

GENERATION OF REACTIVE CYCLOPENTADIENYLCOBALT(I) DERIVATIVES BY REDUCTION OF DICYCLOPENTADIENYLDICOBALT TETRAIODIDE

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Summary

Reduction of $[(C_5H_5)CoI_2]_2$ by sodium amalgam in toluene in the presence of 1,3-butadiene, 1,3-cyclohexadiene or 1,5-cyclooctadiene affords the corresponding cyclopentadienylcobalt(I) diolefin complexes in high yields. Reduction of $[(C_5H_5)CoI_2]_2$ in the presence of 2-butyne yields the binuclear metallocyclic compound $(C_5H_5)_2Co_2(C_4(CH_3)_4)$, previously characterized as a structurally fluxional catalyst for alkyne cyclotrimerisation, as the major product; a trinuclear dicarbyne compound, $(C_5H_5)_3Co_3(C-CH_3)_2$, is obtained as a minor product. With diphenylacetylene, the analogous phenylcarbyne derivative $(C_5H_5)_3Co_3(C-C_6H_5)_2$, previously obtained from thermal reaction with $(C_5H_5)Co(CO)_2$, is obtained along with the major product, the tetraphenylcyclobutadiene complex $(C_5H_5)Co(C_4(C_6H_5)_4)$. Pathways and intermediates for these reactions are discussed.

Introduction

Reactions of cyclopentadienylcobalt(I) derivatives with unsaturated substrate molecules are of considerable utility for the clarification of elementary organometallic reaction mechanisms [1–3] as well as for application as a synthetic tool [4–6]. Cyclopentadienylcobalt dicarbonyl is generally used as a starting material for the generation of reactive species involved in catalytic or stoichiometric substrate transformations. The generation of reactive intermediates from $(C_5H_5)Co(CO)_2$, either by thermal or photochemical CO expulsion, is frequently complicated, however, by the simultaneous formation of bi- or polynuclear carbonyl derivatives [7–9].

We now describe a convenient alternative route to a variety of reactive $(C_5H_5)Co^I$ derivatives, by way of reduction of $[(C_5H_5)CoI_2]_2$ (1) in the presence of unsaturated ligand or substrate molecules. The iodide complex 1 is

readily available from $(C_5H_5)Co(CO)_2$ by direct oxidation with I_2 [10,11] and subsequent refluxing in petroleum ether [12]. $[(C_5H_5)CoI_2]_2$ is quite stable and can even be handled in the presence of air without noticeable deterioration; it has, however, been reported by Roe and Maitlis [12] to decompose to $(C_5H_5)_2Co^+$ and CoI_2 in coordinating solvents. The bromide and chloride derivatives exhibit this instability to an even greater degree, whereas pentamethylcyclopentadienylcobalt(III) halides do not decompose in this manner [12]. From this observation, the impression might arise that unalkylated cyclopentadienylcobalt(III) dihalide compounds are not useful as starting materials for the generation of $(C_5H_5)Co^I$ derivatives by reactions comparable to those of their peralkylated counterparts [13]. We have found, however, that **1** can easily be reduced to form a number of $(C_5H_5)Co^I$ derivatives in high yields.

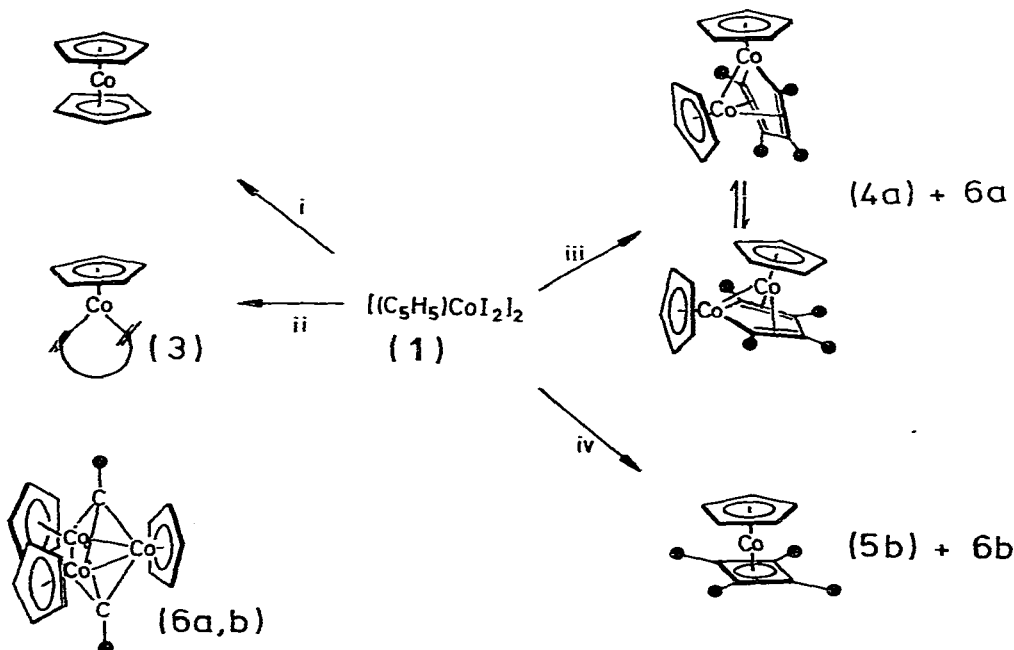
Results and discussion

Reduction of **1** with sodium amalgam in toluene or benzene suspension under an Ar or N_2 atmosphere yields cobaltocene in about 10% yield as the only isolatable product. This observation is in accord with the known tendency of **1** to decompose with formation of $(C_5H_5)_2Co^+$ [12].

If the reduction of **1** is carried out in the presence of 1,3-butadiene, 1,3-cyclohexadiene or 1,5-cyclooctadiene, however, the corresponding $(C_5H_5)Co^I$ diolefin complexes [14] are obtained after removal of solvent and subsequent sublimation, in yields of 50 to 70%.

SCHEME 1

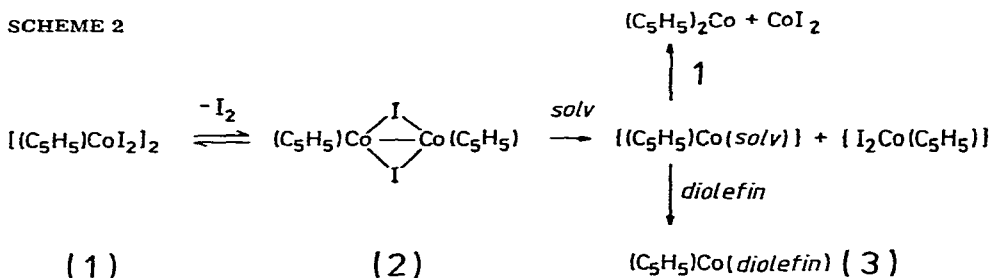
PRODUCTS OBTAINED BY REDUCTION OF $[(C_5H_5)CoI_2]_2$ WITH SODIUM AMALGAM IN TOLUENE SUSPENSION AT ROOM TEMPERATURE.



i) in the absence of additional substrates, ii) in the presence of excess 1,3-butadiene, 1,3-hexadiene or 1,5-cyclooctadiene, iii) in the presence of excess 2-butyne, iv) in the presence of excess diphenylacetylene. (4a, 6a: $\bullet = CH_3$; 5b, 6b: $\bullet = C_6H_5$.)

Apparently, diolefins can intervene in the decomposition pathway of 1 in such a way as to suppress the otherwise predominant disproportionation reaction. In this respect, it is noteworthy that in the mass spectrum of 1 one observes strong ion currents corresponding to I_2^+ and to $(C_5H_5)_2Co_2I_2$ (2), both of which appear to arise from a thermal decomposition of the parent compound. We must assume, therefore, that the binuclear cobalt^{II} iodide compound 2 is present in equilibrium with 1. It is reasonable to assume that 2 can be cleaved by suitable donor or solvent molecules in an asymmetric mode to yield $(C_5H_5)Co^{III}I_2$ and $(C_5H_5)Co^I$ fragments. In the absence of stabilizing ligands, the latter fragment appears to attach itself to the C_5H_5 -ring of excess 1 or 2, thus yielding cobaltocene and CoI_2 under the reducing conditions employed. In the presence of a coordinating olefin, however, the $(C_5H_5)Co^I$ moiety available from 2 would evidently be trapped to give the corresponding olefin complex and thus be precluded from intermolecular C_5H_5 exchange. The $(C_5H_5)CoI_2$ fragment thereby released could then be recycled, probably via its dimer, to produce additional $(C_5H_5)Co^I$ diolefin reduction product.

SCHEME 2



We have further utilized the availability of $(C_5H_5)Co^I$ fragments in these reaction systems to synthesize the binuclear metallocycle 4 in high yields by carrying out the reduction of 1 in the presence of 2-butyne. Compound 4 has previously been obtained, together with $(C_5H_5)Co(CO)_2$, by reduction of $(C_5H_5)Co(CO)I_2$ in the presence of 2-butyne [15]. Compound 4 is structurally fluxional, its two sets of C_5H_5 protons becoming equivalent on the NMR time scale at about 100–120°C; within the same temperature range, 4 is a true catalyst for the cyclotrimerisation of 2-butyne to hexamethylbenzene in the sense that unchanged 4 is quantitatively recovered at the end of the catalytic reaction [15]. The present carbonyl-free reduction reaction followed by sublimation at 35–40°C gives the binuclear compound 4 in 60–70% yield, practically free of side products.

A red-brown solid, which sublimes at 50–55°C appears as a minor product (3–5%), is found by mass spectrometry to have the composition $(C_5H_5)_3Co_3(C_4H_6)$. Its 1H NMR shows only two signals at $\delta = 4.62$ and 2.45 ppm. The intensity ratio of 5 : 2 supports the assignment of these signals to 15 equivalent C_5H_5 and 6 equivalent CH_3 hydrogen positions. In view of the close analogy to the related silylcarbyne complexes 6 ($R = Si(CH_3)_3$), recently reported by Vollhardt et al. [16], this compound can be confidently identified as the bis-(methylcarbyne) complex $(C_5H_5)_3Co_3(C-CH_3)_2$ (6a).

This assignment is further supported by the observation that reduction of 1

in the presence of diphenylacetylene similarly gives, along with the major product, the tetraphenylcyclobutadiene complex $(C_5H_5)Co(C_4(C_6H_5)_4)$ (5) [17], the analogous, purple biscarbyne complex $(C_5H_5)_3Co_3(C-C_6H_5)_2$ (6b), previously obtained by Vollhardt et al. [16] by thermal reaction of diphenylacetylene with $(C_5H_5)Co(CO)_2$.

Apparently, a $[(C_5H_5)Co^I]_n$ moiety generated under reducing conditions from 1 or 2, like that arising from thermal degradation of the dicarbonyl $(C_5H_5)Co(CO)_2$ at higher temperatures [16], is capable of cleaving the alkyne triple bond into two alkyl- or aryl-substituted carbyne units.

Experimental

All manipulations of air-sensitive compounds were carried out under inert gas, using Schlenk tube techniques.

The preparations of $(C_5H_5)Co(CO)I_2$ and $[(C_5H_5)CoI_2]_2$ were based on the procedure described in refs. 9, 10 and 11. Diphenylacetylene, 1,3-butadiene and octacarbonyldicobalt for the syntheses of $(C_5H_5)Co(CO)_2$ were purchased from Fluka AG, Switzerland. Bidentate olefins (1,3-cyclohexadiene and 1,5-cyclooctadiene), 2-butyne and alumina were purchased from EGA-Chemical KG (Germany), Chemicals Procurement Laboratories Inc. (USA) and Merck (Germany), respectively. All solvents used for this work were doubly distilled and dried with butyllithium or methylithium.

Reduction of $[(C_5H_5)CoI_2]_2$ in toluene

1. *Under vacuum.* A mixture of $[(C_5H_5)CoI_2]_2$ (0.76 g, 1.00 mmol) and sodium amalgam (4.5 mmol Na) in about 40 ml of toluene were stirred under vacuum overnight. An orange-brown solution was obtained after filtration. The solution was evaporated to dryness and a dark solid was sublimed under vacuum at room temperature. It was identified as $(C_5H_5)_2Co$ by its mass spectrum. Yield: 0.01 g, 5.3% based on $[(C_5H_5)CoI_2]_2$. The same observations and

TABLE 1

1H NMR AND MASS SPECTRA OF PRODUCTS OBTAINED BY REDUCTION OF $[(C_5H_5)_5CoI_2]_2$ IN THE PRESENCE OF 2-BUTYNE AND OF DIPHENYLACETYLENE

Compound	1H NMR in C_6D_6 (r.t.; δ in ppm)	mass spectra (I.P. = 70 eV)	cf. ref.
$(C_5H_5)_2Co(C_4(CH_3)_4)$ (4a)	4.73 (5)	356 (100, M^+) 354 (9) 288 (37) 231 (74) 189 (62)	15
	4.34 (5) } C_5H_5		
	2.53 (6) } CH_3		
	1.64 (6)		
$(C_5H_5)_3Co_3(C-CH_3)_2$ (6a)	4.62 (15) C_5H_5	426 (93, M^+) 370 (88) 247 (36) 189 (100)	—
	2.45 (6) CH_3		
$(C_5H_5)_3Co_3(C-C_6H_5)_2$ (6b)	4.92 (15) C_5H_5	550 (100, M^+) 370 (24) 247 (15) 189 (60)	16
	~8 mult. (10) C_6H_5 ^a		

^a In acetone- d_6 .

products were obtained when the reduction was carried out under N_2 or H_2 .

2. *In the presence of a bidentate olefin.* Eight mmol of a bidentate olefin (1,3-butadiene, 1,3-cyclohexadiene or 1,5-cyclooctadiene) were introduced, by vacuum distillation, into the mixture of $[(C_5H_5)CoI_2]_2$, sodium amalgam and toluene described above. The mixture was stirred overnight. After filtration and removal of solvent, a $(C_5H_5)Co$ (diene) complex was obtained which was then purified by vacuum sublimation. $(C_5H_5)Co$ (1,3-butadiene), $(C_5H_5)Co$ (1,3-cyclohexadiene) and $(C_5H_5)Co$ (1,5-cyclooctadiene) were identified by comparison of their IR, NMR and mass spectra with those reported in the literature [14,18]. The yields obtained for these three compounds, after purification by sublimation, were 64, 47 and 70%, respectively.

3. *In the presence of 2-butyne.* A mixture of $[(C_5H_5)CoI_2]_2$ (0.76 g, 1 mmol), sodium amalgam (4.5 mmol) and 2-butyne (6 mmol), in about 40 ml toluene, was stirred overnight. After filtration and removal of the solvent, hexamethylbenzene, complex 4 [15] and complex 6a were sublimed at room temperature, 35–40° C and 50–55° C, respectively. For physical data of complex 6a see Table 1. Yields: hexamethylbenzene, 2–10%; $[(C_5H_5)Co]_2(C_4(CH_3)_4)$, 60–75%; $[(C_5H_5)Co]_3(C-CH_3)_2$, 3–5%.

4. *In the presence of diphenylacetylene.* A mixture of $[(C_5H_5)CoI_2]_2$ (0.76 g, 1 mmol), sodium amalgam (4.5 mmol) and diphenylacetylene (0.90 g, 5.06 mmol) in about 40 ml toluene was stirred overnight. After filtration and removal of solvent, unreacted diphenylacetylene was sublimed at 40° C under vacuum. The residue was dissolved in 8 ml of toluene and filtered. The gray residue was identified as hexaphenylbenzene by its mass spectrum. The brown filtrate was chromatographed on an alumina column using petroleum ether (b.p. 50 to 70° C) as the eluent. Two bands, yellow and purple, were detected. The yellow material was identified as $(\eta$ -cyclopentadienyl)(η -tetraphenylcyclobutadiene)cobalt [17] by its mass spectrum. The purple material obtained after removal of solvent, was sublimed at 90° C under vacuum. It was characterized as 6b [16] by its NMR and mass spectra (see Table 1). Yields: hexaphenylbenzene, 0.03 g (0.056 mmol, 3.5%, based on 1); $(C_5H_5)Co(C_4(C_6H_5)_4)$, 0.19 g (0.396 mmol, 20%), $[(C_5H_5)Co]_3(C-C_6H_5)_2$, 0.016 g (0.029 mmol, 4.5%).

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References

- 1 D.R. McAlister, J.E. Bercaw and R.G. Bergman, *J. Amer. Chem. Soc.*, **99** (1977) 1666.
- 2 E.R. Evitt and R.G. Bergman, *J. Amer. Chem. Soc.*, **101** (1979) 3973.
- 3 H.E. Bryndza and R.G. Bergman, *J. Amer. Chem. Soc.*, **101** (1979) 4766.
- 4 Y. Wakatsuki and H. Yamazaki, *Tetrahedron Letters*, (1973) 3383; *Synthesis*, (1976) 26; *J. Organometal. Chem.*, **139** (1977) 157, 169; *J. Chem. Soc. Dalton*, (1978) 1278; *J. Amer. Chem. Soc.*, **101** (1979) 1123.
- 5 H. Bönnemann, *Angew. Chem.*, **90** (1978) 517.
- 6 K.P.C. Vollhardt, *Accts. Chem. Res.*, **10** (1977) 1.

- 7 R.B. King, *Inorg. Chem.*, 5 (1966) 2227.
- 8 K.P.C. Vollhardt, J.E. Bercaw and R.G. Bergman, *J. Organometal. Chem.*, 97 (1975) 283.
- 9 W.S. Lee and H.H. Brintzinger, *J. Organometal. Chem.*, 127 (1977) 87.
- 10 R.E. Heck, *Inorg. Chem.*, 4 (1965) 855.
- 11 R.B. King, *Inorg. Chem.*, 5 (1966) 82.
- 12 D.M. Roe and P.M. Maitlis, *J. Chem. Soc. (A)*, (1971) 3173.
- 13 M.L.H. Green and R.B.A. Pardy, *J. Chem. Soc. Dalton*, (1979) 355.
- 14 R.B. King, P.M. Treichel and F.G.A. Stone, *J. Amer. Chem. Soc.*, 83 (1961) 3593.
- 15 W.S. Lee and H.H. Brintzinger, *J. Organometal. Chem.*, 127 (1977) 93.
- 16 J.R. Fritch and K.P.C. Vollhardt, *Angew. Chem.*, 92 (1980) 570.
- 17 M.D. Rausch and R.A. Genetti, *J. Org. Chem.*, 35 (1970) 3888.
- 18 K. Yasufuka and H. Yamazaki, *Organ. Mass. Spect.*, 3 (1970) 23.