Notes

\( \sigma \)-Bonded organometallic complexes of iron and cobalt derived from 2, 3-bis(bromomethyl)quinoxaline

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2, 3-Bis(bromomethyl)quinoxaline reacts with disodium tetracarbonylferrate at ambient temperature to give 2-bromoethyl, 3-\( \sigma \)-methylene quinoxaline sodium tetracarbonylferrate (I) and 2, 3-bis(\( \sigma \)-methylene)quinoxalinenetetacarbonyliron(II) whereas with disodium cyclopentadienylnonacarbonylcobalt, it gives only 2, 3-bis(\( \sigma \)-methylene)quinoxalinecyclopentadienylnonacarbonylcobalt(III). The complex I undergoes conversion into II in refluxing cyclohexane. The treatment of 2, 3-bis(bromomethyl)quinoxaline with sodium tetracarbonylcobaltate yields 2, 3-bis(\( \sigma \)-methylene)quinoxalineoctacarbonyldicobalt(IV).

The synthesis of transition metal-carbon \( \sigma \)-bonded organometallics using halogeno organic ligands and metal carboxylate anions and their facile thermal or photochemical conversion into the \( \pi \)-complexes have been reported by us\(^1\)-\(^4\). Herein we report the results of our investigation on the reactions of 2, 3-bis(bromomethyl)quinoxaline with metal carboxylate anions such as Na\(_2\)[Fe(CO)\(_4\)], Na\(_2\)[CpCo(CO)\(_6\)] and Na[Co(CO)\(_4\)]. The main objective was to see the effect of the presence of heteroatoms in the aromatic ring on the synthesis of transition metal-carbon \( \sigma \)-bonded compounds. We have also studied the \( \pi \) conversion behaviour of the complexes to show that such a process is not feasible due to the presence of heteroatoms in the aromatic ring.

Experimental

All the reactions and operations were conducted under nitrogen atmosphere. The infrared spectra were recorded on a PE-983 spectrophotometer. The PMR spectra were recorded on a Varian XL-200 or a Bruker AM-300 instrument and the mass spectra on a high resolution mass spectrometer. Tetrahydrofuran was freshly distilled over sodium and benzophenone prior to use. 2,3-bis(bromomethyl)quinoxaline (Aldrich) was used as such. The metal carboxylates Na\(_2\)[Fe(CO)\(_4\)], Na\(_2\)[CpCo(CO)\(_6\)] and Na[Co(CO)\(_4\)] were prepared according to the known procedures.

Reaction of Na\(_2\)[Fe(CO)\(_4\)] with 2, 3-bis(bromomethyl)quinoxaline

To a suspension of Na\(_2\)[Fe(CO)\(_4\)] (1.09 g, 5.1 mmol) in THF (30 ml) was added dropwise a solution of 2, 3-bis(bromomethyl)quinoxaline (1.77 g, 5.6 mmol) in THF (30 ml). After stirring at room temperature for 24 h, the solvent was removed in vacuo and the residue extracted with diethyl ether and filtered on kieselguhr. The filtrate was concentrated under reduced pressure to give a yellow solid which was chromatographed over a column of silica gel (60-120 mesh). Elution with pet. ether/diethyl ether mixture (1:1, v/v) gave two yellow bands. The first band on removal of solvent in vacuo afforded 2, 3-bis(\( \sigma \)-methylene)quinoxaline-tetracarbonyliron(II) as yellow crystals (0.040 g, 6%) from pentane. [Found: C, 52.21; H, 2.82; N, 8.71. Req'd for C\(_{14}\)H\(_8\)N\(_2\)O\(_4\)Fe: C, 51.88; H, 2.49; N, 8.65%]. IR (in cyclohexane): v(CO) 1957 and 1934 cm\(^{-1}\); PMR (CDCl\(_3\)): \( \delta \) 2.75 (s, 4H), 7.71-7.74 (m, 2H) and 8.0-8.1 (m, 2H); MS: m/z 324 (M\(^+\), 296 (M\(^+\)-CO), 268 (M\(^+\)-2CO), 240 (M\(^+\)-3CO), 212 (M\(^+\)-4CO), 156 (M\(^+\)-Fe + 4CO). The second band on removal of solvent gave 2-bromomethyl, 3-\( \sigma \)-methylenequinoxaline sodium tetracarbonylferrate as yellow crystals (0.44 g, 24%) from diethyl ether. [Found: C, 52.21; H, 2.82; N, 8.71. Req'd for C\(_{14}\)H\(_8\)N\(_2\)O\(_4\)Fe: C, 51.88; H, 2.49; N, 8.65%]. IR (in cyclohexane): v(CO) 1957 and 1934 cm\(^{-1}\); PMR (CDCl\(_3\)): \( \delta \) 2.89 (s, 2H), 4.76 (s, 2H), 7.71-7.74 (m, 2H) and 8.0-8.20 (m, 2H); MS: m/z 405 (M\(^+\), 377 (M\(^+\)-CO), 349 (M\(^+\)-2CO), 321 (M\(^+\)-3CO), 293 (M\(^+\)-4CO).

Synthesis of 2, 3-bis(\( \sigma \)-methylene)quinoxaline-cyclopentadienylnonacarbonylcobalt(III)

A solution of 2, 3-bis(bromomethyl)quinoxaline (1.01 g, 3.2 mmol) in THF (30 ml) was added dropwise to a suspension of Na\(_2\)[CpCo(CO)\(_6\)] (0.64 g, 3.12 mmol) in THF (30 ml). After stirring at room temperature for 24 h, the solvent was removed in vacuo and the residue extracted with diethyl ether and filtered on kieselguhr. The filtrate was concentrated under reduced pressure to give a yellow solid which was chromatographed over a column of silica gel (60-120 mesh). Elution with pet. ether/diethyl ether mixture (1:1, v/v) gave two yellow bands. The first band on removal of solvent in vacuo afforded 2, 3-bis(\( \sigma \)-methylene)quinoxalineoctacarbonyldicobalt(IV) as yellow crystals (0.230 g, 24%) from pentane. [Found: C, 62.55; H, 4.6; N, 9.3. Req'd for C\(_{16}\)H\(_8\)CoN\(_2\)O: C, 62.34; H, 4.26; N, 9.09%]. IR (in cyclohexane): v(CO) 1983 cm\(^{-1}\); PMR (CDCl\(_3\)): \( \delta \) 2.74 (s, 5H), 2.79 (s, 4H), 7.69-7.72 (m, 2H).
7.97-8.03 (m, 2H); MS: m/z 308 (M+), 280 (M+ - CO), 215 (M+ - (CO + Cp)), 156 (M- (CO + Cp + CO)).

**Synthesis of 2, 3-bis(σ-methylene)quinoxalineoctacarbonyldicobalt(IV)**

To a suspension of Na[Co(CO)₄] (1.34 g, 6.91 mmol) in THF (40 ml) was added dropwise a solution of 2, 3-bis(bromomethyl)quinoxaline (1.15 g, 3.64 mmol) in THF (30 ml). After adopting the same procedure as described above, it yielded 2, 3-bis(σ-methylene)-quinoxaline (IV) as orange crystals (0.425 g, 25%). [Found: C, 43.85; H, 1.92; N, 6.15. Reqd. for C₁₈H₁₂Co₂N₂O₈: C, 43.40; H, 1.62; N, 5.62%]. IR (in cyclohexane): v(CO) 2035 and 1970 cm⁻¹; PMR(CDCl₃): δ 2.71 (m, 4H), 7.62-7.65 (m, 2H), 7.94-7.97 (m, 2H); MS: m/z 386 (M⁺ - 4CO), 327 (M⁺ - 4CO + Co), 299 (M⁺ - 5CO + Co), 271 (M⁺ - 6CO + Co), 243 (M⁺ - 7CO + Co), 215 (M⁺ - 8CO + Co).

**Thermal conversion of I to II**

A suspension of I (0.105 g, 0.25 mmol) in cyclohexane (30 ml) was heated at 80° for 5 h. The solvent was removed under reduced pressure and chromatographic separation of the residue over a silica gel column and eluting with a mixture of petroleum ether (40-60°)/diethyl ether (3:1, v/v) yielded II (0.04 g, 50%) and unconverted I (0.01 g).

7.97-8.03 (m, 2H) and IV [δ 2.71 (m, 2H), 7.62-7.65 (m, 2H) and 7.94-7.97 (m, 2H) are similar. The low-field multiplets at δ 7.7 and 8.0 have been assigned to the four aromatic protons and remain unshifted from those of the free ligand. The high-field singlet at δ 2.8 is attributable to the metal carbon a-bonded methylene protons. Similar chemical shifts for a-bonded methylene protons have been reported for closely related compounds 1-4. In the PMR spectrum of I, the singlet at δ 6.76 is due to the methylene protons from which the bromine atom has not been abstracted and remains almost unshifted from that of the free ligand (δ 6.94). The mass spectrum of II showed the molecular ion peak at m/z 324 and that of I showed the highest peak at m/z 405 corresponding to the anionic part [C₇H₆N₂CH₂BrCH₂Fe(CO)₄]. The sequential loss of four CO groups was observed from both 324 and 405; the presence of Fe(CO)₄ moieties in these complexes is thus evident. The mass spectrum of III exhibited the molecular ion peak at m/z 308 and other important peaks due to the successive loss of CO, Cp and Co. In its mass spectrum, IV did not show the molecular ion peak at m/z 498; instead it exhibited peaks at 386 arising due to rapid loss of four CO groups. The other important peaks at m/z 327, 299, 271, 243 and 215 were due to the successive loss of Co and 4CO groups. The fragmentation pattern is characteristic of metal carbonyl organometallic complexes. The proposed structures for I-IV are also consistent with the 18-electron rule. Examples of formation of metal carbon σ-bonds from the reactions of organic halides with metal carbonylates are well established 1-4. Compound I provides an interesting example of an intermediate in which only one of the two bromine atoms have been abstracted.

Compounds II and III do not convert into the corresponding π-compounds by elimination of CO. This finding is different from those observed for the compounds 1, 2-bis(σ-methylene)benzene-tetracarbonyldicobalt, 1, 2, 4, 5-tetrakis(σ-methylene)benzene-octacarbonyldiiron and 1, 2, 3, 4, 5, 6-hexakis(σ-methylene) benzene-dodecacarbonyltririron which are known to undergo facile conversion into π-bonded complexes under specific reaction conditions 1-3. This study clearly indicates that such transformation into a π-bonded compound is not feasible if the benzene ring contains hetero atoms such as nitrogen. Apparently the reason for nonconversion of the σ-bonded complexes II and III to respective π-complexes is not difficult to perceive. On conversion to a π-complex, the σ-complexes II and III will have to undergo drastic bonding rearrangement including the formation of nitrogen to nitrogen bonds in the new complex.
bond across the ring giving rise to considerable strain in the molecular framework as shown for II in Scheme 1. Under these circumstances the σ-complexes II and III will simply choose not to undergo any π-conversion at all.

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References