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IRON DIARYLS WITH METAL–CARBON σ-BONDS

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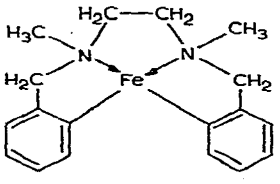
SUMMARY

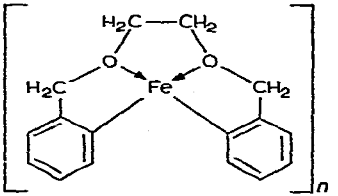
Syntheses, properties and determination of the configuration of the compounds (I), (II) and (III) are described. The possibilities for bonding are briefly discussed.

INTRODUCTION

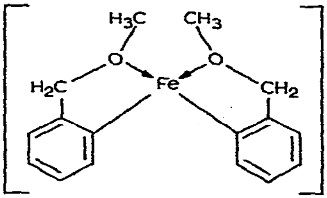
Numerous organoiron compounds, in which carbon monoxide molecules of iron carbonyls or derivatives of iron carbonyls are partially substituted by alkyl, aryl or the analogous fluoro-organic groups, have been made since the first compound of this type[1] was synthesized[2,3]. The existence of the iron–carbon σ-bond was proved in some of these compounds not only from conclusions of spectroscopic data but also by X-ray structure determinations[4]. On the other hand, diethylbis(bipyridine)iron[5] and bis(pentachlorophenyl)bis(diethylphenylphosphine)iron[6] are the only known iron dialkyls and iron diaryls, respectively, which are stable at room temperature and which are reliably characterised.



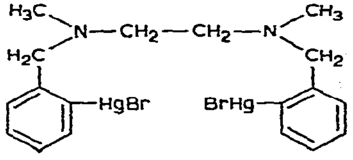
$FeC_{18}H_{22}N_2$ (I)
Dark-red crystals



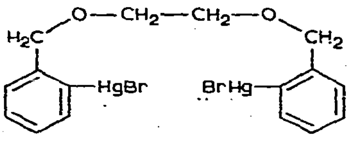
$FeC_{16}H_{16}O_2$ (II)
Yellow-green powder



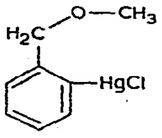
$FeC_{16}H_{18}O_2$ (III)
Dark-green powder



(X)



(XI)



(XII)

Now the compounds (I), (II) and (III) have been synthesized in the present work[7] by reacting an excess of the Grignard compounds of N,N'-dimethyl-N,N'-bis-

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(*o*-bromobenzyl)ethylenediamine (IV), 1,2-bis(*o*-bromobenzyloxy)ethane (V) and *o*-bromobenzyl methyl ether (VI) with anhydrous iron(II) chloride in tetrahydrofuran. The compounds (I)–(III) are extremely sensitive to moisture and air, which must be carefully excluded during the syntheses and handling. Compound (I)–(III) are completely decomposed between 120 and 160° in an inert atmosphere, but they are stable at room temperature for months under dried argon or nitrogen.

Compound (I) can be isolated in the form of ruby crystals, which are soluble in a number of organic solvents (tetrahydrofuran, benzene, dioxane, ethylene glycol dimethyl ether, diethyl ether, cyclohexane, isooctane; arranged in the order of decreasing solubility). Measurements of electric conductivity in pyridine and tetrahydrofuran showed that (I) is a non-electrolyte. Determinations of the molecular weight in benzene indicated that the compound is a monomolecular species in that solvent. During investigations with a magnetic balance, (I) was found to have a magnetic moment of 4.45 Bohr magnetons, equivalent to four unpaired electron spins.

Compound (II) and (III) differ from (I) in astonishing ways, but the former two resemble each other in many of their properties: in their color (yellow green and green, respectively), their manner of synthesis, their insolubility in such usual solvents as tetrahydrofuran, benzene or dioxane and in their extreme sensitivity to air, which makes their handling more difficult than for (I). The remarkable insolubility prevented determinations of their molecular weights, but the non-electrolytic character of (II) in pyridine was proved. Compound (II) dissolves slightly in pyridine to form dark red solutions. Attempts to determine the magnetic moments of these compounds did not succeed because there were disturbances caused by metallic iron, which could not be separated by recrystallization because of the mentioned insolubility. The amount of iron included in (II) was so small that it was not evident analytically, whereas 2–3 % of metallic iron was found in (III), which was synthesized several times under carefully controlled conditions. In (III), the presence of iron was demonstrated by analytical iron and carbon determinations of absolutely halogen free samples, by electron spin resonance and Mößbauer investigations, and by the evolution of hydrogen, which was observed during the addition of acid to products of a methanolysis performed previously. The reason for this impurity was not found. Pure samples of (VI) (purity checked by vapour-phase chromatography) yielded (III) containing the mentioned 2–3 % of metallic iron.

The configuration of the organoiron compounds and the existence of the metal–carbon σ-bonds were proved by chemical and physical investigations. After quantitative analysis, the compounds were cleaved at their metal–carbon bonds with methanol or mercury(II) halides. The resulting amine, ethers and arylmercury halides were isolated as completely as possible, were analyzed, and then, to prove their identity, were synthesized in an independent way. Syntheses were performed, for example, by reacting the Grignard compounds of the starting materials (IV)–(VI) with methanol or mercury(II) halides. Infrared spectra and physical data were compared so far as possible with data in the literature. Transition metal–carbon σ-bonds are known to be cleaved without gas evolution by methanol as well as by mercury(II) halides[8]. Infrared spectra of the organoiron compounds (I)–(III), the starting materials (IV)–(VI) and the products *N,N'*-dimethyl-*N,N'*-dibenzylethylenediamine (VII), 1,2-bis(benzyloxy)ethane (VIII), benzyl methyl ether (IX), (X), (XI), and (XII), which were isolated during the cleavage attempts mentioned above, were recorded in the range of 4000–400 cm^{-1}. Comparisons showed that an absorption band at $\tilde{\nu}$ 444–435 cm^{-1} appeared only in the spectra of the organoiron compounds. Therefore, it seems reasonable to assign those bands to the excitation of vibrations of the iron–carbon σ-bonds.

Electron spin resonance investigations of powder samples of (I)–(III) in sealed capillaries resulted in broad signals at room temperature, whereas ionic iron(II) compounds show resonance signals only at −190°. Iron π-complexes are normally diamagnetic, with the exception of bis(hexamethylbenzene)iron(0)[9]. The magnetic moment of 4.45 Bohr magnetons, which was determined for (I), can be interpreted in terms of the valence bond model, if one assumes a $3d^6$ $4s^2$ $4p^2$ or $3d^6$ $4s^2$ $4p^6$ effective electron configuration of the iron atom. The first of the two arrangements should have two electrons with antiparallel spins in the $4p$ orbital. These could result from the combination of iron(II) with aryl groups, each of which should contribute two electrons, if we include the electrons contributed by the ligands during the formation of the σ-bonds. The result would be two sp-hybridized bonds at the iron, which are not usually observed in the known iron(II) compounds. The $3d^6$ $4s^2$ $4p^6$ electron configuration could be found if two additional complex bonds from the heteroatoms of the organic groups brought four additional electrons to the disposal of the iron. This electron configuration is more probable. In this case, the organoiron compounds should be distorted, tetrahedral chelate complexes, which contain sp^3-hybridized bonds and resemble compounds of aluminium[10,11], beryllium[12], chromium[13,14] and cobalt[15] synthesized earlier. Examinations of Stuart–Briegleb models of (I) showed that this compound should be a racemic mixture of optical isomers in which the iron atom is screened off completely only on one side by methyl, ethylene, and tolylene groups. At the unshielded side of the molecule, addition reactions of small molecules or reactions with multiple bonds seem possible with the iron atom as reaction center. Proof of coordination bonds to the iron atom of the compounds (I)–(III) was not obtained definitely. Such information will probably come only from a complete X-ray structure determination, which will be done in the near future. Some indications from chemical and physical experiments are as follows:

(1). A 1:1 complex of iron(II) chloride and *N*,*N'*-dimethyl-*N*,*N'*-bis(*o*-bromobenzyl)-ethylenediamine (IV) was isolated from the dark red brown solutions of tetra-

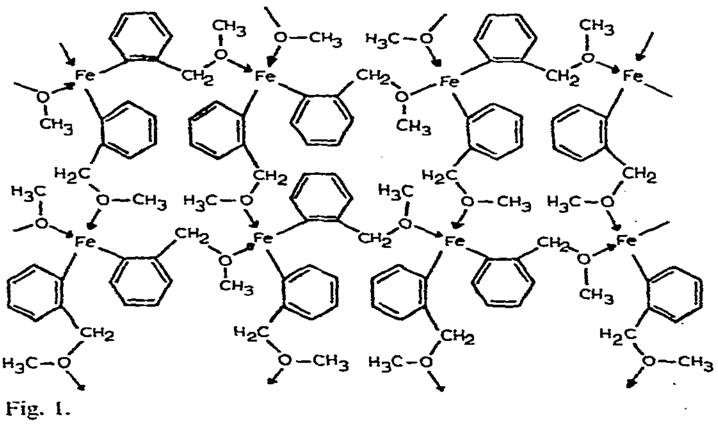

Fig. 1.

hydrofuran. The solid, dried complex had a brownish-white colour. It resembles a recently synthesized complex of iron(II) bromide and *N,N,N',N'*-tetramethylethylenediamine, which was made in a completely different way[16], in its colour and sensitivity to intruding moisture and air.

(2). The observed insolubility of the two oxygen-containing compounds (II) and (III) points to the presence of coordination polymers, which could have the constitution as described in Fig. 1.

(3). Results of Mößbauer investigations, which will be reported separately in the near future[17], give some indications that coordination bonds are likely.

Electron spin resonance studies of dilute (10^{-2}–10^{-4} *M*) solutions of (I) in benzene did not yield the hyperfine structure splitting of the broad resonance signal which might be expected from the presence of the two nitrogen atoms with nuclear spin. This expected splitting was also not observed when dilute solutions of similar chromium compounds[14] were investigated for purposes of comparison. It was impossible to get evidence of the coordination bonds by infrared spectroscopy because there was no suitable apparatus available. It is known[18] that the vibrations of transition metal–heteroatom bonds in complexes cause absorptions in the range of 400–200 cm^{-1}.

Another possibility to demonstrate the existence of these bonds, by use of nuclear magnetic resonance, seems to be excluded for the only soluble compound, (I), because of its paramagnetism. Evidence for the existence of bonds between cobalt and nitrogen atoms was obtained by this elegant method in the case of the diamagnetic tris{5-tert-butyl-2-[(dimethylamino)methyl]phenyl}cobalt[15].

EXPERIMENTAL

All reactions of organometallic compounds were carried out under purified nitrogen or argon in carefully dried solvents. Compounds (IV)–(VI) were synthesized by methods already reported in the literature[19,20].

Compound (I)

One suspended 1.2 g (0.05 g-atom) of magnesium, activated with iodine, in 30 ml of tetrahydrofuran in a three-necked flask, equipped with gas inlet tube, reflux condenser and dropping funnel. The magnesium was reacted with a solution of 7.1 g (0.017 mole) of (IV) in 40–50 ml of tetrahydrofuran. The solution of the Grignard compound was added during 1.5 h to a stirred and cooled (with ice–salt mixture) suspension of 1.5–1.6 g (nearly 0.012 mole) of anhydrous iron(II) chloride in 30 ml of tetrahydrofuran. The stirring was continued after finishing the addition for 90 min in the ice bath and then for 12 h at room temperature. After completion of the reaction in this way the main part (75%) of the tetrahydrofuran was removed under vacuum and then 40 ml of dioxane (purified with benzophenone and sodium) were dropped into the stirred solution at 40°. The resulting precipitate was filtered off using a fritted-glass filter (G3 size) after at least 2 h of standing and discarded. The volume of the dark red filtrate was reduced to 10–15 ml in vacuum at a maximum temperature of 50°. The concentrated solution was stored then in a refrigerator for at least 12 h. One filtered the contents of the flask after thawing through a fritted-glass filter (G3 size) and dried the red crystallized precipitate by removing the adherent solvent with an oil pump. The yield of this already fairly pure product, which contained about 15% of iron, was 78% (average). One added 10 ml of dioxane, stirred thoroughly at 60° for a short time, filtered again through a small fritted-glass filter, dried the filtered solid with an oil pump and stored the filtrate in a refrigerator for at least 12 h. From this filtrate crystals were isolated, which contained 16.5–17.0% of iron, whereas the crystals from the first filtration were pure (I) and did not contain even trace amounts of halogen ions. (Found: C, 66.93; H, 6.85; Fe, 17.21; N, 8.58; mol.wt. cryoscopic in benzene, 330±5. $C_{18}H_{22}FeN_2$ calcd.: C, 67.06; H, 6.88; Fe, 17.37; N, 8.69%; mol.wt., 322.)

Compound (II)

One reacted 1.2 g (0.05 g-atom) of magnesium in 20 ml of tetrahydrofuran with 6.7 g (0.017 mole) of (V) dissolved in 45 ml of tetrahydrofuran. The resulting Grignard solution was dropped during 45–60 min into a stirred and cooled suspension of 1.5 g (0.012 mole) of anhydrous iron(II) chloride in 30 ml of tetrahydrofuran. Then the mixture was stirred another 2 h at low temperature and, for 8–15 h, at room temperature before one filtered through a fritted-glass filter. The brown-black filtrate was discarded and the dark residue washed several times with small amounts of tetrahydrofuran. During this operation, the solid was stirred thoroughly with a magnetic stirring bar. After the tetrahydrofuran filtrate became colourless, the washed precipitate was freed of the adherent solvent with an oil pump. One obtained a yellow-green product (yield about 70%), nearly free of halogen ions, and containing 17.7–18.1% of iron. Traces of halogen in the organoiron compound could be removed by treatment on a fritted-glass plate modified for extraction. The extraction with tetrahydrofuran was done under low vacuum at temperatures lower than 50° to avoid possible thermal decomposition at high temperatures. (Found: C, 65.05; Fe, 18.77. $C_{16}H_{16}FeO_2$ calcd.: C, 64.90; Fe, 18.86%.)

Compound (III)

One reacted 0.8 g (0.033 g-atom) of magnesium turnings in 15 ml of tetrahydrofuran with a solution of 5 g (0.025 mole) of (VI) in 25 ml of tetrahydrofuran and dropped the resulting Grignard solution, under vigorous stirring, into 1.0–1.2 g (0.01 mole) of iron(II) chloride at −20°. The addition required 40–70 minutes. Stirring was continued for 2.5 h at low temperature and then for 12–15 h at room temperature before one filtered through a fritted-glass filter. The remaining precipitate was purified in the same manner as was (II). The yield was 60%. One could remove traces of halogen from (III), as well as (II), by extraction with tetrahydrofuran. (Found: C, 62.12; Fe, 20.5–22.0. $C_{16}H_{18}FeO_2$ calcd.: C, 64.44; Fe, 18.73%.)

The carbon percentage was determined using a sample which contained 22.0% of iron, corresponding to 96.73% of (III) and 62.33% of carbon.

Decomposition of (I) with methanol

Under nitrogen, 3.2 g of I was decomposed with methanol freed of air. After the addition of hydrochloric acid, the solvent was removed, the residue treated with a sodium hydroxide solution, the iron oxide hydrates filtered off and the filtrate extracted five times with diethyl ether. The combined ether extracts were used to extract the precipitate of the iron oxide hydrates in a Soxhlet apparatus. The ether layer was dried over potassium hydroxide, filtered, the ether removed and the remaining oil (2.83 g) fractionated to obtain *N,N'*-dimethyl-*N,N'*-dibenzylethylenediamine, b.p. 133°/0.12 mm, n_D^{22} 1.5441, yield 1.56 g (59%).

Decomposition of (II) with methanol

Compound (II) (1.56 g) in a small amount of tetrahydrofuran, was decomposed with air free methanol without observation of gas evolution. The organic solvents were distilled off, diluted sulfuric acid added and the aqueous phase extracted several times with ether. The combined ether layers were dried over calcium chloride, filtered and the ether removed. The remaining oil (1.20 g) was distilled under vacuum to obtain 1,2-bis(benzyloxy)ethane, b.p. 128°/0.05 mm, n_D^{22} 1.5452, yield 1.01 g (79%).

Decomposition of (III) with methanol

In the manner previously described for (II), 2.49 g of (III) was decomposed and processed to yield benzyl methyl ether, b.p. 57.5–59°/13 mm, $n_D^{19.5}$ 1.5027, yield 1.50 g (73%).

Decomposition of (I) with mercury(II) bromide

Compound (I) (2.15 g) was transferred from a storage container to a stirred solution of 9.0 g of mercury(II) bromide in tetrahydrofuran. At once, decoloration and formation of a grey-white precipitate were observed. The solution was stirred for several hours in the dark before filtration. The filtered solid and the oily residue remaining after evaporation of tetrahydrofuran from the filtrate were each washed six times with 50 ml portions of hot water to remove adherent mercury(II) bromide. Afterwards, both products were extracted with isopropanol for several hours. After distillation of the solvent, one obtained inhomogenous materials, which were discarded; 1.55 g of substance from the oily residue, which were insoluble in isopropanol, were similarly useless. Some of the solid (2.0 g) originally filtered from the tetrahydrofuran also did not dissolve in isopropanol. That material was washed with very dilute hydrochloric acid, water and acetone. The latter grey-white product, which was soluble in pyridine, started to sinter at 177° and melted at 182–183° with decomposition. Analyses showed that it was compound (X). (Found: C, 26.42; H, 3.04; N, 3.39. $C_{18}H_{22}Br_2Hg_2N_2$ calcd.: C, 26.13; H, 2.68; N, 3.38%.)

Decomposition of (II) with mercury(II) bromide

As described above, 1.75 g of (II) was decomposed with 6.5 g of mercury(II) bromide. One isolated 3.43 g (yield 72%) of (XI), m.p. 170–173°, which was soluble in pyridine, insoluble in benzene and ethanol. (Found: C, 23.74; H, 2.06. $C_{16}H_{16}Br_2Hg_2O_2$ calcd.: C, 23.99; H, 2.01%.)

Decomposition of (III) with mercury(II) chloride

Decomposition of 1.42 g of (III) with 7.0 g of mercury(II) chloride in tetrahydrofuran produced 1.62 g of (XII) which was purified by washing with hot water to remove the unreacted mercury(II) chloride and then by recrystallization from butanol or ethanol (yield 67%), m.p. 122°. (Found: C, 26.85; H, 2.98; OCH_3, 8.69. C_8H_9ClHgO calcd.: C, 26.93; H, 2.54; OCH_3, 8.68%.)

$Fe(C_{18}H_{22}N_2Br_2)Cl_2$

A dark oil remained if one stirred 1.3 g (0.01 mole) of iron(II) chloride and 2.8 g (0.006 mole) of (IV) in 200 ml of tetrahydrofuran for several hours, filtered off the excess of iron(II) chloride and removed the solvent from the cognac coloured filtrate. The oily residue became solid after some time and was dried by evacuating the adherent tetrahydrofuran. The solid looked like sand and was a 1:1 addition complex of iron(II) chloride and (IV), sensitive to moist air. (Found: C, 38.75; H, 4.10; Fe, 10.08; N, 5.14. $C_{18}H_{22}Br_2Cl_2FeN_2$ calcd.: C, 39.10; H, 4.01; Fe, 10.10; N, 5.07%.)

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