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MONO-μ-HYDRIDO COMPLEXES OF PENTAMETHYLCYCLOPENTADIENYLCOBALT

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Summary

The complex $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ reacts with Cl_2 and with Br_2 to give $[(\eta^5\text{-}C_5Me_5)CoCl(\mu\text{-}Cl)]_2$ and $(\eta^5\text{-}C_5Me_5)Co(CO)Br_2$, respectively. The latter was converted into the dimeric species $[(\eta^5\text{-}C_5Me_5)CoBr(\mu\text{-}Br)]_2$. The reaction of dimeric pentamethylcyclopentadienylcobalt complexes $[(\eta^5\text{-}C_5Me_5)CoX(\mu\text{-}X)]_2$ (X = Cl, Br, I) with potassium hydroxide gives the mono-μ-hydrido complexes $[(\eta^5\text{-}C_5Me_5)CoX]_2(\mu\text{-}H)(\mu\text{-}X)$.

Introduction

Oxidative addition of pseudohalogens to the dicarbonylpentamethylcyclopentadienylcobalt complex $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ leads to the elimination of a carbonyl group and formation of the corresponding pseudohalogens derivatives of cobalt(III) [1–3]. The complex $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ reacts in a similar way with I_2, to give the $(\eta^5\text{-}C_5Me_5)Co(CO)I_2$ derivative, from which the dimeric $[(\eta^5\text{-}C_5Me_5)COI(\mu\text{-}I)]_2$ can be prepared [4]. This dimeric compound is of great utility in synthesis of organocobalt derivatives [5]. The analogous dimeric Rh and Ir complexes $[(\eta^5\text{-}C_5Me_5)MX(\mu\text{-}X)]_2$ (X = Cl, Br, I) can be used to make the mono-μ-hydrido complexes $[(\eta^5\text{-}C_5Me_5)MX]_2(\mu\text{-}H)(\mu\text{-}X)$ [6], which act as catalysts in olefin hydrogenation [7].

In extension of the earlier studies we describe below: (1) The oxidative addition reactions of Cl_2 and Br_2 to $(\eta^5\text{-}C_5Me_5)Co(CO)_2$, carried out the way described for I_2 [4]; (2) The synthesis of the dimeric complexes $[(\eta^5\text{-}C_5Me_5)CoX(\mu\text{-}X)]_2$ (X = Cl, Br); and (3) The preparation from the dimeric species of the mono-μ-hydrido complexes, $[(\eta^5\text{-}C_5Me_5)CoX]_2(\mu\text{-}H)(\mu\text{-}X)$ (X = Cl, Br, I).

Discussion of results

The reaction of $(\eta^5\text{-}C_5Me_5)Co(CO)_2$, in ether solution with Br_2 or I_2 under N_2 results in loss of a carbonyl group and precipitation of solids of the stoichiometry $(\eta^5\text{-}C_5Me_5)Co(CO)X_2$ (X = Br, I). In the reaction with Cl_2 complete total de-

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carbonylation occurs, as shown by the absence of any ν(CO) band in the IR spectrum, and the dimeric complex of stoichiometry $[(\eta^5\text{-}C_5Me_5)CoCl(\mu\text{-}Cl)]_2$ is obtained directly. Formation of the analogous complexes of bromine and iodine requires refluxing of solutions of the monomeric $(\eta^5\text{-}C_5Me_5)Co(CO)X_2$ complexes (X = Br, I) in light petroleum; this is consistent with the greater tendency of chlorine than of bromine and iodine to form bridging bonds. (We should mention that these compounds were synthesized very recently by a more complex procedure [8].) The mono-μ-hydrido complexes $[(\eta^5\text{-}C_5Me_5)CoX]_2(\mu\text{-}H)(\mu\text{-}X)$ (X = Cl, Br, I) are obtained by treatment of the dimeric species $[(\eta^5\text{-}C_5Me_5)CoX(\mu\text{-}X)]_2$ with KOH in isopropyl alcohol.

All the new complexes obtained are hygroscopic and sparingly soluble in solvents such as CH_2Cl_2 or acetone. These IR spectra show, in the 4000–200 cm^{-1} range, the characteristic bands of the pentamethylcyclopentadiene ligand with C_{5v} symmetry [9,10]. Table 1 lists the vibrations frequencies arising from the carbonyl ligand, together with those corresponding to metal–hydride and metal–halogen bonds. The frequency range of ν(CO) band for $(\eta^5\text{-}C_5Me_5)Co(CO)X_2$ (X = Br, I) is characteristic of terminal ligands, and the frequencies ν(Co–CO) and δ(Co–CO) bands appear in the 500–465 cm^{-1} range, in agreement with published data [11]. There is a band at 248 cm^{-1} which can be assigned to the stretching vibration ν(Co–Br). The ν(Co–I) stretching vibration was not observed, since it would appear below 200 cm^{-1}. The spectra of the di-μ-halobis[halo(pentamethylcyclopentadienyl)]cobalt complex, $[(\eta^5\text{-}C_5Me_5)CoX(\mu\text{-}X)]_2$ (X = Cl, Br), show bands at 309 and 342 cm^{-1} (X = Cl) and 230 and 265 cm^{-1} (X = Br), which are ascribed to the presence of both bridging and terminal Co–X bonds in the molecule. The values of the ratios $\nu(Co\text{–}Cl)_b/\nu(Co\text{–}Cl)_t$ (0.90), $\nu(Co\text{–}Br)_b/\nu(Co\text{–}Br)_t$ (0.84) and $\nu(Co\text{–}Br)_t/\nu(Co\text{–}Cl)_b$ (0.77) are in accord with literature data [12].

Finally, the spectra of the mono-μ-hydrido complexes $[(\eta^5\text{-}C_5Me_5)CoX]_2(\mu\text{-}H)(\mu\text{-}X)$ (X = Cl, Br, I) show bands, at 300 and 350 cm^{-1} (X = Cl) and 235 and 270 cm^{-1} (X = Br), which are assigned to bridging and terminal Co–X bonds, the ratios previously mentioned have values rather similar to those above. No ν(Co–H) bands are observed in the 2200–1600 cm^{-1} range, characteristic of terminal Co–H bonds,

TABLE 1. IR SPECTRAL DATA FOR THE COMPLEXES OBTAINED [a]

	ν(CO)	ν(Co-CO) δ(Co-CO)	ν(Co-X)	ν(Co-H-Co)
$Cp^{\star}Co(CO)Br_2$	2060 vs	495 vs 465 vs	248 m	
$Cp^{\star}Co(CO)I_2$	2030 vs	500 s 470 vs		
$[Cp^{\star}CoCl_2]_2$			342 m (t) 309 m (b)	
$[Cp^{\star}CoBr_2]_2$			265 m (t) 235 w (b)	
$[(Cp^{\star}Co)_2HCl_3]$			350 m (t) 300 m (b)	1108 vw, br, 840 w
$[(Cp^{\star}Co)_2HBr_3]$			270 m (t) 235 w (b)	1100 vw, br, 836 w
$[(Cp^{\star}Co)_2HI_3]$				1096 vw, br, 834 w

[a] $Cp^{\star} = \eta^5\text{-}C_5Me_5$. t = terminal; b = bridge.

but there is a very weak broad band in each case in the 1108–1096 cm^{-1} range which can be assigned to the ν(Co–H–Co) vibration. There is another weak band in the 840–834 cm^{-1} range which may also be ascribed to (Co–H–Co) vibrations in accord with previous assignments [13,14]. The assignment of the bands corresponding to M–H–M vibrations in the IR spectrum is difficult and unfortunately, we were unable to obtain Raman spectra because the complexes were decomposed by the radiation.

The ^1H NMR spectrum ($CDCl_3$, 200 MHz) of the complex (η^5-C_5Me_5)Co(CO)Br_2 shows a singlet at δ 1.85 arising from the 15 equivalent methyl hydrogens. The spectra of the dimeric complexes [(η^5-C_5Me_5)CoX]$_2$ show a singlet at δ 1.20 (X = Cl), δ 1.30 (X = Br) and δ 1.90 (X = I), arising from the 30 equivalent methyl hydrogens. The mono-μ-hydrido complexes [(η^5-C_5Me_5)CoX]$_2$(μ-H)(μ-X) show a singlet at δ 1.01 (X = Cl), δ 1.30 (X = Br), δ 1.80 (X = I), from the 30 equivalent methyl hydrogens. In the three cases a singlet from hydridic hydrogen appears at highfield δ 38.28; the intergrations are in the expected 30/1 ratio.

Experimental

All reactions were carried out under oxygen-free N_2. The pentamethylcyclopentadiene [15] and the (η^5-C_5Me_5)Co(CO)$_2$ [16,17] were prepared by published procedures. The microanalyses were performed by the Dpto. Química Inorgánica de la Facultad de Ciencias de la Universidad de Alcalá de Henares (Madrid, Spain). The cobalt was determined by titration of the Co-EDTA complex in presence of NET as indicator. The halogens were determined gravimetrically by the Volhard method.

The IR spectra were recorded in the range 4000–200 cm^{-1} on a Nicolet DX instrument using Nujol and Hostaflon mulls between CsI windows. ^1H NMR spectra were recorded on a Bruker WH-200-SY spectrometer.

Preparation of (η^5-C_5Me_5)Co(CO)Br_2

The complex η^5-C_5Me_5Co(CO)$_2$ (1.5 g, 6 mmol) was dissolved in Et_2O (30 cm^3) saturated with oxygen-free N_2 in a two-neck flask (100 cm^3) fitted with a N_2 inlet, magnetic stirrer and pressure equalized dropping funnel. Neat bromine (0.3 cm^3, 6 mmol) was slowly added dropwise. A violet solid immediately appeared and CO was evolved. The solid was filtered off, washed with Et_2O and dried in vacuum. The yield was 1.9 g (85%). (Found: C, 33.84; H, 3.97; Br, 40.20; Co, 15.36. $C_{11}H_{15}OBr_2Co$ calcd.: C, 34.58; H, 3.93; Br, 41.86; Co, 15.45%. ^1H NMR ($CDCl_3$): δ 1.85 (15H, C_5Me_5)) ppm.

Preparation of [(η^5-C_5Me_5)Br(μ-Br)Co]$_2$

A suspension dibromo(carbonyl)pentamethylcyclopentadienylcobalt (0.9 g, 2 mmol) in light petroleum (30 cm^3; b.p. 100–120°C) was refluxed. The colour of the solid changed immediately from violet to green. After 1 h the green solid was isolated. The yield was 0.68 g (98%). (Found: C, 32.80; H, 4.29; Br, 44.73; Co, 16.55. $C_{20}H_{30}Br_4Co_2$ calcd.: C, 33.92; H, 4.24; Br, 45.18; Co, 16.68%. ^1H NMR ($CDCl_3$): δ 1.30 (30H, 2C_5Me_5)) ppm.

Preparation of [(η^5-C_5Me_5)Cl(μ-Cl)Co]$_2$

Chlorine was bubbled through a solution of (η^5-C_5Me_5)Co(CO)$_2$ (1.5 g, 6 mmol) in Et_2O (30 cm^3). The green solid which separated was filtered off, washed with Et_2O, and dried in vacuum. The yield was 1.55 g (98%). (Found: C, 44.20; H, 5.70;

Cl, 26.35; Co, 22.09. $C_{20}H_{30}Cl_4Co_2$ calcd.: C, 45.31; H, 5.66; Cl, 26.80; Co, 22.28%. ^{1}H NMR ($CDCl_3$): δ 1.20 (30H, $2C_5Me_5$)) ppm.

Preparation of $[(\eta^5\text{-}C_5Me_5)CoCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$

A solution of $[(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)Co]_2$ (0.5 g, 1 mmol) and KOH (0.079 g, 1.4 mmol) in isopropyl alcohol (30 cm^3) was stirred for 2 h. The green solid was filtered off, washed with isopropyl alcohol and dried in vacuum. The yield was 0.34 g (70%). (Found: C, 47.51; H, 6.40; Cl, 21.04; Co, 23.59; $C_{20}H_{31}Cl_3Co_2$ calcd.: C, 48.46; H, 6.26; Cl, 21.50; Co, 23.82%. ^{1}H NMR ($CDCl_3$): δ 1.01 (30H, $2C_5Me_5$), 38.28 (1H, H^-) ppm.

Preparation of $[(\eta^5\text{-}C_5Me_5)CoBr]_2(\mu\text{-}H)(\mu\text{-}Br)$

By the procedure described above, a dark green solid was obtained from $[(\eta^5\text{-}C_5Me_5)Co(\mu\text{-}Br)Br]_2$ (0.35 g, 0.5 mmol) and KOH (0.040 g, 0.7 mmol) in isopropyl alcohol. The yield is 0.22 g (70%). (Found: C, 37.65; H, 4.98; Br, 37.98; Co, 18.57. $C_{20}H_{31}Br_3Co_2$ calcd.: C, 38.18; H, 4.93; Br, 38.14; Co, 18.77%. ^{1}H NMR ($CDCl_3$): δ 1.30 (30H, $2C_5Me_5$), 38.28 (1H, H^-) ppm.

Preparation of $[(\eta^5\text{-}C_5Me_5)CoI]_2(\mu\text{-}H)(\mu\text{-}I)$

By a similar procedure a green solid was obtained from $[(\eta^5\text{-}C_5Me_5)Co(\mu\text{-}I)I]_2$ (0.5 g, 0.6 mmol) and KOH (0.048 g, 0.8 mmol) in isopropyl alcohol. The yield was 0.32 g (75%). (Found: C, 30.89; H, 3.96; I, 49.03; Co, 15.21. $C_{20}H_{31}I_3Co_2$ calcd.: C, 31.17; H, 4.02; I, 49.45; Co, 15.30%. ^{1}H NMR ($CDCl_3$): δ 1.80 (30H, $2C_5Me_5$), 38.28 (1H, H^-) ppm.

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