Synthesis & Reactions of Some Cyclobutadiene Complexes of Cobalt

JASIM U AHMAD, SHARIFF E KABIR & SAYED S ULLAH*
Department of Chemistry, Jahangirnagar University, Savar, Dhaka (Bangladesh)

Received 13 April 1987; revised and accepted 15 June 1987

Optimum conditions for the stepwise synthesis of the cyclobutadiene complexes $\text{C}_4\text{H}_4\text{Co}_2(\text{CO})_6\text{I}$ and $\text{C}_4\text{H}_4\text{Co}(\text{CO})_2\text{HgCo}(\text{CO})_4\text{II}$ have been established. Their common iodine derivative, $\text{C}_4\text{H}_4\text{Co}(\text{CO})_2\text{I}$, on reaction with $\text{PPh}_3$, $\text{CH}_3\text{MgI}$ and $\text{HgCo}(\text{CO})_4\text{II}$ gives the substitution product $\text{C}_4\text{H}_4\text{Co}(\text{CO})\text{PPh}_3\text{I}$, methyl derivative $\text{C}_4\text{H}_4\text{Co}(\text{CO})\text{CH}_3\text{I}$ and the heteronuclear complex $\text{C}_4\text{H}_4\text{Co}_2\text{Hg}(\text{CO})_5\text{PPh}_3\text{VIII}$, respectively. The reaction of $\text{C}_4\text{H}_4\text{Co}_2(\text{CO})_6\text{I}$ with triphenylmethyl tetrafluoroborate gives the butadienyl salt $[\text{C}_4\text{H}_4\text{Co}(\text{CO})_3]_+$ (IV). When (III) is reacted with $\text{PPh}_3$ and $\text{AgPF}_6$, a mixture of phosphine substituted butadienyl salt $[\text{C}_4\text{H}_4\text{Co}(\text{CO})\text{PPh}_3\text{I}]$ and the phosphine substituted iodo derivative (V) is obtained. Appropriate reaction schemes have been proposed on the basis of IR and PMR evidences.

Although free cyclobutadiene has, at best, a transient existence, it can be stabilized with various transition metals to give rise to many interesting complexes. Ever since its stabilization in the form of cyclobutadienetricarboxyliron in the mid sixties, a vast amount of literature has been produced on various complexes of cyclobutadiene. We report in this paper the details of the synthesis of cyclobutadienetricarboxylcobalt(I) and its reactions with various reagents. Although the preparation of (I) was reported in a communication some years ago, there was no mention of the suitable reaction conditions. As we required (I) as a precursor for further work, we have attempted to find the optimum reaction conditions for its preparation. A preliminary report of the reaction of (I) with triphenylmethyl tetrafluoroborate has appeared.

Materials and Methods

Preparation of 3,4-Dichlorocyclobutene

3,4-Dichlorocyclobutene was prepared by the method described in the literature. A higher percentage of dichlorocyclobutene was obtained in the pyrolysate of the Diels-Alder adduct by lowering the pyrolysation temperature from 200° to 190°. The isomer dichlorobutadiene and dichlorocyclobutene were conveniently separated by column chromatography [SiO$_2$, solvent pet ether (b.p. 30-40°)] instead of spinning band column distillation. The purity of dichlorocyclobutene (55% yield; m.p. 5°) was checked spectroscopically; PMR: $\delta$ 6.28 (2H, d) and 5.15 (2H, d). Thin film IR was identical with the reported values.

Reaction of dichlorocyclobutene with sodium tetra-carboxylcobaltate

The sodium salt was prepared by the vigorous stirring together of Na/Hg (1.501 g) and Co$_3$(CO)$_8$ (9.998 g) for 10 hr in THF (150 ml). After completion of salt formation, the grey yellow solution was washed with fresh mercury. Then it was treated with dichlorocyclobutene (2.502 g) under varying experimental conditions. Optimum yield of $\text{C}_4\text{H}_4\text{Co}(\text{CO})_2\text{Co}(\text{CO})_4\text{I}$, was obtained by stirring the reaction mixture at 70° for 12 hr. After completion of the reaction, THF was removed in vacuo.

The viscous reaction mass was extracted 2-3 times with pet ether (b.p. 30-40°). The pet ether extract was chromatographed on neutral alumina and eluted with ethyl acetate (5%) in pet ether. The first band gave a brown oil (0.208 g) which is thought to be the intermediate $\text{A}$ (Scheme 1).

The second band (yellow), on removal of the solvent, gave bright yellow crystals (m.p. 55°) of $\text{C}_4\text{H}_4\text{Co}(\text{CO})_2\text{HgCo}(\text{CO})_4\text{II}$, (0.998 g); IR: $\nu$CO at 2065, 2035, 2005 and 1960 cm$^{-1}$; PMR: (C$_6$D$_6$) $\delta$ 3.40 (s) (Found: C, 22.8; H, 0.7; Cl requires: C, 22.3; H, 0.75%); it also gave the tests for Hg.

The third band (orange red) gave $\text{C}_4\text{H}_4\text{Co}(\text{CO})_2\text{HgCo}(\text{CO})_4\text{II}$.
Co(OC)₄(I) (1.113 g) as bright red crystals (m.p. 34°); IR: v(CO) at 2968, 2038, 2025, 1960 and 1940 cm⁻¹; PMR: (C₆D₆)b₃.7(s).

Its mass spectrum showed (M⁺-CO) and subsequent loss of five carbonyl groups. The fourth band, which was eluted with ethyl acetate, gave Hg[Co(OC)₄]₂ as orange crystals (0.512 g; m.p., 82°).

If the reaction was carried out at room temperature for a longer period (72 hr), the yield of (II) increased while that of (I) decreased.

Reaction of intermediate A' with NaCo(OC)₄

The above 'intermediate A' (0.090 g) was stirred with a solution NaCo(OC)₄ in THF (30 ml) for 12 hr. The reaction was monitored by IR which showed the formation of complex (I). After removal of the solvent, the residue was chromatographed as above to get C₂H₄Co(OC)₂—Co(OC)₄(I).

Reaction of C₂H₄Co(OC)₂—Co(OC)₄(I) and Hg[Co(OC)₄]₂

The complex(I) (0.050 g) and Hg[Co(OC)₄]₂ (0.101 g) were stirred in 30 ml of cyclohexane. IR monitoring clearly showed the formation of (II) and Co₂(OC)₈. After 48 hr, C₂H₄Co(OC)₂—HgCo(OC)₄ (0.056 g) was isolated by chromatography.

Reaction of C₂H₄Co(OC)₂—Co(OC)₄(I) with iodine

To a solution of complex (I) (1.022 g) in 75 ml of chloroform, iodine (0.201 g in 50 ml chloroform) was added dropwise over a period of 30 min and the reaction mixture was stirred for another 40 min and brought to room temperature. Chloroform was removed and the reaction mass was extracted with ether. Removal of ether gave C₂H₄Co(OC)₂—I(III), (0.981 g, 92%); IR: v(CO) 2070(s) and 2040(s) cm⁻¹; PMR: δ4.70 as dark red crystals, m.p. 84°.

Reaction of C₂H₄Co(OC)₂—I(III) with PPh₃

Complex (III) (0.210 g) and PPh₃ (0.220 g) were allowed to react in TFH at room temperature for 12 hr. After removal of the solvent and crystallization from ether C₂H₄Co(OC)₂PPh₃(V) (0.190 g) was obtained as dark red crystals (m.p. 192°; v(CO): 2005(s) cm⁻¹; PMR: 64.70 as dark red crystals; 8 2.95 (s)).

Reaction of C₂H₄Co(OC)₂—I(III) with CH₃MgI

To a solution of C₂H₄Co(OC)₂ (0.40 g), CH₃MgI (from 0.120 g CH₃I) in diethyl ether was added dropwise at -60° in 30 min. The reaction solution turned grey. After 30 min, water was added to the solution to decompose excess CH₃MgI and the reaction mass was extracted with ether. The ether extract was dried over MgSO₄. Removal of the solvent left a very small
amount (0.05 g) of a brown oil. This was filtered through neutral alumina in pentane solution to retain unreacted C4H4Co2(CO)8. Removal of pentane resulted in a pale yellow and very volatile oil; IR: νCO at 2045 and 2010 cm⁻¹; PMR: δ 3.60 (s) and 0.90 (s).

**Reaction of C4H4Co2(CO)8(II) with triphenylmethyl tetrafluoroborate**

The complex(II) (0.342 g) and triphenylmethyl tetrafluoroborate (0.304 g) were stirred together in 25 ml of dichloromethane. After 6 hr, the reaction mass was filtered, dry diethyl ether was added to the filtrate when an yellow precipitate was obtained. This was dissolved in dichloromethane and an aqueous solution of NH4PF6 (0.165 g) was added to get [(C4H4Co(CO)3)PF6 (0.12 g, 35%) as pale yellow solid; IR: νCO at 2150 (m) and 2105 (s) cm⁻¹; PMR: (acetone-δ6) 6.08 (Found: C, 25.2; H, 1.65. C12H16CoF6O3P requires: C, 24.75; H, 1.2%).

**Results and Discussion**

The reaction of 3,4-dichlorocyclobutene with NaCo(CO)4 prepared from Co2(CO)8 and sodium amalgam in tetrahydrofuran yields, in addition to C4H4Co2(CO)4(I), another complex C4H4Co2(CO)4—HgCo(CO)4(II) (m.p. 55°, yellow crystals) under varying experimental conditions. PMR signal for the cyclobutadiene proton in (II) does not vary significantly (~3.4) from that of complex(I) (~3.7). The slight upfield shift may indicate the electron donating nature of the HgCo(CO)4 group. The formation of (I) is thought to take place via an intermediate metal-carbon σ-complex as shown in Scheme 1.

Although we have no firm evidence for the intermediates A and B, spectroscopic evidence points towards the presence in solution of, at least, one intermediate, probably 'A'. In the process of isolation by chromatography the first fraction was found to be a brown and very unstable oil having two sharp ν(CO) bands at 2078 and 2005 cm⁻¹ characteristics of a Co(CO)4 moiety attached to a ligand. It could not be due to Hg[Co(CO)4]2 since this was isolated at a later stage under much enhanced conditions of solvent polarity.

The PMR in C5D5 shows three signals at δ 6.7 (2H, m) 4.9 (1H, broad singlet) and 2.2 (1H, m). The signal at δ 6.7 can be assigned to the olefinic protons, the signal at δ 4.9 can be due to the CHCl group; in the precursor, C2H4Cl, such protons occur at δ 5.15. The signal at δ 2.2 is thought to be due to the metal-bonded CH: a characteristic upfield shift will be expected in this case. In one instance it was also possible to observe another compound along with 'A' which could be the intermediate 'B' (Scheme 1). Its PMR along with signals due to 'A' showed two triplets at δ 8.0 (2H, t) and 5.85 (2H, t) [ν(CO) 2078, 2020, 2005, and 1940 cm⁻¹]. The signal at δ 8.0 could be due to protons of the olefinic bond attached to the metal atom. Furthermore, when 'A' was separately treated with NaCo(CO)4, it gave the complex C4H4Co2(CO)4—Co(CO)4(I). The formation of complex (II) can be rationalized as being a further reaction of (I) with Hg[Co(CO)4]2 present in the reaction medium. And this was found to be the case when these components were reacted separately (Scheme 1). Complex(I) reacts with I2 quantitatively to give cyclobutadienecobaltidicarbonyliodide(III). We have found that complex(II) also reacts with I2 to give a quantitative yield of (III). Compound C4H4Co2(CO)4(I) reacts with triphenylmethyl tetrafluoroborate to give the cationic species [C4H4Co(CO)3]+(IV), isolated as the hexafluorophosphate salt. The spectroscopic properties (IR and PMR) of this cation are similar to those of the isoelectronic cation [C4H4Fe(CO)2NO]+ (ref. 9).

Complex (III) is amenable to carbonyl substitution by triphenylphosphine as well as to formation of a cationic species formed by triphenylphosphine displacement of iodide in the presence of a halide acceptor (AgPF6) (Scheme 2). Compound (V) is an air-stable dark red crystalline solid (m.p. 192°). It PMR signal at δ 4.25 (s) shows an upfield shift due to substitution by a σ-donor.

The cationic compound(VI) is an air-stable pale yellow solid which shows PMR signals at δ 7.40 (15H, m) and 5.18 (4H, s) thus exhibiting the effect of phosphine substitution.

Attempts to prepare the analogous cationic cyclobutadienetricarbonylcobalt complex according to the equation:

\[
\text{C}_4\text{H}_4\text{Co(CO)}_2\text{I} + \text{AgPF}_6 \rightarrow [\text{C}_4\text{H}_4\text{Co(CO)}_3]\text{PF}_6
\]

were unsuccessful. The cationic complex(VI) under-
goes further substitution by triphenylphosphine, although very slowly, to give rise to the monocarbonyl-

bisdiphosphine substituted cationic complex \([\text{C}_4\text{H}_4\text{Co( CO)}(\text{PPh}_3)_2\text{PF}_6]\) (VII). Its IR and PMR indicate effects of further phosphine substitution.

The phosphine substituted monocarbonyl iodide complex (V) reacts with Hg[Co(CO)_4]_2 to give a phosphine substituted dicobalt complex \(\text{C}_4\text{H}_4\text{Co( CO)}(\text{PPh}_3)_2\text{HgCo( CO)}(\text{CO})_4\) (VIII). Nucleophilic attack on the cationic complex (VI) with sodium borohydride indicates the formation of a neutral complex in very small amounts. There was no evidence for a hydride peak in the PMR spectrum, but it may be that the amount of resulting complex \(\text{C}_4\text{H}_4\text{CoH( CO)}(\text{CO})_2\text{PPh}_3\) (IX) was much too small for the sensitivity of 90 MHz instrument.

The dicarbonyl iodide complex (III) is also amenable to nucleophilic attack by methylmagnesium iodide affording \(\text{C}_4\text{H}_4\text{Co}(\text{CO})_2\text{CH}_3\) (X). The neutral complex (X) is a very volatile pale yellow oil and has been characterised only on the basis of IR and PMR evidences (see experimental section). This reactivity of (III) is compatible with its ability to undergo substitution by triphenylphosphine.

The reactions of (III) described above are summarised in Scheme 2.

\(\nu(\text{ CO})\) of the complexes:

It is interesting to note that by examining the \(\nu(\text{ CO})\) (Fig. 1) of the parent complex (I) and some of its derivatives, it is possible to assign the various \(\nu(\text{ CO})\) modes.

It may be seen that the \(\nu(\text{ CO})\) frequencies of the three complexes in the region 2000-1900 cm \(^{-1}\) are lowered in accordance with the presence of a \(\sigma\)-donor attached to the \(\text{C}_4\text{H}_4\text{Co( CO)}(\text{CO})_2\) moiety. This is expected because \(\sigma\)-donating substituent is directly attached to the cobalt and hence changes in \(\nu(\text{ CO})\) should be more pronounced here. Based on this observation, it can be assumed that the \(\nu(\text{ CO})\) frequencies exhibited in the region 2000-1900 cm \(^{-1}\) are due to the carbonyl groups in the \(\text{C}_4\text{H}_4\text{Co( CO)}(\text{CO})_2\) fragment and the frequencies in the region 2100-2000 cm \(^{-1}\) are due to \(\text{Co( CO)}_4\) or HgCo(CO)_4 moieties.

\(\nu(\text{ CO})\) frequencies of complexes (I), (II), (VIII) and Hg[Co(CO)_4]_2 showing the effect of a \(\sigma\)-donor substituent

**Acknowledgement**

Part of this work was done at the laboratory of Prof P L Pauson, Department of Pure and Applied Chemistry, Strathclyde University. One of us (SSU) thanks the Association of Commonwealth Universities for a fellowship.

**References**