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Bi- and trinuclear σ-aryl complexes of iron and manganese

Galina A. Artamkina and Irina P. Beletskaya*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation.
Fax: +7 095 939 3618; e-mail: beletska@org.chem.msu.ru

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The binuclear and trinuclear aryl σ-complexes of iron and manganese have been prepared by the palladium-catalysed reactions of *m*-diiodobenzene, *p*-diiodobenzene or 1,3,5-triiodobenzene with cyclopentadienyldicarbonyliron and manganese pentacarbonyl anions.

The preparation of polynuclear arene complexes with sp^2-transition metal bonds is not only an interesting synthetic goal but also a problem of practical importance because these complexes exhibit valuable physico-chemical properties. These complexes can be used in the development of new materials for non-linear optics or as liquid crystals, catalysts, and sensors.[1–5]

The interaction of aryl halides with transition metal carbonyl anions (carbonylates) is the simplest method for the synthesis of the σ-aryl derivatives of transition metals. However, carbonylates do not enter nucleophilic substitution reactions with non-activated aryl halides.[6–9] Thus, it was found[8] that the yield of the σ-aryl complex of iron in the reaction of supernucleophilic iron carbonylate $[CpFe(CO)_2]^-$ with iodobenzene was 2%, whereas only traces of a binuclear complex were obtained in the reaction with diiodobenzene.[9]

Previously, such polynuclear complexes were usually prepared by the two-step synthesis including the preparation and decarbonylation of acyl metal complexes.[9–17]

$$L_mM^- + Ar(COCl)_n \longrightarrow Ar(COML_m)_n \xrightarrow{\Delta \text{ or UV}} Ar(ML_m)_n,$$

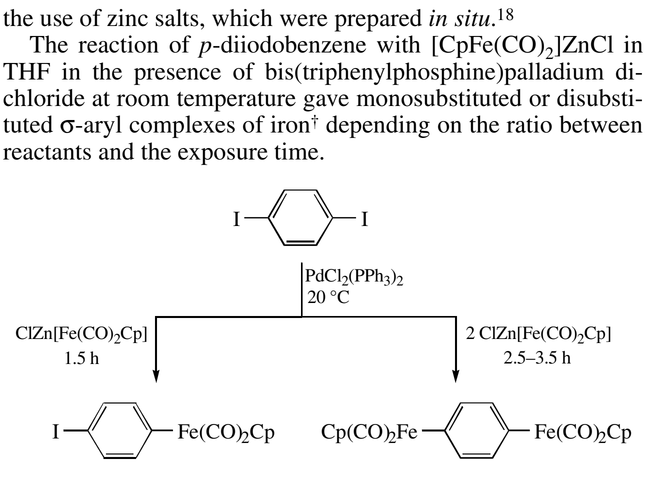
where $n = 1–3$.

A number of binuclear and trinuclear manganese, rhenium, and iron complexes with aryl bridges were prepared using this method. The total yields of the complexes varied within a range of 26–62%. Note that not always the parent acyl metal complexes can be prepared and successfully decarbonylated.[9,13,14]

Previously,[18,19] we found that the cross-coupling reaction of aryl and vinyl halides with carbonylates in the presence of palladium or nickel complexes can be used for the synthesis of the mononuclear σ-aryl and σ-vinyl complexes of transition metals. In this work, we attempted to apply this reaction to the synthesis of the binuclear and trinuclear arene complexes of iron and manganese.

The dicarbonylcyclopentadienyliron anion is most reactive among transition metal carbonylates. According to Dessy *et al.*,[20] its nucleophilicity in reactions with alkyl halides is higher than that of manganese carbonylate by six orders of magnitude: $CpFe(CO)_2^-$ (7.0×10^7) > $Mn(CO)_5^-$ (77) > $Co(CO)_4$ (1). At the same time, this anion is a good reducing agent. We found that side reactions associated with reduction can be eliminated with the use of zinc salts, which were prepared *in situ*.[18]

The reaction of *p*-diiodobenzene with $[CpFe(CO)_2]ZnCl$ in THF in the presence of bis(triphenylphosphine)palladium dichloride at room temperature gave monosubstituted or disubstituted σ-aryl complexes of iron[†] depending on the ratio between reactants and the exposure time.

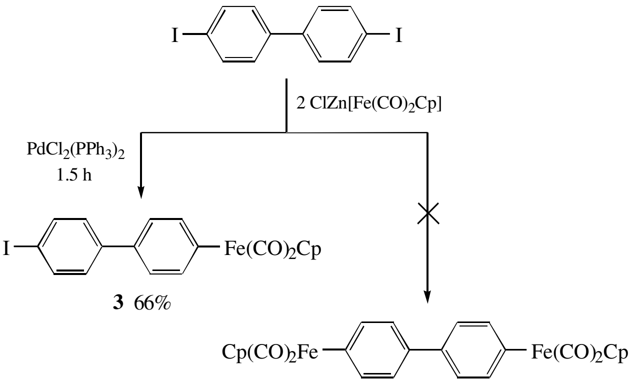


1 70–75%

2 70–80%

Evidently, the second step (the formation of the binuclear iron carbonyl complex) is much slower than the first step because of the strong donor effect of the $CpFe(CO)_2$ group.[21–23]

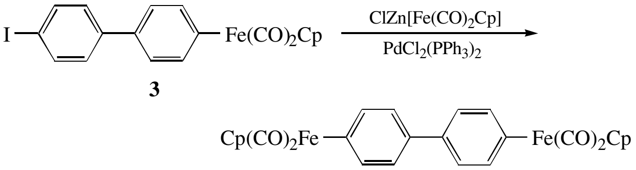
Surprisingly, in the case of *p,p′*-diiodobiphenyl, only monosubstituted product **3** was formed even in the presence of 2 equiv. of iron carbonylate.



3 66%

4

With the use of the $Pd_2(dba)_3{\cdot}CHCl_3$ complex of zero-valent palladium (dba is dibenzylideneacetone) in the presence of trifurylphosphine, the formation of binuclear complex **4** was also not observed, whereas the yield of complex **3** significantly decreased (36%). An increase in the reaction time to 5 h also resulted in a decrease in the yield of complex **3** (18%). We synthesised complex **4** in a low yield (20%) from isolated mononuclear complex **3**.



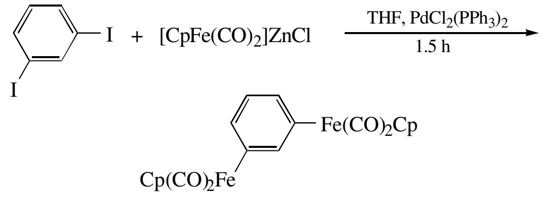
3

4 20%

[†] *General procedure of cross-coupling reactions.*

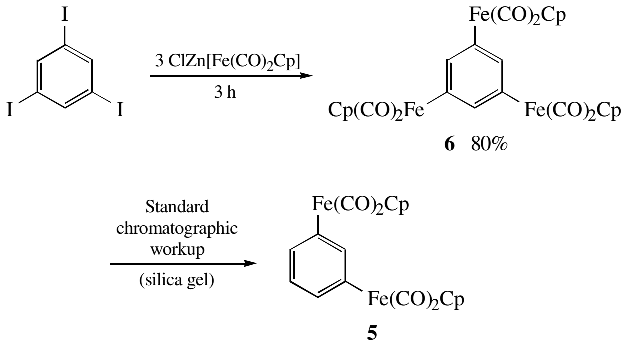
All operations with the solutions of carbonylate salts and reaction products were performed using standard vacuum-line / argon atmosphere techniques. The solvent (THF) was vacuum transferred to the reaction vessel. The reaction was performed in an apparatus that consisted of two vessels joined with a tube with a sealed glass filter. The corresponding dimer was reduced in a reaction vessel with intense stirring {0.07–0.08 cm^3 of an $NaK_{2.8}$ alloy were taken per 0.5 mmol of the dimer $[CpFe(CO)_2]_2$ or $Mn_2(CO)_{10}$; the reaction time was 1 h to 1 h 10 min}. The resulting solution was filtered into the other vessel in which the reaction was performed. A portion of $ZnCl_2$ was loaded into this vessel and sublimed onto the walls; thin-walled glass beads with sealed portions of the substrate and the catalyst were also placed in the reaction vessel; these beads were broken using a ground-glass hook. The reactant concentration in solution was 0.1–0.2 mol dm^{-3}. The course of the reaction was monitored by TLC (Silufol UV-254) with sampling at regular intervals in a flow of argon. After completion of the reaction, the reaction mixture was evaporated with a small amount of silica gel and chromatographed on a column with SiO_2 (L = 40/100 or 60/200).

In contrast, the reaction of iron carbonylate with *m*-diiodobenzene [in the absence of conjugation with the $CpFe(CO)_2$ group] gave only binuclear complex **5** regardless of the ratio between reactants.



5 75%

According to ^1H NMR-spectroscopic data, the reaction of 1,3,5-triiodobenzene with 3 equiv. of $[CpFe(CO)_2]ZnCl$ resulted in the formation of trinuclear complex **6** in a quantitative yield.

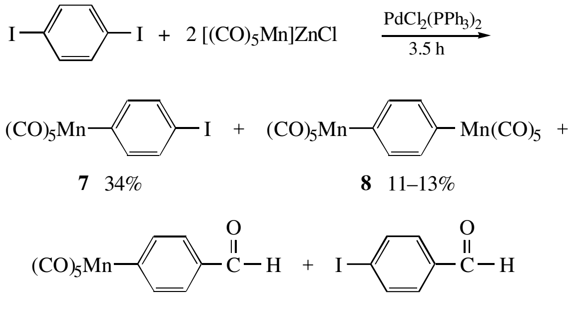


6 80%

5

The ^1H NMR spectrum exhibited two singlets at 6.99 (3H) and 4.85 ppm (5H); in this case, the signal of parent triiodobenzene was absent. However, only 1,3-binuclear complex **5** (40–60%) was obtained with the use of a standard chromatographic procedure on silica gel, which was used previously for separating σ-aryl complexes.[†] Complex **5** was identical to that obtained from *m*-diiodobenzene, that is, one $CpFe(CO)_2$ group was eliminated. This by-process was removed by passing the reaction mixture through a thin bed of Al_2O_3 before chromatographing (on a column with SiO_2). In this case, complex **6** was obtained in 80% yield. It is interesting to note that the complex thus purified underwent no degradation on passing it through SiO_2. The degradation of the complex on SiO_2 is possibly catalysed by some Pd species, which are removed by filtration through Al_2O_3.

As would be expected, the reactivity of the zinc salt of manganese carbonylate was found to be much lower than that of $[CpFe(CO)_2]ZnCl$. Nevertheless, the conversion of the reaction with *p*-diiodobenzene in the presence of $PdCl_2(PPh_3)_2$ as a catalyst (at a 1:2 ratio between the reactants) was 60% for 3.5 h. However, as distinct from reactions with iron carbonylate, the formation of a mixture of products (**7**–**10**) was observed.



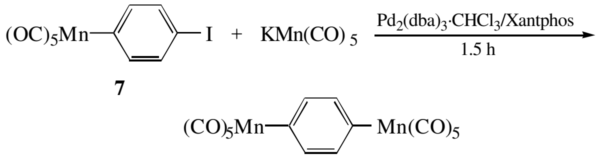
7 34% **8** 11–13%

9 13% **10** traces

Although the total yield of products was reasonably high (60%, **7**–**10**) in the catalysis with $PdCl_2(PPh_3)_2$, the yield of binary complex **8** was much lower (11–13%) than that of mononuclear complex **7** (34%). Note that the formation of two aldehydes **9** and **10** was observed along with substitution products. However, these products were formed in the course of chromatographing the reaction mixture rather than in the course of the reaction.[‡]

Our attempts to change the ratio between mono- and disubstitution products by varying the nature of the catalyst [Pd_2dba_3/$(Fur)_3P$, Ph_3As], solvent (diethyl ether), and temperature (–30 °C) were unsuccessful. A decrease in the carbonylate concentration, namely, the reaction in THF at equimolar ratios between reactants had also insignificant effect on the ratio between products **7** and **8**. Monoarylated complex **7** was obtained in a reasonably high yield (60%) by adding the potassium salt of manganese carbonylate at equimolar ratios between the reactants. As mentioned above, with the use of the zinc salt, the product yield in the cross-coupling reaction of iron carbonylate with iodobenzene was much higher than that with the use of the potassium salt.[18] Because manganese carbonylate is a weaker nucleophile and reductant than iron carbonylate, it is better to use the potassium salt in reactions with its participation.

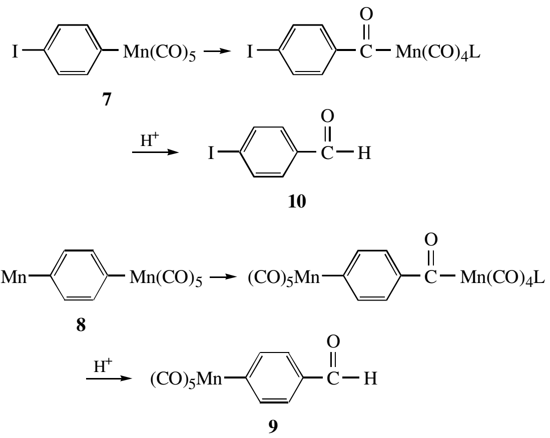
Thus, under the tested conditions, binuclear complex **8** was formed in a low yield. Moreover, it gave rearrangement products upon chromatographing. Our attempt to improve the yield of the disubstitution product by using $Pd_2(dba)_3 \cdot CHCl_3$/L as a catalyst, where L = Fur_3P, BINAP, were unsuccessful. A binuclear complex was prepared with the use of Xantphos as a ligand; the reaction occurred almost quantitatively and resulted in the formation of complex **8** in 82% yield. *p*-Diiodobenzene can also serve as the initial substrate in the reaction, although the yield of complex **8** was lower in this case. The resulting product was prevented from decomposition in the course of chromatographing by the filtration of the reaction mixture, which was twofold diluted with light petroleum, through a thin bed of SiO_2.



7

8 82%

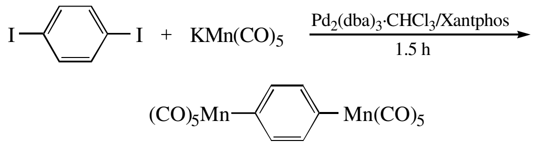
[‡] *p*-(Pentacarbonylmanganese)benzaldehyde **9** and *p*-iodobenzaldehyde **10** were detected in the reaction products after chromatographing on a column with SiO_2. Evidently, they are formed from complexes **7** and **8**, respectively, by an aryl–acyl rearrangement.



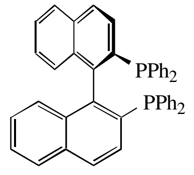
7 **10** **8** **9**

These rearrangements are known for almost all transition metals;[24] they readily occur with alkyl complexes and much more difficult with aryl complexes.

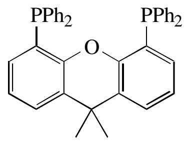
The IR spectrum of the reaction mixture before chromatographing exhibited no characteristic bands of aldehyde (1720 cm^{-1}) and acyl groups (~1587 cm^{-1}).[9] Carbonyl bands were also absent from the reaction performed in a CO atmosphere. This fact allowed us to conclude that aldehydes **9** and **10** were formed on the column in the course of chromatographing the reaction mixture. However, our attempts to perform an aryl–acyl rearrangement by stirring the reaction mixture with silica gel before chromatographing was unsuccessful.



8 63%

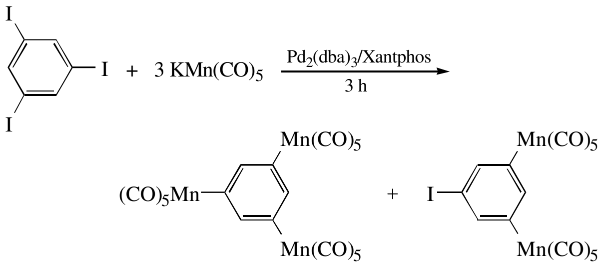


BINAP



Xantphos

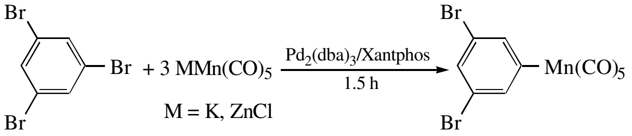
The use of Xantphos as a ligand allowed us to obtain trinuclear manganese complex **11** in good yield in the reaction with 1,3,5-triiodobenzene, although the binuclear complex **12** was detected along with the target product.



11 50%

12 25%

Under the same conditions, only one bromine atom was replaced in 1,3,5-tribromobenzene, and 1,3,5-dibromo(pentacarbonylmanganese)benzene **13** was formed. Complex **13** was also formed in the same yield in the reaction of 1,3,5-tribromobenzene with the zinc salt of manganese carbonylate.



13 60%

All the binuclear and trinuclear complexes were characterised by ^{1}H NMR spectroscopy and mass spectrometry; their characteristics were consistent with published data.[9] In conclusion, note that a number of new mononuclear iron and manganese complexes and a binuclear manganese complex containing halogens at the benzene ring were prepared in the course of this study. All these complexes were characterised by elemental analysis, IR spectroscopy and ^{1}H NMR (and, in some cases, ^{13}C NMR) spectroscopy.

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