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Reaction of Benzoyl Chloride with Collman's Reagent, $Na_2Fe(CO)_4$. Synthesis and Crystal Structure of the Unexpected Organoiron Product, a New Binuclear Complex with a Triply Coordinated Oxygen Atom, $Fe_2(CO)_6(\mu\text{-}C_2Ph_2O)$

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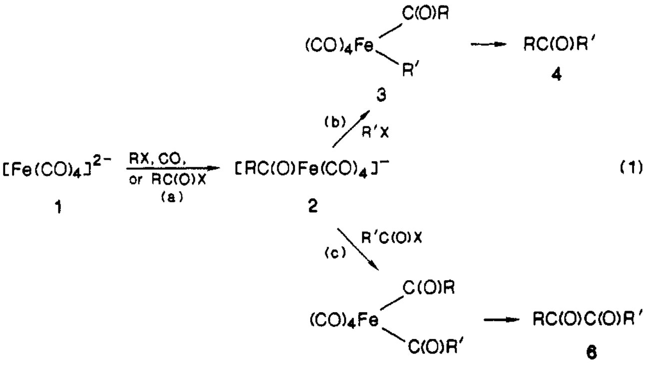
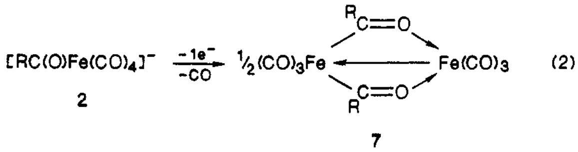
Summary: The reaction of $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$ with 2 molar equiv of PhC(O)Cl in tetrahydrofuran affords the complex $Fe_2(CO)_6(\mu\text{-}C_2Ph_2O)$ (**9**) with a triply coordinated oxygen atom along with PhC(O)O(Ph)C═C(Ph)OC(O)Ph (**8**). Compound **9** was characterized by a single-crystal X-ray diffraction analysis. Chemical and ESR observations suggest that this reaction is initiated by a single-electron-transfer process between $Na_2Fe(CO)_4$ and PhC(O)Cl.

The reaction sequence (1a) and (1b) has proved to be very useful for the synthesis of ketones **4**.[1] The first step



(1a) was shown to be of the S_N2-type (two electron transfer) with alkyl halides,[2] and the second step (1b) probably involves the intermediate **3**. A recent review by Lukehart[3] has drawn attention to transition-metal diacyl complexes, and the question is whether or not intermediates of type **5**[4] are involved in the synthesis of α-diketones on reaction of acyl chlorides with anion **2**. This reaction gives very poor yields of α-diketones **6** according to the few available reports.[5] Furthermore, it also has been shown that anions **2**, on oxidation with one-electron oxidizing agents, form dinuclear complexes of type **7** (eq 2).[6,7]



In an effort to gain a better understanding of reaction sequence (1a) and (1c); i.e., when the organic reagent is an acyl halide, we have studied the reaction of an excess of benzoyl chloride with dianion **1**. The observed results were rather unexpected.

Reaction of 0.640 g (1.85 mmol) of $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$[8] with 2 molar equiv of benzoyl chloride in tetrahydrofuran (THF) at 0 °C under a nitrogen atmosphere showed, after 30 min by IR spectroscopy, complete disappearance of dianion **1** and the expected presence of anion **2** (R = Ph).[9] An IR spectrum of the red solution obtained after 24 h exhibited no trace of this anion; only new bands around 2000 cm^{-1} were observed. Only traces of benzil (**6**: R = R′ = Ph) were detected (TLC and GC). Analysis of the gaseous atmosphere by IR spectroscopy showed not only the presence of CO but also the presence of CO_2.[10] After evaporation of the liquid mixture to dryness, addition of hexane, and filtration and concentration of the hexane solution, the diester $PhO_2CC(Ph)$═C(Ph)OC(O)Ph (**8**) was isolated as beige crystals.[11] Chromatography (Al_2O_3, CH_2Cl_2/C_6H_{12}, 1:9) of the hexane solution yielded an organometallic complex, **9**, which gave red crystals on recrystallization from hexane–methylene chloride (20:1).

The NMR data[12] revealed for **9** a structural dissymmetry that was confirmed by X-ray crystallography.[13] Its molecular structure is shown on Figure 1, together with the atom numbering scheme and selected bond distances and angles. An organic moiety, Ph_2C_2O, is unsymmetrically coordinated to two linked $Fe(CO)_3$ units. This organic group is σ-bonded to Fe(2) by the C(7) carbon and π-

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[4] Complex **5** was obtained for R = $n\text{-}C_3F_7$. It underwent smooth decarbonylation on gentle heating. Hensley, D. W.; Wurster, W. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1981**, *20*, 645.

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[10] CO_2 was separated from CO by trapping with $Ca(OH)_2$ and then evolved by HCl. The amount of CO_2 was determined by using a Toepler pump and corresponded to 1 mol/mol of **9**.

[11] **8**: IR (ν_{CO}, CH_2Cl_2) 1704 (s) cm^{-1}; $^{13}C\{^1H\}$ NMR (25.05 MHz, $CDCl_3$) 164.3 (CO_2), 138.9 (C═C) ppm; mass spectrum (EI, 70 eV), *m/e* 420 (M^+), 299 $(M - PhCO_2)^+$. Anal. Calcd for $C_8H_{20}O_4$: C, 80.0; H, 4.8. Found: C, 80.6; H, 5.1.

[12] **9**: IR (ν_{CO}, hexane) 2074 (m), 2034 (vs), 2001 (s), 1996 (s), 1979 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.4 (s), 7.3 (s); $^{13}C\{^1H\}$ NMR (25.05 MHz, CD_2Cl_2) δ 207 (CO); the carbonyl groups are fluxional over the range +30 to −80 °C; mass spectrum (EI, 70 eV), *m/e* 474 (M^+), 445.9186 (calcd for $(M - CO)^+C_{19}H_{10}O_6{}^{56}Fe_2$ *m/e* 445.9176), 418 $(M - 2CO)^+$, 390 $(M - 3CO)^+$, 362 $(M - 4CO)^+$, 334 $(M - 5CO)^+$, 306 $(M - 6CO)^+$, 178 $(M - 6CO - Fe_2O)^+$, 128 $(M - 6CO - C_2Ph_2)^+$; 50–100% estimated yields by IR before chromatography. When yields were less than 100%, there was no further reaction between remaining reagents **2** and PhC(O)Cl. After chromatography **9** was recovered as an oil and its isolation as crystals is very difficult. **9** does not react with PhC(O)Cl nor with CO.

[13] Crystal data: $Fe_2O_7C_{20}H_{10}$, M_r 474; monoclinic space group $P2_1/c$; $a = 15.724$ (5) Å, $b = 9.685$ (3) Å, $c = 13.204$ (4) Å, $\beta = 104.38$ (5)°; $V = 1947.8$ (8) $Å^3$; $Z = 4$, $d_{calcd} = 1.62$ $g \cdot cm^{-3}$; $\mu = 15.26$ cm^{-1}. A red parallelepiped of approximate dimensions 0.3 × 0.2 × 0.2 mm was selected: Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Mo Kα, λ = 0.709 26 Å. The structure was solved by the Patterson method. A total of 3828 reflections were collected of which 2403 ($I > 3\sigma(I)$) were used to give $R = 0.039$ and $R_w = 0.044$.

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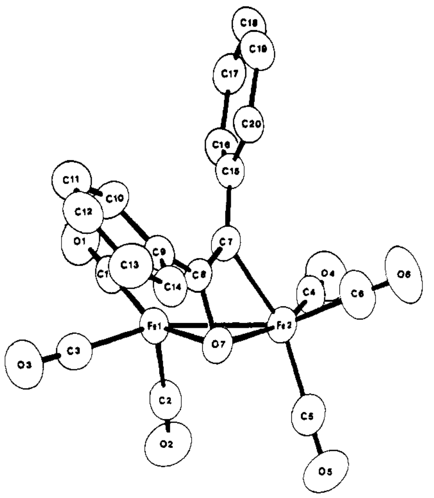


Figure 1. The molecular structure of **9**. Selected bond lengths (Å): Fe(1)–Fe(2), 2.461 (1); Fe(1)–O(7), 1.982 (3); Fe(2)–O(7), 1.994 (3); Fe(1)–C(7), 2.104 (4); Fe(1)–C(8), 2.028 (4); Fe(2)–C(7), 1.962 (4); O(7)–C(8), 1.383 (5); C(7)–C(8), 1.399 (5). Selected bond angles (deg): Fe(2)–Fe(1)–O(7), 51.98 (7); O(7)–Fe(2)–C(7), 67.9 (1); Fe(1)–O(7)–Fe(2), 76.49 (9); O(7)–C(8)–C(7), 105.2 (3). Hydrogen atoms have been omitted for clarity.

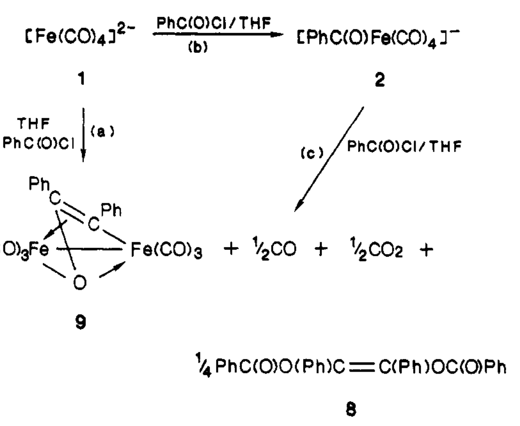
bonded by the C(7)–C(8) bond to Fe(1), and the oxygen O(7) is three-coordinated to C(8), Fe(1), and Fe(2). The bond lengths C(7)–C(8), 1.399 (5) Å, and C(8)–O(7) 1.383 (5) Å, are within the range for a coordinated double C–C bond and a very elongated double C–O bond, respectively.[14] The Fe–Fe distance is 2.461 (1) Å, within the range of distances found for other dinuclear $Fe_2(CO)_6$ units.[15] The mode of bonding of the organic ligand allows each iron atom to have a 18-valence-electron configuration taking into account the metal–metal bond. This unusual structure is a rare example of a three-coordinated oxygen atom in a diiron structure.[14,16]

We tentatively assign the following stoichiometry to this puzzling reaction (Scheme I), which did not give very reproducible yields of **8** and **9** despite carefully controlled experimental conditions.

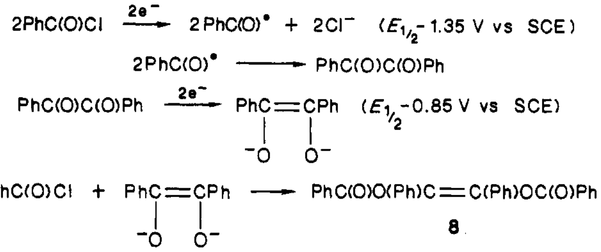
As implied in Scheme I, the carbon–carbon coupling of two acyl groups to give the organic moiety of **9** induces the loss of one oxygen atom which is recovered in carbon dioxide.

The following findings suggest a radical mechanism for the reactions shown in Scheme I. (i) The observed yields of **8** and **9** were not very reproducible according to the above-mentioned procedure. Also, prior preparation of anion **2** (the Na^+ salt according to reaction b (Scheme I) or the PPN^+ salt[9] after metathesis of the Na^+ cation or the Li^+ salt[6] by adding phenyllithium on $Fe(CO)_5$), storage for a few hours, and subsequent addition of PhC(O)Cl resulted in a very slow reaction or in no reaction at all. (ii) Electroreduction of benzoyl chloride[17] gives diester **8** (Scheme II). Thus, the proposed electron-transfer mechanism of reactions of Scheme I merits consideration.

Scheme I



Scheme II



$$2PhC(O)Cl \xrightarrow{2e^-} 2PhC(O)^\bullet + 2Cl^- \quad (E_{1/2}\ -1.35\ V\ vs\ SCE)$$

$$2PhC(O)^\bullet \longrightarrow PhC(O)C(O)Ph$$

$$PhC(O)C(O)Ph \xrightarrow{2e^-} Ph\underset{\underset{^{-}O}{|}}{C}=\underset{\underset{O^-}{|}}{C}Ph \quad (E_{1/2}\ -0.85\ V\ vs\ SCE)$$

$$2PhC(O)Cl + Ph\underset{\underset{^{-}O}{|}}{C}=\underset{\underset{O^-}{|}}{C}Ph \longrightarrow \underset{\mathbf{8}}{PhC(O)O(Ph)C=C(Ph)OC(O)Ph}$$

(iii) ESR examination of samples of freshly prepared reaction mixtures (a or b) (Scheme I) showed for some hours, in frozen solutions as well as at room temperature, the appearance of two close signals (g = 2.044 and g = 2.052) that are due to iron-containing radicals.

The simplest radical that could be derived from dianion **1** is $Fe(CO)_4^{\bullet -}$ formed by a one-electron-transfer process to benzoyl chloride. Unfortunately, the ESR characterization of this species is still unknown: very careful experiments made by Krusic and co-workers[18] showed that, consistent with one of the signals observed in this paper, mild oxidation of anion **1** gives an ESR signal with g = 2.039, which is ascribable to the $Fe_2(CO)_8^{\bullet -}$ radical anion.[19] The ESR signal of the radical $PhC(O)Fe(CO)_4^\bullet$ as observed by Krusic and co-workers[20] (g = 2.049 at −80 °C) also is consistent with one of our observed signals, although its formation in significant quantities under our conditions should have resulted in the coupling product **7** (rather stable for $R = C_6H_5$)[6] which, however, we never observed by in situ IR examination of the reaction mixtures.

In conclusion, although there is little doubt that the generation of compound **8** (Scheme I) is the result of an electron-transfer process involving benzoyl chloride, the nature of the reactive iron carbonyl radical formed in this process is not understood thus far. Also, the role of such radical intermediates in the generation of the binuclear complex **9** is unclear.

Registry No. **8**, 96276-54-9; **9**, 110098-08-3; Fe, 7439-89-6; benzoyl chloride, 98-88-4.

Supplementary Material Available: Tables of bond distances and angles and positional and thermal parameters for **9** (4 pages); a listing of structure factor amplitudes for **9** (8 pages). Ordering information is given on any current masthead page.

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