

## 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.

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### 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.

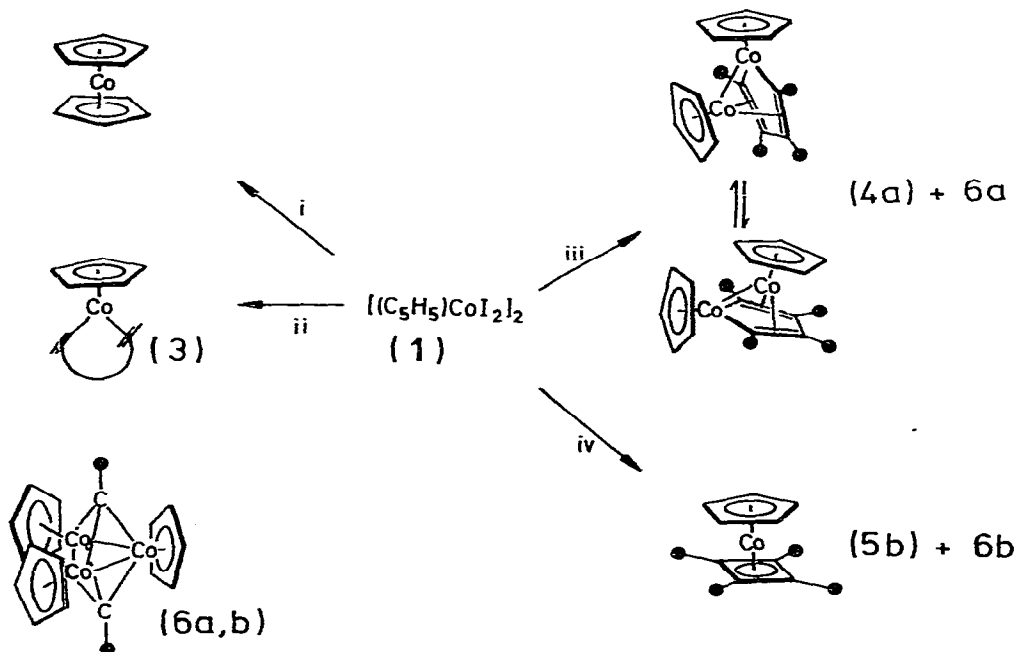
### Results and discussion

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

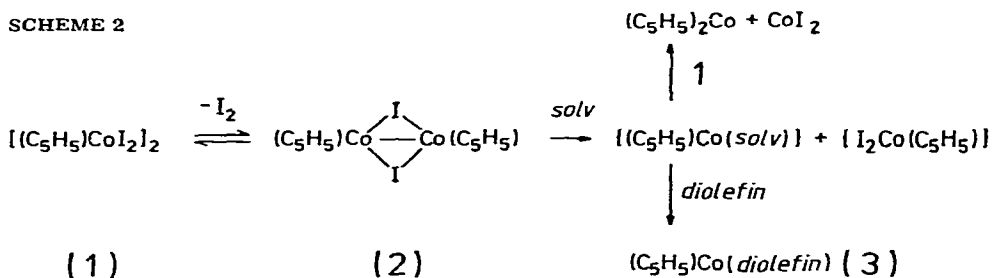
PRODUCTS OBTAINED BY REDUCTION OF  $[(C_5H_5)CoI_2]_2$  WITH SODIUM AMALGAM IN TOLUENE SUSPENSION AT ROOM TEMPERATURE.



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<sup>II</sup> 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 methylolithium.

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

<sup>a</sup> 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)( $\eta$ -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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