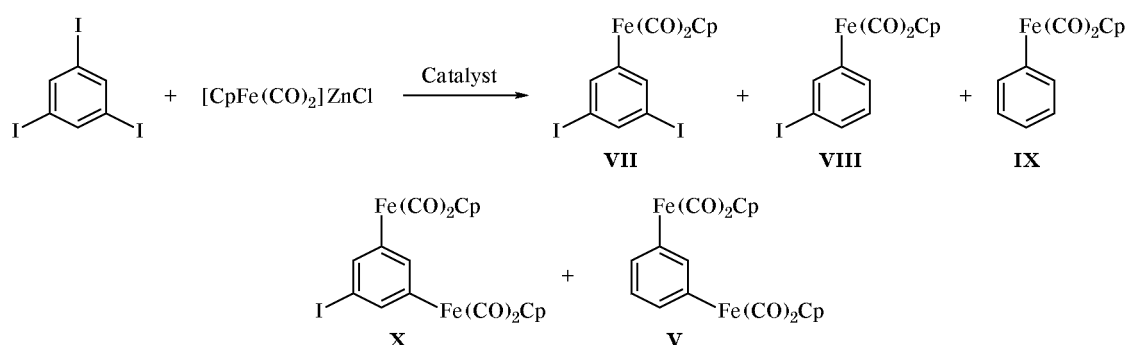
Scheme 4.



Scheme 5.



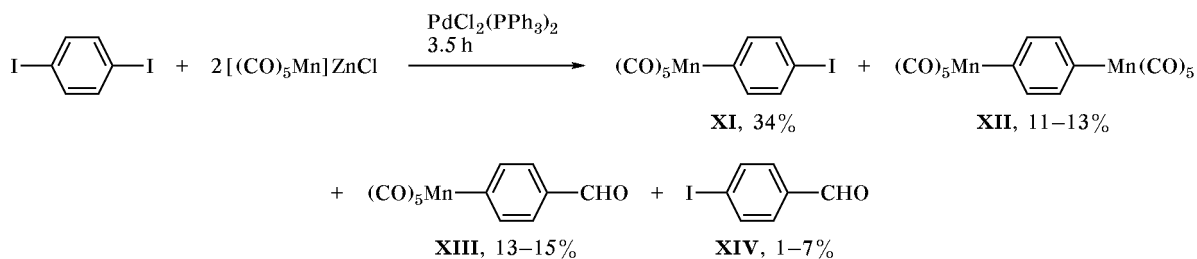
Scheme 6.



we isolated complex **VI** in 80% yield (Scheme 5). It was interesting that complex **VI** isolated as described above no longer underwent decomposition on passing through silica gel. When the reaction was performed with an equimolar ratio of 1,3,5-triiodobenzene and iron carbonylate, no selective formation of the corresponding mononuclear complex was observed, but a mixture of products **V** and **VII–X** was obtained, presumably as a result of consecutive substitution and reduction processes (Scheme 6). Here, the reaction carried out by standard procedure afforded mainly dinuclear complexes **V** and **X** (~41%); when the zinc salt was gradually added to the reaction mixture, mononuclear complexes **VII–IX** were detected in an overall yield of ~14%.

As expected, the reactivity of pentacarbonylmanganese zinc salt was much lower than the reactivity of  $[\text{CpFe}(\text{CO})_2]\text{ZnCl}$ . Nevertheless, with  $\text{PdCl}_2(\text{PPh}_3)_2$  as catalyst, the substrate conversion was 80% in 3.5 h. Unlike the reaction with iron carbonylate, a mixture of products **XI–XIV** was obtained (Scheme 7, see table, run no. 1). Although the overall yield of complexes **XI–XIV** in the reaction catalyzed by  $\text{PdCl}_2(\text{PPh}_3)_2$  was fairly good (60%; 74% on the reacted initial compound), the yield of dinuclear complex **XII** (11–13%) was considerably lower than the yield of mononuclear complex **XI** (34%). It should also be noted that, after chromatographic treatment, the reaction mixture obtained from *p*-diiodobenzene and  $[\text{Mn}(\text{CO})_5]\text{ZnCl}$  contained pentacarbonyl(*p*-formyl-

Scheme 7.



Reaction of *p*-diiodobenzene with  $[\text{Mn}(\text{CO})_5]\text{M}$ , 20°C

Run no.	Ratio ArX- [ $\text{Mn}(\text{CO})_5$ ]M	M	Catalyst, L (mol %)	Time, h	Solvent	Conver- sion, %	Yield, <sup>a</sup> %			
							XI	XII	XIII	XIV
1	1:2	ZnCl	$\text{PdCl}_2(\text{PPh}_3)_2$	3.5	THF	80	34 (42)	11 (13)	13 (16)	Traces
2	1:2	ZnCl	$\text{Pd}_2(\text{dba})_3\text{CHCl}_3$	1	THF	86	15 (18)	9 (10)	15 (18)	4.3
3	1:2	ZnCl	$\text{Pd}_2(\text{dba})_3\text{CHCl}_3,$ $\text{Ph}_3\text{As}$	1	THF	84	28 (33)	–		
4 <sup>b,c</sup>	1:1	ZnCl	$\text{Pd}_2(\text{dba})_3\text{CHCl}_3,$ $\text{Ph}_3\text{As}$	5	THF	35	12			
5 <sup>c</sup>	1:2	ZnCl	$\text{PdCl}_2(\text{PPh}_3)_2$	18	Ether	14	11			
6 <sup>d</sup>	1:1	ZnCl	$\text{PdCl}_2(\text{PPh}_3)_2$	4	THF	73	35 (47)	12		
7 <sup>d</sup>	1:1	K	$\text{PdCl}_2(\text{PPh}_3)_2$	0.75	THF	90	60	3.1		

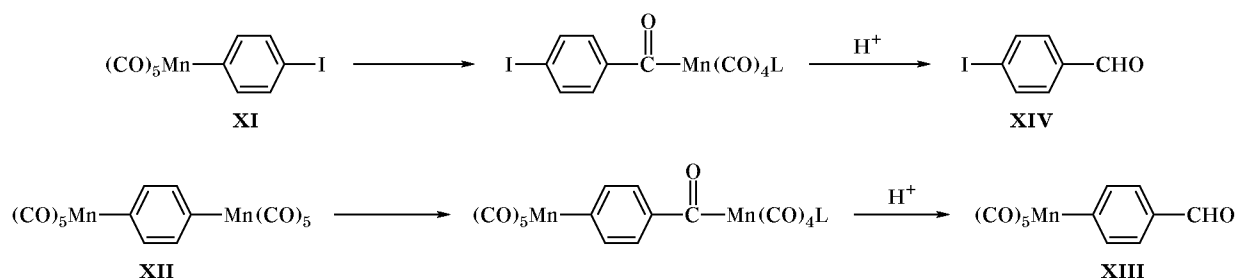
<sup>a</sup> In parentheses are given the yields calculated on the converted *p*-diiodobenzene.<sup>b</sup> At -30°C.<sup>c</sup> Products **XII–XIV** were not analyzed.<sup>d</sup> Products **XIII** and **XIV** were not analyzed.

phenyl)manganese (**XIII**) and *p*-iodobenzaldehyde (**XIV**). Obviously, these compounds were formed via aryl–acyl rearrangement from complexes **XI** and **XII**, respectively (Scheme 8; see table, run nos. 1, 2). Such rearrangements are known for almost all transition metals [24]; they occur fairly readily with alkyl complexes but are much more difficult with aryl complexes. The IR spectrum of the reaction mixture before chromatographic treatment contained no bands assignable to aldehyde ( $1720\text{ cm}^{-1}$ ) or acyl group ( $1587\text{ cm}^{-1}$  [12]). No carbonyl bands were observed in the IR spectrum of the mixture obtained in the reaction carried out in a CO atmosphere. These

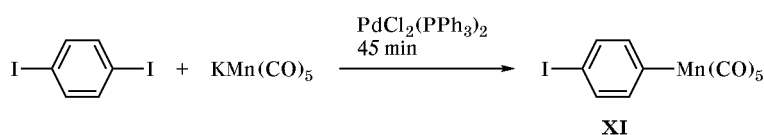
findings indicate that aldehydes **XIII** and **XIV** are formed during chromatography on silica gel. However, our attempt to effect the rearrangement before chromatographic treatment by adding silica gel to the reaction mixture failed.

We also tried to control the ratio of mono- and disubstitution products by varying the ligand nature (run nos. 2, 3), solvent (run no. 5), and temperature (run no. 4), but no success was achieved in these attempts. Reduction of the carbonylate concentration by carrying out the reaction in THF with equimolar amounts of the reactants had no appreciable effect on the ratio of products **XI** and **XII** (see table, run no. 6).

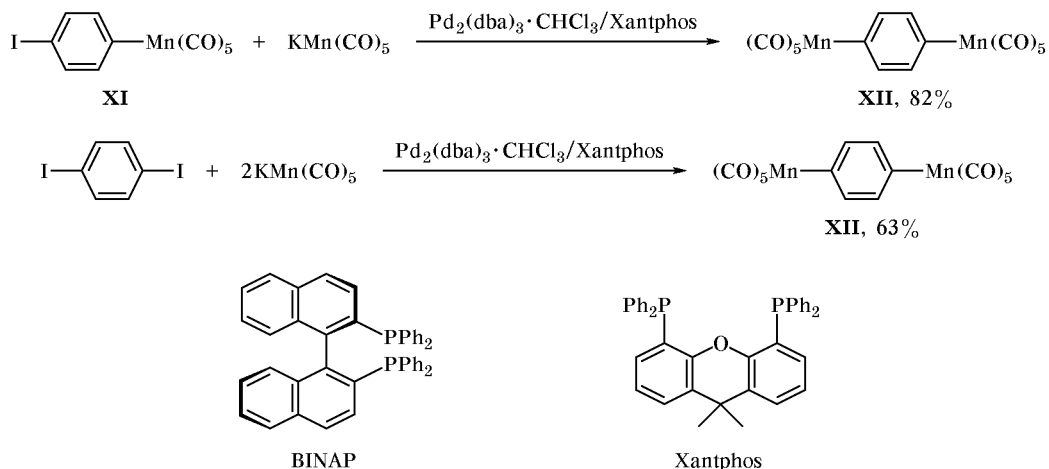
Scheme 8.



Scheme 9.



## Scheme 10.



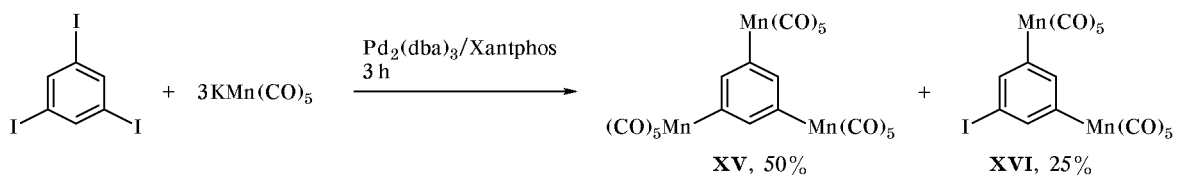
We succeeded in obtaining mononuclear complex **XI** in a sufficiently good yield (60%) by reaction of *p*-diiodobenzene with an equimolar amount of manganese carbonylate potassium salt (Scheme 9). According to our previous data, in the cross coupling of iron carbonylate with iodobenzene the corresponding zinc salt ensured much greater yield of the product than that obtained with the potassium salt [20]. Presumably, the reason is that manganese carbonylate is a weaker reducing agent than iron carbonylate.

Thus, under the above conditions dinuclear complex **XII** is formed in a poor yield and, furthermore, it undergoes rearrangement during chromatography. Therefore, we then focused on searching for conditions for the transformation of mononuclear complex **XI** into dinuclear complex **XII** and optimal procedure for isolation of the latter. For this purpose, complex **XI** was brought into reactions with zinc and potas-

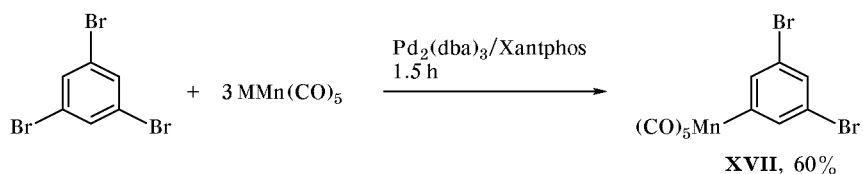
sium manganese carbonylates in the presence of such catalysts as  $\text{PdCl}_2(\text{PPh}_3)_2$  and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3/\text{L}$ , where  $\text{L} = \text{Fur}_3\text{P}$  or BINAP. We succeeded in synthesizing dinuclear complex **XII** with Xantphos as ligand. The reaction was characterized by almost quantitative conversion, and complex **XII** was formed in 82% yield. *p*-Diiodobenzene can also be used as initial compound, though in this case the yield of **XII** is lower (63%) (Scheme 10). The product can be isolated without decomposition by diluting the reaction mixture with an equal volume of petroleum ether and passing the resulting mixture through a thin layer of silica gel.

Xantphos as ligand turned out to be also useful in the synthesis of trinuclear manganese complex **XV** from 1,3,5-triiodobenzene. The reaction was accompanied by formation of dinuclear complex **XVI** (Scheme 11). An analogous reaction with 1,3,5-tri-

## Scheme 11.



## Scheme 12.



M = K, ZnCl.

bromobenzene resulted in replacement of only one bromine atom to afford 3,5-dibromophenylpentacarbonylmanganese (**XVII**) (yield 60%). Complex **XVII** was also obtained in a similar yield by reaction of 1,3,5-tribromobenzene with manganese carbonylate zinc salt (Scheme 12).

Thus we have synthesized a number of new mononuclear iron and manganese complexes. Such transition metal complexes having halogen atoms in the aromatic ring, as well as the dinuclear manganese complex, attract interest as starting materials for the synthesis of polyheteronuclear complexes.

## EXPERIMENTAL

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian VXR-400 spectrometer using signals from residual protons in the deuterated solvent as internal reference. The IR spectra were measured on a UR-20 spectrometer from solutions in  $\text{CCl}_4$  or THF. The mass spectra (electron impact, 70 eV) were obtained on an MS-890 instrument with direct sample admission into the ion source ( $150^\circ\text{C}$ ).

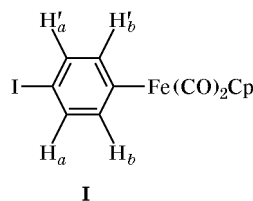
Tetrahydrofuran and diethyl ether were stored under reduced pressure over potassium diphenylketyl. The procedures for purification of zinc(II) chloride,  $[\text{CpFe}(\text{CO})_2]_2$ , and  $\text{Mn}_2(\text{CO})_{10}$  were given in [20, 21].

### Typical procedure of cross coupling reaction.

All operations with solutions of carbonylate salts and reaction products were carried out in a high vacuum or under argon. The solvent (THF) was condensed and evaporated using a vacuum line. The reactions were carried out in a setup consisting of two parts which were connected with a tube having a glass filter inside it. The corresponding metal carbonyl dimer was reduced in one part of the setup under vigorous stirring: 0.07–0.08 ml of  $\text{NaK}_{2,8}$  alloy was required to reduce 0.5 mmol of  $[\text{CpFe}(\text{CO})_2]_2$  or  $\text{Mn}_2(\text{CO})_{10}$  (reaction time 60 to 70 min). In some experiments with a larger amount of the reducing agent, the reaction time was shortened to 10–20 min. A test experiment with pentafluoropyridine showed almost complete absence (according to chromatographic data) of  $\text{Mn}_2(\text{CO})_{10}$  in a solution of the corresponding anion. The resulting solution was filtered into the second part where the cross coupling was performed. It was preliminarily charged with  $\text{ZnCl}_2$  (deposited onto walls by sublimation) and thin-walled glass balls containing the substrate and catalyst. The balls were broken with the aid of a hook which was rotated through a ground joint. The reactant concentration was 0.1–0.2 M. Solutions of potassium salts were stirred with  $\text{ZnCl}_2$  over a period of 10–20 min, and balls containing the

substrate and catalyst were broken. The progress of the reaction was monitored by TLC on Silufol UV-254 plates; sample were withdrawn intermittently with a syringe in a stream of argon. When the reaction was complete, the mixture was evaporated with a small amount of silica gel which was then transferred to a silica gel column (L 40/100 or 60/200  $\mu\text{m}$ ).

**Synthesis of mononuclear iron complex from *p*-diiodobenzene and  $[\text{CpFe}(\text{CO})_2]\text{ZnCl}$**  (substrate-to-anion ratio 1:1). Amounts of the reactants:  $[\text{CpFe}(\text{CO})_2]_2$ , 0.089 g (0.25 mmol); *p*- $\text{IC}_6\text{H}_4\text{I}$ , 0.17 g (0.52 mmol);  $\text{NaK}_{2,8}$ , 0.04 ml;  $\text{ZnCl}_2$ , 75 mg (0.55 mmol);  $\text{PdCl}_2(\text{PPh}_3)_2$ , 7 mg (0.01 mmol, 2 mol %). Reaction time 1.5 h. We isolated initial *p*-diiodobenzene (eluent hexane) and, in succession, complexes **I** and **II** (eluent hexane–ether, 2:1): *p*- $\text{IC}_6\text{H}_4\text{Fe}(\text{CO})_2\text{Cp}$  (**I**), yield 0.140 g (74%).  $^1\text{H}$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 7.219 s ( $\text{H}_a$ ), 7.230 s ( $\text{H}_b$ ), 5.1 (Cp). IR spectrum ( $\text{CH}_2\text{Cl}_2$ ),  $\nu$ ,  $\text{cm}^{-1}$ : 2026 v.s., 1971 v.s. Mass spectrum,  $m/z$ : 380  $[\text{M}]^+$ , 352  $[\text{M} - \text{CO}]^+$ , 324  $[\text{M} - 2\text{CO}]^+$ , 197  $[\text{M} - 2\text{CO} - \text{I}]^+$ , 121  $[\text{CpFe}]^+$ , 76  $[\text{C}_6\text{H}_4]^+$ , 56  $[\text{Fe}]^+$ . Found, %: C 41.27; N 2.34.  $\text{C}_{13}\text{H}_9\text{FeIO}_2$ . Calculated, %: C 41.01; N 2.39. *p*- $\text{Cp}(\text{CO})_2\text{FeC}_6\text{H}_4\text{Fe}(\text{CO})_2\text{Cp}$  (**II**), yield 10 mg (9%). Mass spectrum,  $m/z$ : 430  $[\text{M}]^+$ , 402  $[\text{M} - \text{CO}]^+$ , 374  $[\text{M} - 2\text{CO}]^+$ , 346  $[\text{M} - 3\text{CO}]^+$ , 318  $[\text{M} - 4\text{CO}]^+$ , 253  $[\text{CpFeC}_6\text{H}_4\text{Fe}]^+$ , 188  $[\text{FeC}_6\text{H}_4\text{Fe}]^+$ , 132  $[\text{FeC}_6\text{H}_4]^+$ , 76  $[\text{C}_6\text{H}_4]^+$ , 56  $[\text{Fe}]^+$ .

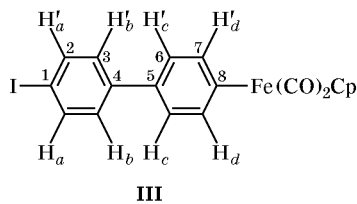


**Synthesis of dinuclear iron complex by reaction of *p*-diiodobenzene with  $[\text{CpFe}(\text{CO})_2]\text{ZnCl}$**  (substrate-to-anion ratio 1:2). Amounts of the reactants: *p*- $\text{IC}_6\text{H}_4\text{I}$ , 0.165 g (0.5 mmol);  $[\text{CpFe}(\text{CO})_2]_2$ , 0.177 g (0.5 mmol);  $\text{ZnCl}_2$ , 0.150 g (1.10 mmol);  $\text{NaK}_{2,8}$ , 0.08 ml;  $\text{PdCl}_2(\text{PPh}_3)_2$ , 14 mg (0.02 mmol, 2 mol %). Reaction time 2.5 h. We isolated initial *p*-diiodobenzene (eluent hexane) and, in succession (eluent hexane–ether, 2:1), *p*- $\text{IC}_6\text{H}_4\text{Fe}(\text{CO})_2\text{Cp}$  (**I**), 0.040 g (21%), and *p*- $\text{Cp}(\text{CO})_2\text{FeC}_6\text{H}_4\text{Fe}(\text{CO})_2\text{Cp}$  (**II**), 150 mg (70%).  $^1\text{H}$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 6.985 (4H), 4.991 (5H) [11]. The mass spectrum was the same as that given above.

**Synthesis of dinuclear iron complex by reaction of *m*-diiodobenzene with  $[\text{CpFe}(\text{CO})_2]\text{ZnCl}$**  (substrate-to-anion ratio 1:2). Amounts of the reactants: *m*- $\text{IC}_6\text{H}_4\text{I}$ , 0.165 g (0.5 mmol);  $[\text{CpFe}(\text{CO})_2]_2$ , 0.177 g

(0.5 mmol); NaK<sub>2,8</sub>, 0.1 ml; ZnCl<sub>2</sub>, 0.150 g (1.10 mmol); PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 14 mg (0.02 mmol, 2 mol %). Reaction time 2 h. *m*-[CpFe(CO)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, yield 0.160 g (75%) (eluent hexane–ether, 2:1). <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>), δ, ppm: 7.542 t (1H, H<sub>a</sub>), 6.982 d.d (2H, H<sub>b</sub>), 6.576 t (1H, H<sub>c</sub>), 4.879 s (10H); *J*<sub>a,b</sub> = 1.6 Hz, *J*<sub>b,c</sub> = 7.2 Hz. <sup>13</sup>C NMR spectrum: 162.309 (C<sup>1</sup>), 144.725 (C<sup>2</sup>), 139.96 (C<sup>3</sup>), 127.944 (C<sup>4</sup>), 217.276 (C=O), 86.315 (Cp). Mass spectrum, *m/z*: 430 [M]<sup>+</sup>, 402 [M – CO]<sup>+</sup>, 374 [M – 2CO]<sup>+</sup>, 346 [M – 3CO]<sup>+</sup>, 318 [M – 4CO]<sup>+</sup>, 253 [CpFeC<sub>6</sub>H<sub>4</sub>Fe]<sup>+</sup>, 188 [FeC<sub>6</sub>H<sub>4</sub>Fe]<sup>+</sup>, 132 [FeC<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 76 [C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 56 [Fe]<sup>+</sup> [11].

**Reaction of *p,p'*-diiodobiphenyl with [CpFe(CO)<sub>2</sub>]ZnCl.** 1. *Substrate–anion ratio 1:2, catalyst PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.* Amounts of the reactants: *p,p'*-IC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>I, 0.203 g (0.5 mmol); [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 0.177 g (0.5 mmol); ZnCl<sub>2</sub>, 0.170 g (1.25 mmol); NaK<sub>2,8</sub>, 0.10 ml; PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 10 mg (0.014 mmol, 1.4 mol %). Reaction time 1 h. We isolated initial *p,p'*-IC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>I, 0.039 g (19%) (eluent hexane), and, in succession (eluent hexane–ether, 2:1): *p,p'*-IC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Fe(CO)<sub>2</sub>Cp (**III**), 0.151 g (66 or 79% with account taken of the conversion), and IFe(CO)<sub>2</sub>Cp, 0.061 g (20%). <sup>1</sup>H NMR spectrum of **III** (acetone-*d*<sub>6</sub>), δ, ppm: 7.208 d (H<sub>a</sub>), 7.389 (H<sub>b</sub>), *J*<sub>a,b</sub> = 8 Hz, 7.542 d (H<sub>c</sub>), 7.784 d (H<sub>d</sub>), *J*<sub>c,d</sub> = 8 Hz, 5.006 (Cp). <sup>13</sup>C NMR spectrum of **III** (acetone-*d*<sub>6</sub>), δ<sub>C</sub>, ppm: 92.003 (C<sup>1</sup>), 125.903 (C<sup>2</sup>), 129.179 (C<sup>3</sup>), 134.885 (C<sup>4</sup>), 141.922 (C<sup>5</sup>), 138.540 (C<sup>6</sup>), 146.116 (C<sup>7</sup>), 148.110 (C<sup>8</sup>), 217 (C≡O), 87 (Cp). IR spectrum of **III**, (CH<sub>2</sub>Cl<sub>2</sub>), ν, cm<sup>-1</sup>: 2023 v.s., 1969 v.s. Mass spectrum of **III**, *m/z*: 456 [M]<sup>+</sup>, 428 [M – CO]<sup>+</sup>, 400 [M – 2CO]<sup>+</sup>, 335 [IC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Fe]<sup>+</sup>, 279 [IC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 208 [C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Fe]<sup>+</sup>, 152 [C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 76 [C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 56 [Fe]<sup>+</sup>. Found, %: C 50.40; H 3.01. C<sub>19</sub>H<sub>13</sub>FeIO<sub>2</sub>. Calculated, %: C 50.03; H 2.87.



2. *Reaction of *p,p'*-IC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Fe(CO)<sub>2</sub>Cp with [CpFe(CO)<sub>2</sub>]ZnCl; catalyst PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.* Amounts of the reactants: *p,p'*-IC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Fe(CO)<sub>2</sub>Cp, 0.082 g (0.18 mmol); [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 0.038 g (0.108 mmol); ZnCl<sub>2</sub>, 0.034 g (0.25 mmol); NaK<sub>2,8</sub>, 0.02 ml; PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 7 mg (0.01 mmol, 5.5 mol %). Reaction time 2.5 h. The reaction mixture was evaporated,

and the residue was subjected to thin-layer chromatography on silica gel (Silpearl) using hexane–ether (3:1) as eluent. Yield of *p,p'*-Cp(CO)<sub>2</sub>FeC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Fe(CO)<sub>2</sub>Cp 0.02 g (20%). Mass spectrum, *m/z*: 506 [M]<sup>+</sup>, 478 [M – CO]<sup>+</sup>, 450 [M – 2CO]<sup>+</sup>, 422 [M – 3CO]<sup>+</sup>, 264 [FeC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Fe]<sup>+</sup>, 208 [C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Fe]<sup>+</sup>, 152 [C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 76 [C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 56 [Fe]<sup>+</sup>.

**Reaction of [CpFe(CO)<sub>2</sub>]ZnCl with 1,3,5-triiodobenzene.** 1. *Substrate–anion ratio 1:3; catalyst PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.* Amounts of the reactants: C<sub>6</sub>H<sub>3</sub>I<sub>3</sub>, 0.182 g (0.4 mmol); [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 0.275 g (0.78 mmol); ZnCl<sub>2</sub>, 0.244 g (1.8 mmol); NaK<sub>2,8</sub>, 0.10 ml; PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 10 mg (0.014 mmol, 1.2 mol %). Reaction time 4 h. Elution with hexane gave initial triiodobenzene, and subsequent elution with hexane–ether (2:1) afforded 1,3-[CpFe(CO)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 0.075 g (44%), [CpFe(CO)<sub>2</sub>]<sub>2</sub>, and IFe(CO)<sub>2</sub>Cp.

2. *Substrate–anion ratio 1:3; catalyst Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>/trifurylphosphine.* Amounts of the reactants: C<sub>6</sub>H<sub>3</sub>I<sub>3</sub>, 0.182 g (0.4 mmol); [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 0.212 g (0.60 mmol); ZnCl<sub>2</sub>, 0.180 g (1.3 mmol); NaK<sub>2,8</sub>, 0.10 ml; Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, 10 mg (0.01 mmol, 0.83 mol %); trifurylphosphine, 8 mg (0.034 mmol, 2.8 mol %). Reaction time 4 h. We isolated 1,3-[CpFe(CO)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 0.100 g (57%); [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 0.080 g (38%); and IFe(CO)<sub>2</sub>Cp.

3. *Synthesis of 1,3,5-tris(cyclopentadienyldicarbonyliron)benzene.* Amounts of the reactants: C<sub>6</sub>H<sub>3</sub>I<sub>3</sub>, 0.068 g (0.15 mmol); [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 0.089 g (0.25 mmol); ZnCl<sub>2</sub>, 0.096 g (0.7 mmol); NaK<sub>2,8</sub>, 0.07 ml; PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 2.9 mg (0.004 mmol, 0.88 mol %); THF-*d*<sub>8</sub> (~2 ml). After 3 h, the solution was filtered under reduced pressure through a layer of glass wool and celite into an NMR ampule. <sup>1</sup>H NMR spectrum (THF-*d*<sub>8</sub>), δ, ppm: 6.99 s (3H) and 4.86 s (5H) [11]; no signal of the initial iodide (δ 8.00 ppm, CDCl<sub>3</sub>) was present. Mass spectrum, *m/z*: 606 [M]<sup>+</sup> [1,3,5-[Fe(CO)<sub>2</sub>Cp]<sub>3</sub>C<sub>6</sub>H<sub>3</sub>]<sup>+</sup>, 578 [M – CO]<sup>+</sup>, 550 [M – 2CO]<sup>+</sup>, 522 [M – 3CO]<sup>+</sup>, 494 [M – 4CO]<sup>+</sup>, 466 [M – 5CO]<sup>+</sup>, 438 [M – 6CO]<sup>+</sup>, 382 [M – 6CO – Fe]<sup>+</sup>, 318 [C<sub>6</sub>H<sub>4</sub>Fe<sub>2</sub>Cp<sub>2</sub>]<sup>+</sup>, 262 [C<sub>6</sub>H<sub>4</sub>CpFeCp]<sup>+</sup>, 186 [FeCp<sub>2</sub>]<sup>+</sup>, 121 [FeCp]<sup>+</sup>.

The reaction mixture was passed through a thin layer of neutral Al<sub>2</sub>O<sub>3</sub>, THF was evaporated, and the dry residue was subjected to column chromatography on silica gel using petroleum ether–ether (1:1) as eluent. Yield 0.073 g (80%).

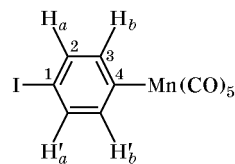
4. *Substrate–anion ratio 1:1; catalyst Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>/AsPh<sub>3</sub>.* Amounts of the reactants: C<sub>6</sub>H<sub>3</sub>I<sub>3</sub>, 0.260 g (0.57 mmol); [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 0.138 g (0.39 mmol); ZnCl<sub>2</sub>, 0.136 g (1.0 mmol); NaK<sub>2,8</sub>, 0.07 ml; Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, 10 mg (0.01 mmol,

1.75 mol %); AsPh<sub>3</sub>, 12 mg (0.04 mmol, 6.6 mol %). Reaction time 1 h. Elution with hexane gave C<sub>6</sub>H<sub>3</sub>I<sub>3</sub>, 0.111 g (43%), and the subsequent elution with hexane–ether (2:1) afforded a yellow fraction which contained (according to the TLC data) five products, one of which was CpFe(CO)<sub>2</sub>I, 0.085 g (33%). The yellow fraction was chromatographed on a Silpearl plate using hexane–ether (4:1) as eluent. The following compounds were isolated (identified by the mass spectra): 1,3-[CpFe(CO)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 0.017 g (13%); 1,3,5-I[Fe(CO)<sub>2</sub>Cp]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 0.073 g (44%); 1,3,5-I<sub>2</sub>[Fe(CO)<sub>2</sub>Cp]C<sub>6</sub>H<sub>3</sub>, 0.006 g (2%); ferrocene, 0.005 g. Mass spectra, *m/z*: 1,3,5-I[Fe(CO)<sub>2</sub>Cp]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>: 556 [M]<sup>+</sup>, 528 [M – CO]<sup>+</sup>, 500 [M – 2CO]<sup>+</sup>, 472 [M – 3CO]<sup>+</sup>, 444 [M – 4CO]<sup>+</sup>, 314 [Fe<sub>2</sub>IC<sub>6</sub>H<sub>3</sub>]<sup>+</sup>, 202 [M – C<sub>6</sub>H<sub>3</sub>]<sup>+</sup>, 127 [I]<sup>+</sup>, 56 [Fe]<sup>+</sup>; 1,3,5-I<sub>2</sub>[Fe(CO)<sub>2</sub>Cp]C<sub>6</sub>H<sub>3</sub>: 506 [M]<sup>+</sup>, 478 [M – CO]<sup>+</sup>, 450 [M – 2CO]<sup>+</sup>, 385 [FeI<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sup>+</sup>, 329 [I<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sup>+</sup>, 127 [I]<sup>+</sup>, 56 [Fe]<sup>+</sup>.

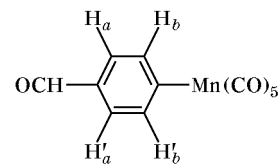
5. *Substrate–anion ratio 1:1; catalyst PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>*. Amounts of the reactants: C<sub>6</sub>H<sub>3</sub>I<sub>3</sub>, 0.260 g (0.57 mmol); [CpFe(CO)<sub>2</sub>]<sub>2</sub>, 0.138 g (0.39 mmol); ZnCl<sub>2</sub>, 0.136 g (1.0 mmol); NaK<sub>2,8</sub>, 0.05 ml; PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 10 mg (0.014 mmol, 2.5 mol %). A solution of the zinc salt [CpFe(CO)<sub>2</sub>]<sub>2</sub>ZnCl in THF was added dropwise over a period of 1 h under argon to a mixture of 1,3,5-triiodobenzene and the catalyst in THF, placed in a two-necked flask. Following a procedure analogous to that described in the preceding experiment, we isolated C<sub>6</sub>H<sub>3</sub>I<sub>3</sub>, 0.140 g (54%); CpFe(CO)<sub>2</sub>I, 0.053 g (29%); 1,3-[CpFe(CO)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, traces; 1,3,5-I[Fe(CO)<sub>2</sub>Cp]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 0.032 g (15%); 1,3,5-I<sub>2</sub>[Fe(CO)<sub>2</sub>Cp]C<sub>6</sub>H<sub>3</sub>, 0.045 g (11%); [CpFe(CO)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; 0.002 g (1.4%); 1,3-I[CpFe(CO)<sub>2</sub>]-C<sub>6</sub>H<sub>4</sub>, 0.006 g (2.8%); and ferrocene, traces. Mass spectra, *m/z*: CpFe(CO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>: 254 [M]<sup>+</sup>, 226 [M – CO]<sup>+</sup>, 198 [M – 2CO]<sup>+</sup>, 142 [FeC<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 56 [Fe]<sup>+</sup>; 1,3-I[CpFe(CO)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>: 380 [M]<sup>+</sup>, 352 [M – CO]<sup>+</sup>, 324 [M – 2CO]<sup>+</sup>, 197 [M – 2CO – I]<sup>+</sup>, 121 [CpFe]<sup>+</sup>, 76 [C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 56 [Fe]<sup>+</sup>.

**Reaction of *p*-diiodobenzene with [Mn(CO)<sub>5</sub>]-ZnCl.** 1. *Substrate–anion ratio 1:2; catalyst PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>*. Amounts of the reactants: *p*-diiodobenzene, 0.165 g (0.5 mmol); Mn<sub>2</sub>(CO)<sub>10</sub>, 0.253 g (0.65 mmol); ZnCl<sub>2</sub>, 0.212 g (1.56 mmol); NaK<sub>2,8</sub>, 0.10 ml; PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 10 mg (0.014 mmol, 1.4 mol %). Reaction time 3.5 h. We isolated in succession (eluent hexane) initial *p*-diiodobenzene, 0.033 g (20%); Mn<sub>2</sub>(CO)<sub>10</sub>, and *p*-IC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub> (XI); the latter product was additionally recrystallized from pentane. Yield of XI 0.07 g (34%). <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>),  $\delta$ , ppm: 7.227 d and 7.449 d (*J*<sub>*a,b*</sub> = 8 Hz). <sup>13</sup>C NMR spectrum (acetone-*d*<sub>6</sub>),  $\delta$ <sub>C</sub>, ppm: 147.941 (C<sup>1</sup>), 140.819 (C<sup>2</sup>), 137.847 (C<sup>3</sup>),

90.545 (C<sup>4</sup>), 215.519 (C≡O). IR spectrum (THF),  $\nu$ , cm<sup>-1</sup>: 2005 sh, 2026 v.s, 2063 w, 2122 m. Mass spectrum, *m/z*: 398 [M]<sup>+</sup>, 370 [M – CO]<sup>+</sup>, 342 [M – 2CO]<sup>+</sup>, 314 [M – 3CO]<sup>+</sup>, 286 [M – 4CO]<sup>+</sup>, 258 [M – 5CO]<sup>+</sup>, 203 [C<sub>6</sub>H<sub>4</sub>I]<sup>+</sup>, 131 [C<sub>6</sub>H<sub>4</sub>Mn]<sup>+</sup>, 55 [Mn]<sup>+</sup>. Found, %: C 33.35; H 1.04. C<sub>11</sub>H<sub>4</sub>IMnO<sub>5</sub>. Calculated, %: C 33.20; H 1.01. Elution with hexane–ether (2:1) gave Mn(CO)<sub>5</sub>I, 0.024 g (7.5%), and a yellow fraction which (according to the TLC data) contained several substances. This fraction was subjected to chromatography on a Silpearl plate using hexane–ether (3:1) as eluent to isolate *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub> and *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>CHO (XIII, a light yellow substance). <sup>1</sup>H NMR spectrum (chloroform-*d*),  $\delta$ , ppm: 7.736 d (H<sub>*a*</sub>), 7.584 d (H<sub>*b*</sub>) (*J*<sub>*a,b*</sub> = 8 Hz), 9.922 s. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2130 s, 2095 s, 2035 s, 2015 s, 1975 s, 1720 s. Also, traces of *p*-IC<sub>6</sub>H<sub>4</sub>CHO and Mn<sub>2</sub>I<sub>2</sub>(CO)<sub>8</sub> (*m/z* 588, M<sup>+</sup>) were detected.



XI



XIII

Yield of *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub> 0.026 g (11%). Mass spectrum, *m/z*: 466 [M]<sup>+</sup>, 438 [M – CO]<sup>+</sup>, 410 [M – 2CO]<sup>+</sup>, 382 [M – 3CO]<sup>+</sup>, 354 [M – 4CO]<sup>+</sup>, 326 [M – 5CO]<sup>+</sup>, 298 [M – 6CO]<sup>+</sup>, 270 [M – 7CO]<sup>+</sup>, 242 [M – 8CO]<sup>+</sup>, 214 [M – 9CO]<sup>+</sup>, 186 [M – 10CO]<sup>+</sup>, 55 [Mn] [11].

Yield of *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>CHO 0.02 g (13%); the product was recrystallized from pentane. Mass spectrum, *m/z*: 300 [M]<sup>+</sup>, 272 [M – CO]<sup>+</sup>, 244 [M – 2CO]<sup>+</sup>, 216 [M – 3CO]<sup>+</sup>, 188 [M – 4CO]<sup>+</sup>, 160 [M – 5CO]<sup>+</sup>, 105 [C<sub>6</sub>H<sub>4</sub>C(O)H]<sup>+</sup>, 76 [C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>, 55 [Mn]. Found, %: C 48.7; H 2.00. C<sub>12</sub>H<sub>5</sub>MnO<sub>6</sub>. Calculated, %: C 48.00; H 1.70.

2. *Substrate–anion ratio 1:2; catalyst Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>/trifurylphosphine*. Amounts of the reactants: *p*-IC<sub>6</sub>H<sub>4</sub>I, 0.165 g (0.5 mmol); Mn<sub>2</sub>(CO)<sub>10</sub>, 0.253 g (0.65 mmol); ZnCl<sub>2</sub>, 0.212 g (1.56 mmol); NaK<sub>2,8</sub>, 0.10 ml; Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, 10 mg (0.01 mmol, 1 mol %); trifurylphosphine, 8 mg (0.034 mmol, 3.4 mol %). Reaction time 1 h. We isolated *p*-I<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 0.016 g (10%), and *p*-IC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>, 0.031 g (15.6%) (eluent hexane). The subsequent elution with hexane–ether (3:1) afforded IMn(CO)<sub>5</sub>, 0.011 g (3.4%); *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>, 0.022 g (9.4%); *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>CHO, 0.023 g (15.2%); and *p*-IC<sub>6</sub>H<sub>4</sub>CHO, 0.005 g (4.3%). The following compounds were



isolated in trace amounts (identified by the mass spectra): *p*-IC<sub>6</sub>H<sub>4</sub>COOH, 248 [M]<sup>+</sup>; *p*-OHCC<sub>6</sub>H<sub>4</sub>CHO, 134 [M]<sup>+</sup>; *p*-OHCC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>CHO, 210 [M]<sup>+</sup>.

3. *Substrate-anion ratio 1:1, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.* Amounts of the reactants: *p*-IC<sub>6</sub>H<sub>4</sub>I, 0.330 g (1 mmol); Mn<sub>2</sub>(CO)<sub>10</sub>, 0.200 g (0.51 mmol); ZnCl<sub>2</sub>, 0.195 g (1.42 mmol); NaK<sub>2,8</sub>, 0.15 ml; PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 11.7 mg (0.016 mmol, 1.6 mol %); THF, 10 ml. The reaction mixture was diluted with an equal volume of petroleum ether, and the resulting solution was passed through a thin layer of silica gel (1.5 cm<sup>3</sup>, 60/200 μm). Further isolation procedure was the same as above. The following compounds were isolated: *p*-I<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 0.090 g (27%); *p*-IC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>, 0.136 g (35%); *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>, 0.028 g (12%) (eluent petroleum ether).

4. *Reaction of p-diiodobenzene with [Mn(CO)<sub>5</sub>]K; reactant ratio 1:1; catalyst PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.* Amounts of the reactants: *p*-IC<sub>6</sub>H<sub>4</sub>I 0.830 g (2.52 mmol); Mn<sub>2</sub>(CO)<sub>10</sub>, 0.488 g (1.25 mmol); PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 25 mg (0.036 mmol, 1.4 mol %); NaK<sub>2,8</sub>, 0.6 ml; THF, 15 ml. The mixture was diluted with an equal volume of petroleum ether and was passed through a small column charged with silica gel (1.5 cm<sup>3</sup>), the solution was evaporated with addition of silica gel, and the residue was separated by column chromatography according to the standard procedure. The following compounds were isolated: eluent petroleum ether: *p*-IC<sub>6</sub>H<sub>4</sub>I, 0.090 g (10%); *p*-IC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>, 0.6 g (60%); eluent petroleum ether-ether (1:1): *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>, 0.018 g (3.1%).

**Reaction of *p*-IC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub> with [Mn(CO)<sub>5</sub>]K in the presence of Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>/Xantphos.** Amounts of the reactants: *p*-IC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>, 0.083 g (0.21 mmol); Mn<sub>2</sub>(CO)<sub>10</sub>, 0.040 g (0.10 mmol); NaK<sub>2,8</sub>, 0.08 ml; Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, 4 mg (2 mol %, 0.0039 mmol); Xantphos, 5 mg (4.4 mol %, 0.0087 mmol); THF, 5 ml. After 1.5 h, the reaction mixture was diluted with an equal volume of petroleum ether, the resulting solution was passed through a thin layer of silica gel (2 cm<sup>3</sup>), and the sorbent was washed with ether. Removal of the solvent gave 0.080 g (82%) of *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>. Its mass spectrum coincided with that reported in [11]. <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>), δ, ppm: 7.28 s.

**Reaction of [Mn(CO)<sub>5</sub>]K with *p*-diiodobenzene in the presence of Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>/Xantphos.** Amounts of the reactants: *p*-IC<sub>6</sub>H<sub>4</sub>I, 0.067 g (0.20 mmol); Mn<sub>2</sub>(CO)<sub>10</sub>, 0.080 g (0.21 mmol); NaK<sub>2,8</sub>, 0.1 ml; Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, 8 mg (1.9 mol %, 0.0077 mmol); Xantphos, 10 mg (4 mol %, 0.017 mmol); THF, 6 ml. After 1.5 h, the mixture was

treated as described in the preceding experiment to isolate 0.060 g (63%) of *p*-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>4</sub>Mn(CO)<sub>5</sub>.

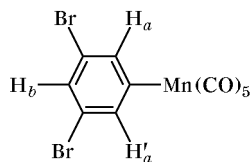
**Reaction of Mn(CO)<sub>5</sub>K with 1,3,5-triiodobenzene.** *Substrate-anion ratio 1:3; catalyst Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>/Xantphos.* Amounts of the reactants: 1,3,5-C<sub>6</sub>H<sub>3</sub>I<sub>3</sub>, 0.124 g (0.27 mmol); Mn<sub>2</sub>(CO)<sub>10</sub>, 0.21 g (0.53 mmol) (30% excess); NaK<sub>2,8</sub>, 0.14 ml; Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, 0.0173 g (0.017 mmol, 2.1 mol %); Xantphos, 0.025 g (0.043 mmol, 5.3 mol %); THF, 8 ml. Reaction time 2.5 h. The reaction mixture was diluted with an equal volume of petroleum ether, the resulting solution was passed through a thin layer of silica gel (2 cm<sup>3</sup>; 60/200 μm) and evaporated, and the residue was subjected to column chromatography on silica gel (60/200 μm) using petroleum ether as eluent to isolate 1,3,5-[(CO)<sub>5</sub>Mn]<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, 0.090 g (50%), and 1,3,5-I[(CO)<sub>5</sub>Mn]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 0.040 g (25%).

<sup>1</sup>H NMR spectrum of 1,3,5-[(CO)<sub>5</sub>Mn]<sub>3</sub>C<sub>6</sub>H<sub>3</sub> (acetone-*d*<sub>6</sub>), δ, ppm: 7.35 s (3H). Mass spectrum, *m/z*: 660 [M]<sup>+</sup>, 605 [M - 2CO + H]<sup>+</sup>, 576 [M - 3CO + H]<sup>+</sup>, 520 [M - 5CO]<sup>+</sup>, 492 [M - 6CO]<sup>+</sup>, 380 [M - 10CO]<sup>+</sup>, 352 [M - 11CO]<sup>+</sup>, 296 [M - 13CO]<sup>+</sup>, 240 [M - 15CO]<sup>+</sup>, 185 [C<sub>6</sub>H<sub>3</sub>Mn<sub>2</sub>]<sup>+</sup>, 131 [C<sub>6</sub>H<sub>4</sub>Mn]<sup>+</sup>, 78 [C<sub>6</sub>H<sub>6</sub>]<sup>+</sup>, 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 55 [Mn]<sup>+</sup>.

<sup>1</sup>H NMR spectrum of 1,3,5-I[(CO)<sub>5</sub>Mn]<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (acetone-*d*<sub>6</sub>), δ, ppm: 7.56 d (2H), 7.73 t (1H) (*J*<sub>H,H</sub> = 1.2 Hz). Mass spectrum, *m/z*: 591 [M]<sup>+</sup>, 563 [M - CO]<sup>+</sup>, 535 [M - 2CO]<sup>+</sup>, 507 [M - 3CO]<sup>+</sup>, 479 [M - 4CO]<sup>+</sup>, 451 [M - 5CO]<sup>+</sup>, 423 [M - 6CO]<sup>+</sup>, 395 [M - 7CO]<sup>+</sup>, 367 [M - 8CO]<sup>+</sup>, 339 [M - 9CO]<sup>+</sup>, 311 [M - 10CO]<sup>+</sup>, 258 [C<sub>6</sub>H<sub>4</sub>MnI]<sup>+</sup>, 204 [PhI]<sup>+</sup>, 182 [MnI]<sup>+</sup>, 55 [Mn]<sup>+</sup>. IR spectrum (THF), ν, cm<sup>-1</sup>: 2123 m, 2115 s, 2060 m, 2030 v.s, 2005 s. Found, %: C 32.50; H 0.47. C<sub>16</sub>H<sub>3</sub>IMn<sub>2</sub>O<sub>10</sub>. Calculated, %: C 32.46; H 0.51.

**Reaction of Mn(CO)<sub>5</sub>K(or ZnCl) with 1,3,5-tri-bromobenzene.** *Substrate-anion ratio 1:3; catalyst Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>/Xantphos.* 1. *Zinc salt.* Amounts of the reactants: 1,3,5-C<sub>6</sub>H<sub>3</sub>Br<sub>3</sub>, 0.042 g (0.133 mmol); Mn<sub>2</sub>(CO)<sub>10</sub>, 0.080 g (0.21 mmol); ZnCl<sub>2</sub>, 0.085 g (0.63 mmol); NaK<sub>2,8</sub>, 0.04 ml; Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, 8.5 mg (0.0082 mmol, 2 mol %); Xantphos, 11 mg (0.019 mmol, 4.75 mol %); THF, 7 ml. After 2 h, the reaction mixture was diluted with an equal volume of petroleum ether, the resulting solution was passed through a thin layer of silica gel (2 cm<sup>3</sup>; 60/200 μm) and evaporated, and the residue was separated by column chromatography on silica gel (60/200 μm) using petroleum ether as eluent to isolate Mn<sub>2</sub>(CO)<sub>10</sub>, 0.008 g (10%); 1,3,5-C<sub>6</sub>H<sub>3</sub>Br<sub>3</sub>, 0.008 g (20%); and 1,3,5-(CO)<sub>5</sub>MnC<sub>6</sub>H<sub>3</sub>Br<sub>2</sub> (XVII), 0.034 g (60%). <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>), δ, ppm: 7.310 t (1H, H<sub>b</sub>), 7.620 d (2H, H<sub>a</sub>) (*J*<sub>a,b</sub> = 2 Hz). IR spectrum

(THF),  $\nu$ ,  $\text{cm}^{-1}$ : 2010 sh, 2030 v.s, 2067 w, 2126 s. Mass spectrum,  $m/z$ : 430  $[M]^+$ , 402  $[M - \text{CO}]^+$ , 374  $[M - 2\text{CO}]^+$ , 346  $[M - 3\text{CO}]^+$ , 318  $[M - 4\text{CO}]^+$ , 290  $[M - 5\text{CO}]^+$ , 236  $[\text{C}_6\text{H}_4\text{Br}_2]^+$ , 155  $[\text{C}_6\text{H}_4\text{Br}]^+$ , 134  $[\text{MnBr}]^+$ , 75  $[\text{C}_6\text{H}_3]^+$ , 55  $[\text{Mn}]^+$ . Found, %: C 30.83; H 0.71.  $\text{C}_{11}\text{H}_3\text{Br}_2\text{MnO}_5$ . Calculated, %: C 30.73; H 0.70.



XVII

2. *Potassium salt*. Amounts of the reactants: 1,3,5- $\text{C}_6\text{H}_3\text{Br}_3$ , 0.045 g (0.14 mmol);  $\text{Mn}_2(\text{CO})_{10}$ , 0.082 g (0.21 mmol);  $\text{NaK}_{2,8}$ , 0.035 ml;  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ , 7.7 g (0.0075 mmol, 1.8 mol %); Xantphos, 10.6 g (0.018 mmol, 4.3 mol %); THF, 8 ml. Reaction time 1.5 h. The reaction mixture was treated as described above to isolate 1,3,5- $\text{C}_6\text{H}_3\text{Br}_3$ , 0.004 g (9%);  $\text{Mn}_2(\text{CO})_{10}$ , 0.008 g (10%); and 1,3,5- $(\text{CO})_5\text{Mn}-\text{C}_6\text{H}_4\text{Br}_2$ , 0.036 g (60%).

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