CoCpBr INTERMEDIATES IN THE CYCLOPENTADIENYLATION OF CoBr$_2$ WITH NaCp

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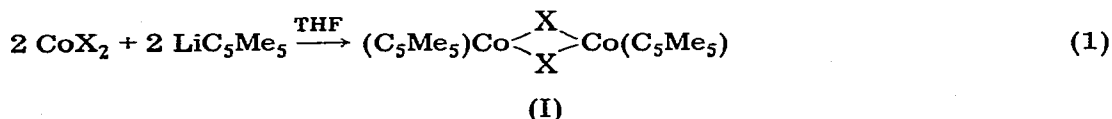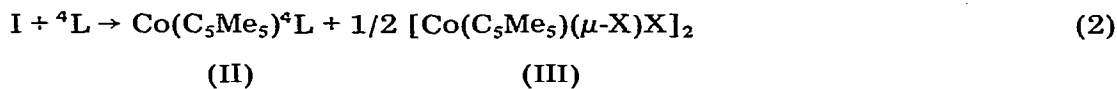
Summary

Reaction of CoBr$_2$ and NaCp (Cp = η^5-C$_5$H$_5$) at low temperature followed by addition of a diene or acetylene gives the complexes CoCp(diene). The scope and mechanism of this novel reaction have been investigated.

Though reaction of transition metal halides with alkali metal cyclopentadienides, in particular NaCp, to give metallocenes, MCp$_2$, is one of the best known reactions in organotransition metal chemistry, very little is known about its mechanism. The displacement of two halides by Cp would be expected to proceed stepwise, but in no case in which the reaction leads to the sandwich molecule (Cr to Ni) has the presence of an intermediate been firmly established. Tsutsui attempted to prove the intermediate formation of σ-Cp complexes in the reaction of FeCl$_3$ and NaCp at low temperatures [1], but because the arguments rested primarily on hydrolysis products, ferrocene and ferricenium were the only characterized organometallic species, the precise nature of the intermediates cannot be regarded as established beyond doubt.

We recently isolated fairly stable dimeric pentamethylcyclopentadienylcobalt halides, [Co(C$_5$Me$_5$)(μ-X)]$_2$ (I, X = Cl, Br) [2] from the reaction of CoX$_2$ and LiC$_5$Me$_5$ in THF between —20 and 20°C. They were crystallized from pentane solution and were shown to be dimeric by mass spectroscopy. Among the reactions these novel cobalt(II) semisandwich complexes were shown to undergo was a valence disproportionation upon addition of two- or four-electron ligands, ^{4}L, as in eq. 2, and a cyclopentadienylation with either NaCp or LiC$_5$Me$_5$ to give pentamethyl- or decamethyl-cobaltocene, IV, as in eq. 3.

$$2 \text{ CoX}_2 + 2 \text{ LiC}_5\text{Me}_5 \xrightarrow{\text{THF}} (\text{C}_5\text{Me}_5)\text{Co} \underset{X}{\overset{X}{<\quad>}} \text{Co(C}_5\text{Me}_5) \tag{1}$$

(I)

(X = Cl, Br)

$$I + {}^4L \rightarrow Co(C_5Me_5){}^4L + 1/2 \ [Co(C_5Me_5)(\mu\text{-}X)X]_2 \tag{2}$$

$$\text{(II)} \qquad\qquad\qquad \text{(III)}$$

$(^4L = 1,5\text{-cyclooctadiene, } 1,3\text{-butadiene a.o.})$

$$I + 2 \ MC_5R_5 \rightarrow 2 \ Co(C_5Me_5)(C_5R_5) \tag{3}$$

$$\text{(IV)}$$

$(M = Na, R = H \text{ or } M = Li, R = Me)$

The demonstration of reaction 3 qualifies complexes I to be regarded as true intermediates in the cyclopentadienylation of cobalt(II) halides to cobaltocenes, with the reaction in the case of the pentamethylcyclopentadienyl ligand being so retarded at the stage of the monocyclopentadienylation as to allow isolation of I. The present article deals with the extension of reaction 1 to use NaCp as the cyclopentadienylating agent. It has been observed [2] that NaCp reacts much more rapidly than LiC_5Me_5 in reaction 3; thus monocyclopentadienyl complexes of type I from NaCp and cobalt(II) halides are to be expected only at low temperatures. If subsequent transformations are analogous to reaction 2 this would lead to cobalt(III) complexes $(CoCpX_2)_n$. The stability of these compounds is known to decrease markedly in the order $X = I > Br \gg Cl$ [3], whereas complexes I become less stable in the sequence $X = Cl > Br \gg I$ [2]. Thus $CoBr_2$ was chosen as a compromise, and was employed as its 1,2-dimethoxy-ethane (DME) adduct, which is readily soluble in THF, enabling homogeneous conditions to be used even at low temperatures.

Results

In a first set of experiments when $CoBr_2 \cdot DME$ was treated with an equimolar amount of NaCp at $-80°C$ in THF the initially clear blue solution rapidly

TABLE 1

REACTION OF $CoBr_2$ DME, NaCp AND NEUTRAL TWO- OR FOUR-ELECTRON LIGANDS IN THF AT -80 TO $20°C$

Run	Ligand	Product	Yield (%)	By-products	Reaction conditions
1	CO	$CoCp(CO)_2$ (V)	17	$CoCp_2$ (traces)	30—40 kPa for 6 h at $-80°C$
2	C_8H_{12} [a]	$CoCp(C_8H_{12})$ (VI)	34	$CoCp_2$, $CoCp(C_5H_6)$ [b]	from -80 to $20°C$ within 3 h
3	C_7H_8 [c]	$CoCp(C_7H_8)$ (VII)	10	$CoCp_2$ (traces) $CoCp(C_5H_6)$ [b]	from -80 to $20°C$ within 1.5 h
4	C_2Ph_2	$CoCp(C_4Ph_4)$ [d] (VIII)	8	$CoCp(C_4Ph_4H_2)$ [e]	from -80 to $10°C$ within 2 h

[a] $C_8H_{12} = 1,5$-cyclooctadiene (COD). [b] $C_5H_6 = 1,3$-cyclopentadiene. [c] $C_7H_8 = 2,5$-bicyclo[2.2.1]hepta-diene (norbornadiene, NBD). [d] $C_4Ph_4 =$ tetraphenylcyclobutadiene. [e] $C_4Ph_4H_2 = 1,2,3,4$-tetraphenyl-1,3-butadiene.

TABLE 2

REACTION OF $CoBr_2 \cdot DME$, NaCp, $CoCp_2$ AND COD IN A MOLAR RATIO OF 2/2.06/0.5/1.16 [a] UNDER VARIOUS CONDITIONS

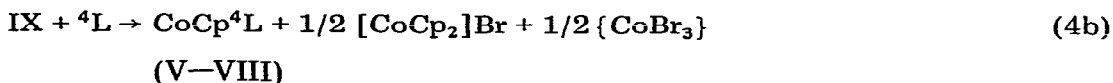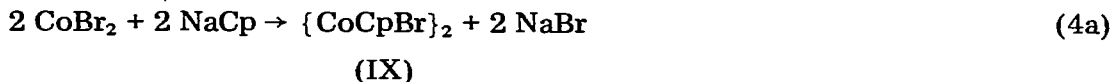| Run	Co^{2+}	$CoCp_2$	$[CoCp_2]^+$	Co [b]	ΣCo [c]	CoCpCOD	(Yield in %)	Conditions
1	0.40	0.17	0.86	0.58	2.47	0.46	(45.3)	$CoCp_2$ added at —80°C prior to NaCp
2	0.25	0.31	0.84	0.59	2.42	0.43	(43)	$CoCp_2$ added at —80°C after the NaCp
3	0.30	0.32	1.17	0.30	2.46	0.37	(37.5)	$CoCp_2$ added at 0°C prior to NaCp at —80°C
4		—	not determined			0.11	(11.5)	molar ratio $CoBr_2$/NaCp as 1/1.5
5		—	not determined			0.08	(8.6)	solvent change to hexane at —80°C
6	0.50	traces	0.90	0.39	1.97	0.18	(18)	LiCp instead of NaCp

[a] The amount of products isolated is given in mmoles as calculated on the basis of these figures. [b] Elementary Co admixed with some CoO. [c] Sum of columns 1—4 and 6.

turned green. Either a diene or tolane, in slight excess, or CO was added, and the mixture allowed to warm slowly to room temperature. After evaporation of THF the neutral diolefin complexes were extracted with pentane or toluene, the solution passed over CuCl to remove any cobaltocene and the product purified by crystallization, chromatography or sublimation. The results are shown in Table 1.

In addition to the products listed in Table 1, $[CoCp_2]^+$ and $CoBr_2$ were frequently isolated from the reaction. As can be seen, even in the most favorable case, involving the good chelating diene 1,5-cyclooctadiene (COD), the yield is less than 50% based on the stoichiometry of eq. 4. To gain a closer insight into the reaction a second series of experiments was run under various conditions with COD as the olefinic component. The work-up procedure was modified (see experimental) to allow for separate quantitative determination of all the principal products. The results are given in Table 2.

Discussion

The products observed in the above reactions can be rationalized in terms of eq. 4, if reduction of Co^{3+} to Co^{2+} during work up at ambient temperature is taken into account.

$$2\,CoBr_2 + 2\,NaCp \rightarrow \{CoCpBr\}_2 + 2\,NaBr \qquad (4a)$$
$$(IX)$$

$$IX + {}^4L \rightarrow CoCp^4L + 1/2\,[CoCp_2]Br + 1/2\,\{CoBr_3\} \qquad (4b)$$
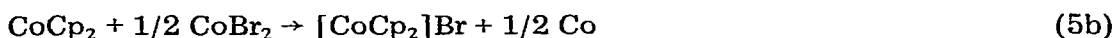$$(V—VIII)$$

Formation of a semi-sandwich complex IX with the metal in the formal oxidation state +2 was expected by analogy with the isolated pentamethyl-cyclopentadienyl compounds I. On addition of the olefin (or CO) it undergoes a valence disproportionation slightly different from that shown in eq. 2 in that cobalt(III) partly appears as $[CoCp_2]^+$ rather than as a (dibromo)cyclopenta-dienide $(CoCpBr_2)_n$. No evidence for the formation of the latter complex was found in any of the experiments.

In the pentamethylcyclopentadienyl system yields of complexes II were around 70% and roughly parallel the proportion of I which can be recovered from a pentane solution. Thus reaction 2 is almost quantitative. The markedly lower yields in the cyclopentadienyl system, in particular those shown in Table 1, may have several causes.

The formation of Co^{3+} in the disproportionation (eq. 4b) must reduce the yield of the diolefin complexes, which are oxidized with potential values around +0.3 V vs. SCE leading to $[CoCp_2]^+$ and Co^{2+} [4]. In the experiments listed in Table 2, 0.5 mol of $CoCp_2$ were added deliberately at the beginning of the reaction to quench the Co^{3+} expected from reaction 4b. As can be seen from comparison of experiment 2 in Table 1 with experiments 1 and 2 in Table 2, the yield of VI is thereby increased by 30%. This effect does not appear when NaCp is present in excess of the stoichiometry in eq. 4 (exp. 4 in Table 2). Instead the yield of VI is decreased, probably due to the formation of $CoCp_2$.

Whereas pentane solutions of I on standing at room temperature slowly deposit complexes III, but no permethylcobaltocene or cobalticenium, the metallocene is formed from NaCp and $CoBr_2$. With the ratio of reactants appropriate to eq. 4a the reaction proceeds as given in eq. 5.

$$\{CoCpBr\}_2 \rightarrow CoCp_2 + CoBr_2 \qquad\qquad (5a)$$

$$CoCp_2 + 1/2\ CoBr_2 \rightarrow [CoCp_2]Br + 1/2\ Co \qquad\qquad (5b)$$

Thus cobalticenium and elementary Co is formed in the redox reaction 5b. The occurrence of reaction 5 has been separately confirmed, and it was found that reaction 5b is slow at low temperature and the relative amounts of $CoCp_2$, $[CoCp_2]^+$ and Co isolated vary with the time of reaction at room temperature.

The formation of decamethylcobaltocene in reaction 3 requires reflux in THF, whereas reaction 2 ($^4L = COD$) is virtually instantaneous at $-30°C$. Thus in the pentamethylcyclopentadienyl system exists a temperature interval between valence disproportionation and cyclopentadienylation of at least 100 K.

In contrast, experiments in which the reaction mixture formed from $CoBr_2$ and NaCp was allowed to warm from $-80°C$ before the diene was added, showed that reaction 5 becomes dominant above $-40°C$. From the rapid colour change on addition of NaCp to the THF solution of $CoBr_2$ at $-80°C$ it is inferred that the formation of IX is still fast at this temperature but reaction 4b is obviously slow, which means that in the cyclopentadienyl system reaction 5 competes with reaction 4 at all temperatures.

As can be seen from run 6 in Table 2 the yield is not improved when the less soluble LiCp is employed. In this case reaction 4a appears to be slower, which leads to a ratio of Co^{2+} and $[CoCp_2]^+$ to VI considerably higher than that found when NaCp is used.

For the structure of cyclopentadienyl(bromo)cobalt (IX) the formula of the dimer in eq. 4a and 5a was written largely by analogy with the complexes established for the pentamethylcyclopentadienyl system. Run 5 in Table 2, in which reaction 4b occurs in a hydration solvent, demonstrates the existence of a neutral, unpolar species for which a formulation as a bromide-bridged dimer analogous to I reasonably accomodates the coordination requirements of the metal. The rather low yield of VI in this experiment is due to extensive decomposition of the unstable intermediate IX during the evaporation, redissolution, and filtration procedures.

In contrast, THF solutions of cyclopentadienyl(bromo)cobalt may well contain monomeric species associated with coordinated solvent, such as CoCpBr-$(THF)_n$; this point awaits further elucidation using the pentamethylcyclopentadienyl system, which is easier to study.

Finally it may be difficult to prove whether complexes I and IX have the cyclopentadienyl ligand σ- or π-bound. In the case of σ-Cp intermediates it is difficult to reconcile the composition of I with a reasonable coordination for the Co. Moreover in this case one would expect the cyclopentadienyl complex IX to be of greater stability than its pentamethyl analog I. The reverse order established experimentally thus strongly favors π-bonding of the cyclopentadienyl ligand.

Experimental

All experiments were performed under purified nitrogen with anhydrous nitrogen-saturated solvents.

Bromo(cyclopentadienyl)cobalt (IX)

A solution of 2.26 g (30 mmol) $CoBr_2 \cdot$ DME (prepared by brominating Co powder in DME, isolated and analyzed for Co) in 30 ml THF was cooled to $-78°$C in a dry ice/acetone bath and a solution of 2.75 g (31 mmol) of NaCp in 30 ml THF was added dropwise with stirring. The resulting green mixture was used for the experiments described below.

Reaction with CO (Table 1, exp. 1)

A Schlenk tube containing the THF solution of IX was connected to a CO supply and stirred under 30—40 kPa CO at $-78°$C for 6 h. Evaporation of the THF at $0°$C followed by extraction of the residue with pentane and evaporation of the pentane left a brown oil (0.44 g, 14%), which was identified from its IR (ν(CO) 2033, 1964 cm^{-1} (CH_2Cl_2)) and ^{1}H-NMR (δ 5.02 (CS_2)) absorptions as CoCp(CO)$_2$ (V).

Reaction with 2,5-bicyclo[2.2.1]heptadiene (NBD) (Table 1, exp. 3)

To the THF solution of IX was added 1.7 ml (16.6 mmol) NBD (a larger excess of the diene leads to extensive polymerization and thus difficulties in the work up) at $-78°$C, and the mixture was allowed to warm to $10°$C during 1.5 h. The THF was evaporated and the residue extracted with 100 ml pentane. The orange-brown solid left after evaporation of the pentane was chromatographed on alumina (2 × 100 cm, 4% H_2O) with pentane as eluent; the first

band eluted gave cyclopentadiene(cyclopentadienyl)cobalt [5] (110 mg, 4%) and the second cyclopentadienyl(norbornadiene)cobalt (VII) [6] (340 mg, 9.6%, m.p. 58—60°C (pentane) m.p. lit. [6] 59—60°C), and traces of cobaltocene were subsequently eluted. The diamagnetic complexes were identified by comparison of their ^{1}H NMR spectra with those of authentic samples.

Reaction with 1,2-diphenylacetylene (Table 1, exp. 4)

To a solution of 30 mmol IX in THF was added 6.73 g (37 mmol) 1,2-diphenylacetylene at —80°C and the mixture allowed to warm to room temperature during 2 h. It was concentrated to 10 ml, and after extraction with 50 ml pentane then with 50 ml toluene, the solid was filtered off and washed with toluene. The pentane extract was passed through CuCl to oxidize cobaltocene, and the eluate was combined with the toluene extracts. After concentration these were chromatographed on alumina (4% H_2O) with pentane/dichloromethane (100/3) as eluent. Two bands were obtained. The first, which was orange, gave after sublimation (170°C/1 Pa) 250 mg (8%) cyclopentadienyl-(tetraphenylcyclobutadiene)cobalt (VIII) [7] (m.p. 258°C, m.p. lit. [7] 256°C), and the second, which was red, after sublimation (175—185°C/1 Pa) gave 130 mg (4%) of cyclopentadienyl(1,2,3,4-tetraphenyl-1,3-butadiene)cobalt [8]. ^{1}H NMR: δ 7.0—6.75 (m, 20 H, Ph), 4.5 (s, 5 H, Cp), 0.10 ppm (s, 2 H, olefin).

Reaction with 1,5-cyclooctadiene (Table 2, exp. 1—4)

After mixing of the reagents as indicated in Table 2 the mixture was warmed to room temperature during 3 h then the THF was evaporated off and the rasidue extracted with 50 ml pentane. The pentane solution was passed through a frit covered with 3 × 2 cm of alumina (4% H_2O) and 2 × 4 cm of powdered CuCl to oxidize the cobaltocene, and then concentrated. Cooling to —80°C gave light brown crystals of cyclooctadiene(cyclopentadienyl)cobalt (VI) [9], which was filtered off. The yields given in Table 2 refer to this fraction, melting at 103—104°C (m.p. lit. [9] 102°C). The mother liquid contained a further 150 mg of VI.

The CuCl was washed with water and $[CoCp_2]^+$ was precipitated as its tetraphenylborate salt from the aqueous solution, and filtered off, dried and weighed (Table 2, column 2). The pentane-insoluble residue from the reaction mixture was treated with water, and the solution was filtered; $[CoCp_2]^+$ was precipitated from the filtrate as the tetraphenylborate salt (Table 2, column 3) and Co^{2+} was determined by complexometric titration (Table 2, column 1). The water-insoluble residue consisted of elementary Co with small parts of cobalt-oxide. It was dissolved in nitric acid and titrated as above (Table 2, column 4).

Literature

1 M. Tsutsui, M. Hancock, J. Ariyoshi and M.L. Levy, J. Am. Chem. Soc., 91 (1969) 5233.
2 U. Koelle, F. Khouzami and B. Fuss, Angew. Chem., 94 (1982) 132; Angew. Chem. Int. Ed. Engl., 21 (1982) 131; Angew. Chem. Suppl., (1982) 230.
3 R.F. Heck, Inorg. Chem., 4 (1965) 855.
4 U. Koelle, Inorg. Chim. Acta, 47 (1981) 13.
5 M.L.H. Green, L. Pratt and G. Wilkinson, J. Chem. Soc., (1959) 3753.
6 R.B. King, P.M. Treichel and F.G.A. Stone, J. Am. Chem. Soc., 83 (1961) 3593.
7 M.D. Rausch and R.A. Genetti, J. Org. Chem., 35 (1970) 3888.
8 A. Nakamura and N. Hagihara, Chem. Abstr., 59 (1963) 14869.
9 A. Nakamura and N. Hagihara, Bull. Soc. Chem. Japan, 33 (1960) 425.