

## $\sigma$ -Bonded organometallic complexes of iron and cobalt derived from 2-bromomethylnaphthalene

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The monoanionic metal carbonylate  $\text{Na}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  reacts with 2-bromomethylnaphthalene at ambient temperature to give  $[(\sigma\text{-C}_{10}\text{H}_7\text{CH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  (I) whereas with  $\text{Na}[\text{Co}(\text{CO})_4]$  at room temperature  $[(\sigma\text{-C}_{10}\text{H}_7\text{CH}_2)\text{Co}(\text{CO})_4]$  (II) is obtained. Irradiation of (I) yields  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  (III) and  $\text{C}_{10}\text{H}_7\text{CH}_2\text{CH}_2\text{C}_{10}\text{H}_7$  (IV). The compounds have been characterized by IR, PMR, mass spectroscopic data and elemental analysis.

The synthesis of transition metal carbon  $\sigma$ -bonded organometallics using metalcarbonylate anions with halogeno organic ligands<sup>1-11</sup> and their facile thermal or photochemical conversion into corresponding  $\pi$  complexes have been reported by us<sup>2-7</sup> and other workers<sup>12</sup>. The involvement of these  $\sigma$ -bonded organometallics in organic synthesis is also well documented<sup>13-17</sup>. In continuation of our studies, we report herein the results of our investigation on the reactions of 2-bromomethylnaphthalene with metal carbonylate anions,  $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  and  $\text{Na}[\text{Co}(\text{CO})_4]$ . The main objective was the synthesis of metal carbon  $\sigma$ -bonded compounds and the photolysis of the  $\sigma$ -bonded compound, I in order to study its potential in organic synthesis.

### Experimental

All the reactions and subsequent work-up were carried out under nitrogen. THF was freshly distilled over sodium benzophenoneketyl prior to use. Hydrocarbon solvents were dried over sodium wire. 2-Bromomethylnaphthalene, dicobaltoctacarbonyl and cyclopentadienyl-irondicarbonyl dimer were purchased from Aldrich and used as such. The metal carbonylates, sodium cyclopentadienyldicarbonylferrate<sup>18</sup> and sodium tetracarbonylcobaltate<sup>19</sup> were prepared according to the known procedures. The infrared spectra were recorded on a Varian XL-200 and Bruker AM-300 instrument and mass spectra on a high resolution mass spectrometer.

### Reaction of 2-bromomethylnaphthalene with $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$

To a suspension of  $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  (1.2 g, 6 mmol) in THF (40 ml) was added dropwise a solution of 2-bromomethylnaphthalene (1.32 g, 6 mmol) in THF (30 ml). The reaction mixture was stirred at room temperature for 20 h. The solvent was removed *in vacuo* and the residue extracted with pet. ether (40-60°C) and filtered on kieselguhr. The filtrate was then concentrated under reduced pressure to give a yellow mass which was chromatographed over a column of silica gel (60-120 mesh). Elution with pet. ether (40-60°C) gave a single yellow band which on removal of solvent *in vacuo* yielded  $[(\sigma\text{-C}_{10}\text{H}_7\text{CH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  (I) as yellow crystals, (yield: 0.80 g, 42%) [Found: C, 67.97; H, 4.54. Req'd. for  $\text{C}_{18}\text{H}_{14}\text{O}_2\text{Fe}$ : C, 67.92; H, 4.40%]. IR (in cyclohexane):  $\nu(\text{CO})$  2075 and 1987  $\text{cm}^{-1}$ ; PMR ( $\text{CDCl}_3$ ):  $\delta$  7.81-7.28 (m, 7H), 3.19 (s, 5H) and 2.55 (s, 2H); MS:  $m/z$  318 [ $\text{M}^+$ ], 290 [ $\text{M}^+ - \text{CO}$ ], 262 [ $\text{M}^+ - 2\text{CO}$ ], 197 [ $\text{M}^+ - (2\text{CO} + \text{Cp})$ ] and 141 [ $\text{M}^+ - (2\text{CO} + \text{Cp} + \text{Fe})$ ].

### Reaction of 2-bromomethylnaphthalene with $\text{Na}[\text{Co}(\text{CO})_4]$

To a freshly prepared yellow suspension of  $\text{Na}[\text{Co}(\text{CO})_4]$  (1.04 g, 5.4 mmol) in THF (30 ml) was added dropwise a solution of 2-bromomethylnaphthalene (1.2 g, 5.4 mmol) in THF (30 ml) and the reaction mixture stirred at room temperature for 24 h. The work-up of the reaction mixture as described above gave a yellow mass. Chromatographic separation over a column of silica gel eluting with pet. ether/diethyl ether mixture (1:1, v/v) yielded  $[(\sigma\text{-C}_{10}\text{H}_7\text{CH}_2)\text{Co}(\text{CO})_4]$  (II) as yellow crystals (yield: 0.485 g, 29%) [Found: C, 57.82; H, 2.96. Req'd. for  $\text{C}_{14}\text{H}_9\text{O}_4\text{Co}$ : C, 57.69; H, 2.88%]. IR (in cyclohexane):  $\nu(\text{CO})$  2071 and 2006  $\text{cm}^{-1}$ ; PMR ( $\text{CDCl}_3$ ):  $\delta$  7.44-7.23 (m, 7H) and 2.43 (s, 2H); MS:  $m/z$  312 [ $\text{M}^+$ ], 284 [ $\text{M}^+ - \text{CO}$ ], 256 [ $\text{M}^+ - 2\text{CO}$ ], 228 [ $\text{M}^+ - 3\text{CO}$ ], 200 [ $\text{M}^+ - 4\text{CO}$ ] and 141 [ $\text{M}^+ - (4\text{CO} - \text{Co})$ ].

### Photochemical conversion of compound I into III and IV

A toluene solution (20 ml) of I (0.26 g, 0.82 mmol) was taken in a Carius tube, flushed with nitrogen and sealed *in vacuo*. The reaction mixture was irradiated with a 125 watt medium pressure mercury lamp for 10 h. The reaction mixture was filtered on kieselguhr. The filtrate on removal of solvent yielded a yellow

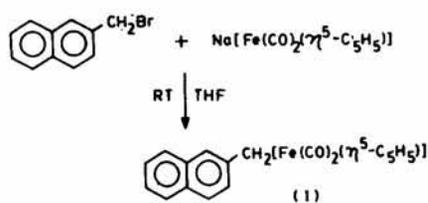
gummy residue which was chromatographed on a silica gel (60-120 mesh) column and eluted with pet. ether to give two distinct bands. The first band on removal of solvent yielded  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  (**III**) (0.03 g, 10%) as yellow crystals. IR (in cyclohexane):  $\nu(\text{CO})$  2006, 1960 and  $1792\text{ cm}^{-1}$ ; PMR ( $\text{CDCl}_3$ ):  $\delta$  4.15 (s, 5H). The second band on removal of solvent yielded white crystals of 1,2-dinaphthylethane,  $\text{C}_{10}\text{H}_7\text{CH}_2\text{CH}_2\text{C}_{10}\text{H}_7$  (**IV**) (0.014 g, 6%). IR (in cyclohexane): 2979, 2682 and  $1600\text{ cm}^{-1}$ ; PMR ( $\text{CDCl}_3$ ):  $\delta$  7.34 (s, 14H) and 2.92 (s, 4H); MS:  $m/z$  282 [ $\text{M}^+$ ], 155 [ $\text{M}^+ - \text{C}_{10}\text{H}_7$ ], 141 [ $\text{M}^+ (\text{C}_{10}\text{H}_7 + \text{CH}_2)$ ], 127 [ $\text{M}^+ - (\text{C}_{10}\text{H}_7 + \text{CH}_2 + \text{CH}_2)$ ].

### Results and discussion

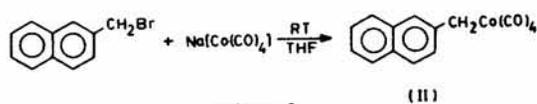
The reaction of 2-bromomethylnaphthalene with  $\text{Na}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  in THF at ambient temperature afforded  $[(\sigma\text{-C}_{10}\text{H}_7\text{CH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  (**I**) as yellow crystals in 42% yield. The IR spectrum of compound **I** in carbonyl stretching region shows two sharp bands at  $2075$  and  $1987\text{ cm}^{-1}$  in agreement with a *cis*-dicarbonyl arrangement. Furthermore, the  $\nu(\text{CO})$  bands are very similar to those reported for the related compounds<sup>1-8</sup>. The PMR spectrum of **I** exhibited signals at  $\delta$  7.28-7.81 (m, 7H), 3.19 (s, 5H) and 2.55 (s, 2H). The low field multiplets at  $\delta$  7.28-7.81 is due to the aromatic protons. The singlet at  $\delta$  3.19 has been assigned to cyclopentadienyl protons whereas the singlet at 2.55 is due to the methylene protons. The upfield shifts of methylene protons ( $\delta$  2.55) of **I** compared to that of the free ligand ( $\delta$  4.65) clearly indicates the formation of Fe-C $\sigma$ -bond via methylene carbon atoms. The high field signal for methylene protons has been observed for analogous complexes<sup>1-11</sup>.

The mass spectrum of **I** showed the molecular ion peak at  $m/z$  318 and the sequential loss of two CO groups, one cyclopentadienyl group and one Fe atom. The elemental analyses are in agreement with the proposed molecular formula for **I**. Thus on the basis of the above spectroscopic evidences and 18-electron rule, structure **I** is suggested for this compound (Scheme 1).

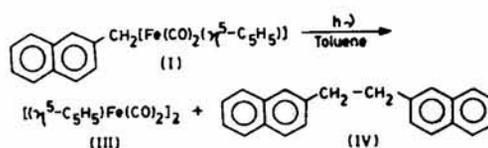
A similar reaction of 2-bromomethylnaphthalene with  $\text{Na}[\text{Co}(\text{CO})_4]$  yielded  $[(\sigma\text{-C}_{10}\text{H}_7\text{CH}_2)\text{Co}(\text{CO})_4]$



Scheme 1



Scheme 2



Scheme 3

(**II**) as yellow crystals in 29% yield. The IR spectrum of complex **II** exhibits two sharp  $\nu(\text{CO})$  bands at  $2071$  and  $2006\text{ cm}^{-1}$  as expected for tetracarbonyl complex with terminal carbonyls<sup>2-4,10</sup>. The PMR spectrum of **II** shows peaks at  $\delta$  7.23-7.44 (m, 7H) and 2.43 (s, 2H). The multiplets at  $\delta$  7.23-7.44 are due to the aromatic protons of naphthalene rings whereas the singlet at  $\delta$  2.45 is assigned to the methylene protons. This type of high field shift for methylene protons has been observed for analogous complexes<sup>2-11</sup>. The mass spectrum of **II** showed molecular ion peak at  $m/z$  312 and the successive loss of four CO groups and one Co atom. The elemental analyses are in agreement with the proposed molecular formula for **II**. Therefore, on the basis of above spectroscopic evidences, structure **II** is suggested for this compounds (Scheme 2).

The photolysis of **I** in toluene yielded  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  (**III**) as yellow crystals and  $\text{C}_{10}\text{H}_7\text{CH}_2\text{CH}_2\text{C}_{10}\text{H}_7$  (**IV**) as white solid (Scheme 3). Compound **III** was identified to be  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  by comparing its IR spectrum [ $\nu(\text{CO})$  bands at 2006, 1960 and  $1792\text{ cm}^{-1}$ ] and PMR spectrum (singlet at  $\delta$  4.15) with those of an authentic sample.

The IR spectrum of **IV** exhibits peaks at 2979, 2982 and  $1600\text{ cm}^{-1}$  which are due to the aromatic groups, the methylene groups and carbon-carbon double bond respectively. The PMR of **IV** shows signals at  $\delta$  7.34 (s, 14H) and 2.92 (s, 4H). The singlet at  $\delta$  7.34 is due to the aromatic protons of naphthalene ring whereas the singlet at 2.92 is assigned to the methylene protons. Similar chemical shift for the methylene protons have been reported for related compounds<sup>13</sup>. The mass spectrum of **IV** showed the molecular ion peak at  $m/z$  282 corresponding to the molecular formula  $\text{C}_{10}\text{H}_7\text{CH}_2\text{CH}_2\text{C}_{10}\text{H}_7$ . The mass fragmentation pattern is also in agreement with the molecular formula. The photolysis of **I** in closed system forms radicals  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  and  $\text{C}_{10}\text{H}_7\text{CH}_2$  which undergo coupling to give  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  (**III**) and  $\text{C}_{10}\text{H}_7\text{CH}_2\text{CH}_2\text{C}_{10}\text{H}_7$  (**IV**). This

observation is similar to that reported by Wrighton *et al.*<sup>13</sup> for the closed system photolysis of  $[(\sigma\text{-C}_6\text{H}_5\text{CH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  (V) in toluene which yielded  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  (III) and  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$  (VI).

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