Synthesis of Tetrakis(\(\sigma\)-methylene) Compounds of Iron & Cobalt Carbonyls & Their Facile Conversion into \(\pi\)-Compounds

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Reactions of disodium tetracarbonylferrate and sodium tetracarbonylcobaltate with tetrabromodurene yield 1,2,4,5-tetrakis(\(\sigma\)-methylene)benzene diironoctacarbonyl(I) and 1,2,4,5-tetrakis(\(\sigma\)-methylene)benzene dicobalt(II) respectively. Under mild condition (40°) the complex(I) undergoes facile conversion into 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane diironhexacarbonyl(III), where a \(\sigma\) to \(\pi\) conversion takes place with the two Fe(CO)\(_3\) moieties separately coordinated to two butadiene fragments exocyclic to the benzene ring giving rise to a Dewar like structure of the benzene ring. Attempts to convert complex(II) into \(\pi\)-form by both photochemical and thermal methods are not successful.

The conversion of \(\sigma\) to \(\pi\) mode of bonding in transition metal organometallics is an important process and is thought to be involved in many transition metal catalyzed reactions\(^1\). In our laboratory we synthesised 4,5-dimethyl(bis \(\sigma\)-methylene)benzene tetracarbonyliron and 1,2-bis(\(\sigma\)-methylene)benzene tetracarbonyliron respectively and studied their conversion by thermal and photochemical methods to \(\pi\)-complexes respectively in which tricarbonyliron moieties hold butadiene fragments in such a manner that benzene ring behaves like a triene ligand\(^2\). In persuance of study along the same line, we recently synthesised 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane diironhexacarbonyl(III), a novel complex in which all the \(\pi\)-electrons of the aromatic ring were involved in coordination with iron in an extra skeletal manner\(^3\). This observation prompted us to synthesise 1,2,4,5-tetrakis(\(\sigma\)-methylene)benzene diironoctacarbonyl(I) to see if this complex actually acts as a precursor in the \(\sigma\) to \(\pi\) conversion process to give the \(\pi\)-complex, 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane diironhexacarbonyl(III). We have also studied the conversion behaviour of analogous cobalt complexes to show that such a conversion is not feasible due to 18-electron rule limitation.

Materials and Methods
All reactions and subsequent handling were carried out in dry oxygen-free nitrogen atmosphere. Infrared spectra were recorded in cyclohexane on a Beckman IR 4220 spectrophotometer. NMR spectra were recorded in CDCl\(_3\) on a Varian EM300 (90 MHz) instrument. Mass spectra were recorded using an MS-12 high resolution spectrometer. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Tetrahydrofuran(THF) was freshly distilled over sodium and benzophenone under nitrogen immediately before use.

Disodium tetracarbonylferrate was prepared as a yellow suspension by a known procedure\(^4\). 1,2,4,5-Tetrakis(bromomethyl)benzene was prepared according to the known procedure\(^5\) and recrystallised from chloroform. Sodium tetracarbonylcobaltate was also prepared by the known procedure\(^6\).

Synthesis of 1,2,4,5-tetrakis(\(\sigma\)-methylene)benzene diironoctacarbonyl(I)

1,2,4,5-Tetrakis(bromomethyl)benzene (3 g, 6.6 mmol) was added to a suspension of disodium tetracarbonylferrate (3.2 g, 14.9 mmol) in THF and stirred under nitrogen atmosphere for 90 min at 0°C. The colour of the reaction mixture changed...
from light yellow to deep yellow, which turned to a reddish brown mass when dried in vacuo. This was then extracted twice with ether (40-60°C), filtered and the filtrate concentrated in vacuo to give a yellow viscous mass which was chromatographed over a column of silica (60-120 mesh) eluting with ether (40-60°C). A distinct yellow band was obtained. This yellow band on removal of solvent yielded yellow needle-like crystals of I, m.p. 101° (0.8 g, 25% based on the ligand) (Found: C, 46.4; H, 2.1. C₁₈H₁₀Fe₂O₅ requires C, 46.4; H, 2.2%).

**Thermal conversion of I into 2,3,5,6-tetramethylene-bicyclo[2.2.0]hexane diironhexacarbonyl**

Complex (I, 1.12 g, 2.4 mmol) was dissolved in cyclohexane (25 ml) and the solution heated at 40°. After 2 hr, almost complete conversion was achieved as indicated by IR. The solvent was removed and the reaction product chromatographed over a column of silica gel eluting with pet ether (40-60°). The resulting red yellow crystals were further purified by recrystallisation from n-pentane at -40°; m.p. 80-82° (0.5 g, 51% based on complex I); IR: 2040 (s) and 1990 (vs) cm⁻¹ (νC=O); PMR: δ 0.1 (d, J = 3 Hz, 4Hₐ), 0.7 (s, 2Hₐ), 1.1 (d, J = 3.5 Hz, 4Hₐ), MS: m/z 410 (M⁺), and 382, 354, 326, 298, 270 and 242 corresponding to stepwise loss of six CO units. These data were in agreement with those reported for the complex 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane diironhexacarbonyl which was reported recently from this laboratory.

**Synthesis of 1,2,4,5-tetrakis(α-methylene tetra-carbonylcobalt)benzene(II)**

To a suspension of sodium tetracarbonylcobaltate (4.56 g, 23.5 mmol) in freshly distilled THF (40 ml) was added dropwise with vigorous stirring, 1,2,4,5-tetrakis(bromomethyl)benzene in THF (40 ml) during 2 hr at room temperature. The colour of the reaction changed from deep yellow to brownish yellow. After completion of the reaction (as revealed by IR) THF was removed in vacuo leaving brownish-yellow mass. This was extracted with n-pentane (2×25 ml), filtered and the filtrate concentrated in vacuo to leave a brownish-yellow solid, which recrystallised from n-pentane as brownish-yellow crystals, m.p. 79-80°.

**Reaction of complex(I) with triphenylphosphine**

Complex (I, 0.5 g, 1.1 mmol) was allowed to reflux with triphenylphosphine (0.6 g, 2.2 mmol) in cyclohexane (100 ml) at 60° for 14 hr under nitrogen atmosphere. The course of the reaction was monitored by IR at thirty-minute interval. After 14 hr the colour of the solution changed into faint yellow. Removal of the solvent in vacuo afforded a yellow crystalline product in 30% yield, m.p. 76-78°; IR: 2030 (s), 1970 (s), 1910 (s) (νC=O) cm⁻¹.

**Results and Discussion**

The structure of complex(I) has been elucidated on the basis of its IR, PMR and mass spectra and elemental analyses. The IR spectrum of I in cyclohexane exhibited two sharp νC=O modes at 2050 and 1995 cm⁻¹. The significant upward shift in this νC=O modes as compared to that (1790 cm⁻¹) in Na₃Fe(CO)₄ (ref. 7) is a clear indication of formation of a neutral complex. The PMR spectrum of I exhibited signals at δ 2.3 (s, 8H) and 7.3 (s, 2H) in the intensity ratio 4:1. These have been assigned to methylene and aromatic protons respectively. The high field signal for methylene protons is also observed for analogous complexes²,⁸. In the mass spectrum, I did not display the molecular ion peak at m/z 466; instead it exhibited peaks at m/z 438 and other peaks due to successive loss of carbonyl moiety.

As expected, complex(I) underwent facile σ-π-conversion at 40° to give the π-complex(III). This change was observed even while recording the PMR spectrum at 25°. The complex(I) undergoes thermal substitution with triphenylphosphine and the IR spectrum of the resulting solid displayed three sharp νC=O bands at 2030, 1970 and 1910 cm⁻¹, in accordance with the spectral data of triphenylphosphine tetracarbonyliron [PPh₃Fe(CO)₄] (ref. 9, 10).

The IR spectrum of complex(II) displayed significant upward shift in νC=O mode [Δν(C=O) = 112, 180 cm⁻¹] indicating the formation of neutral complex. The PMR spectrum of II exhibited signals at δ 1.5 (s, 8H) and 7.3 (s, 2H) with the intensity ratio 4:1. The low field signal at δ 7.3 is clearly due to two aromatic protons. The high field singlet at δ 1.5 accounts for the presence of magnetically equivalent methylene protons. The mass spectrum did not exhibit any molecular ion peak. Successive loss of neutral carbon monoxide gave peaks at m/z 545, 517, 489, 428, 400 corresponding to a series of unimolecular reactions. The peaks at m/z 458, 271 and 88 were due to loss of three cobalt atoms from m/z 517, 330 and 147 respectively. These decomposition products are characteristic of cobaltcarbonyl complexes¹⁰ indicating the presence of four Co(CO)₄ moieties where the metal atoms are bonded through Co-C σ-bonds.
Attempts to convert complex(II) into its π-form by both thermal and photochemical methods were not successful. This may be due to the fact that the resulting π-complex does not satisfy the 18-electron rule, which is a general condition for the stability of organometallic complexes of transition metals.

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References

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