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OXIDATIVE ADDITION REACTIONS TO Cp'Co(CO)L ($Cp' = C_5H_4CH_3$; L = CO, PPh_3 AND TETRACYANOETHYLENE) WITH XCN (X = Br, I)

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Summary

Oxidative addition of XCN (X = Br, I) to Cp'Co(CO)L (L = CO, PPh_3) leads to the formation of Cp'CoL(CN)X. The complexes C_p'CoTCNE(L) do not react with XCN.

Introduction

Werner et al. have extensively studied the Lewis base behaviour of cobalt complexes such as C_5R_5CoLL' (R = H, Me; L = CO, C_2H_4; L' = PMe_3, $P(OMe)_3$). These complexes react with an electrophile to form a new bond to the metal [1–4].

We previously described oxidative additions to $Cp'Co(CO)_2$ ($Cp' = C_5H_4CH_3$) [5]. We now present the results of a study of oxidative additions of XCN (X = Br, I) to the complexes Cp'Co(CO)L (L = CO, PPh_3, TCNE) and Cp'Co(PPh_3)TCNE (TCNE = tetracyanoethylene), in order to study the influence of a σ-donor (PPh_3) and a strong π-acceptor (TCNE) ligand on the reactivity; TCNE is known to be a stronger π-acceptor ligand than carbonyl [6].

Discussion of results

Addition of ethereal solutions of XCN (X = Br, I) to solutions of $Cp'Co(CO)_2$ and Cp'Co(CO)PPh_3 in the same solvent, under N_2, results in loss of CO and precipitation of solids of the stoichiometry Cp'Co(CO)(CN)X or Cp'Co(PPh_3)(CN)X.

The complexes Cp'Co(L)TCNE (L = CO, PPh_3) were made by reaction of Cp'Co(CO)L with TCNE in benzene solution. After addition of a solution of XCN (X = Br, I) in ether to a suspension of Cp'Co(L)TCNE (L = CO, PPh_3) in the same solvent followed by a period at room temperature or under reflux, the starting complexes were recovered unchanged, showing that oxidative addition to Cp'Co(L)TCNE (L = CO, PPh_3) does not occur.

The IR data for the isolated compounds are listed in Tables 1 and 2.

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TABLE 1

IR SPECTRAL DATA (cm^{-1}) (R = $C_5H_4CH_3$)

$RCo(CO)_2$	$RCo(CO)(CN)Br$	$RCo(CO)(CN)I$	$RCo(CO)TCNE$	Assignment
	2154 s	2173 vs	2221,2175 vs	$\nu(CN)$
2022,1957 vs	2104 s	2116 s	2070 vs	$\nu(CO)$
471 m	480 w	477 w	477 m	$\nu(Co-CO)$
410 w	420 w	419 w	419 m	$\nu(Co-CN)$ $\delta(Co-CO)$
	400 m	398 m	390 w	$\delta(Co-CN)$
	354 m	352 m		$\nu(Co-Olefin)$
	266 m			$\nu(Co-Br)$

In all cases the IR spectrum displays, in the 4000–200 cm^{-1} range, the characteristic bands of the methylcyclopentadiene ligand with C_s symmetry [7,8]. The range of the $\nu(CN)$ and $\nu(CO)$ bands is typical of terminal ligands [9]. The $\nu(CN)$ vibration frequency is higher for the carbonyl complexes than for the analogous triphenylphospine derivatives. This is in agreement with the greater donor capacity of the triphenylphosphine, which leads to an increase in the π-back bonding Co → CN.

The spectra of the triphenylphosphine derivatives display bands at ca. 1120, 725 and 445 cm^{-1} which can be assigned to $\nu_1(PC)$, $\nu_2(PC)$ and $\nu_3(PC)$, respectively. These bands are at higher frequencies than those from the free PPh_3 as a result of coordination to the metal [10]. The bands corresponding to $\nu(Co-CO)$, $\nu(Co-CN)$ and to the deformations of these bonds appear in the 480–350 cm^{-1} range [9]. The spectra of $Cp'Co(L)(CN)Br$ (L = CO, PPh_3) show bands at 266 and 260 cm^{-1}, respectively, which are ascribed to $\nu(Co-Br)$ vibration.

In the complexes $Cp'Co(CO)TCNE$ and $Cp'Co(PPh_3)TCNE$ bonding of the TCNE to the cobalt through a nitrogen atom is ruled out because the $\nu(CN)$ frequencies (2221, 2175 and 2218, 2160 cm^{-1}, respectively) are lower than those in TCNE itself (2257, 2220 cm^{-1}). In nitrile complexes there is usually an increase in the $\nu(CN)$ frequency relative to that for the uncoordinated nitrile [11]. Furthermore, the $\nu(CO)$ frequency (2070 cm^{-1}) in $Cp'Co(CO)TCNE$ is higher than for the

TABLE 2

IR SPECTRAL DATA (cm^{-1}) (R = $C_5H_4CH_3$)

$RCo(CO)PPh_3$	$RCo(PPh_3)(CN)Br$	$RCo(PPh_3)(CN)I$	$RCo(PPh_3)TCNE$	Assignment
	2146 s	2140s	2218,2160 vs	$\nu(CN)$
1929,1914 vs				$\nu(CO)$
1127 m	1120 vs	1121 vs	1120 s	$\nu_1(PC)$
719 vs	725 vs	723 s	725 s	$\nu_2(PC)$
445 m	445 w	445 w		$\nu_3(PC)$
400 m	468 vw	470 w	476 w,br	$\nu(Co-CO)$ $\nu(Co-CN)$
	458 w	458 w		$\delta(Co-CO)$
375 w	370 w	375 w	388 w	$\delta(Co-CN)$
355 m				$\nu(Co-olefin)$
	260 w			$\nu(Co-Br)$

TABLE 3

IR ν(CO) FREQUENCIES (cm^{-1}) (R = $C_5H_4CH_3$)

	$RCo(CO)_2$	$RCo(CO)PPh_3$	RCo(CO)TCNE
Solid	2022 vs(B_1),1957vs(A_1)	1929vs,1914vs(A′)	2070vs (A′)
$CHCl_3$	2021 vs(B_1), 1956vs(A_1)	1914 vs(A′)	2076vs (A′)
CH_3CN	2018 vs(B_1),1953 vs(A_1)	1916 vs(A′)	

$Cp'Co(CO)_2$ (ν(CO): 2022, 1957 cm^{-1}), indicating that the coordinated TCNE is a stronger π-acceptor ligand than carbonyl. The ν(C=C) vibration frequency which should be lower than that of free TCNE (1570 cm^{-1}) [12], is not observed in the spectra of these complexes, probably because it would be weak in the IR and may be masked by methylcyclopentadiene ligand vibrations. The fact that these compounds were not oxidised by XCN (X = Br, I) indicates that they are markedly stabilized by the TCNE owing to its strong π-acceptor capacity.

The IR spectra of the complexes Cp′Co(CO)L (L = CO, PPh_3 and TCNE) were recorded with $CHCl_3$ and CH_3CN solutions, in order to study the influence of the solvent on the ν(CO) frequency (Table 3). As can be seen, the value of ν(CO) is not influenced by the solvent polarity and is lowered as the acidic character of the ligand L decreases (TCNE > CO > PPh_3). The observed bands are consistent with those expected from group theory, C_{2v} symmetry for $Cp'Co(CO)_2$ and C_s symmetry for Cp′Co(CO)L (L = PPh_3, TCNE) (local symmetry). The two bands observed for the complex $Cp'Co(CO)PPh_3$ in the solid state can be attributed to lattice distortions.

The ^1H NMR spectra were obtained for $CDCl_3$ solutions, and assignments were made on basis of an AA′BB′ system, in agreement with literature data [13]. The spectrum could not be obtained for the complex Cp′Co(CO)ICN because it decomposes in solution.

Experimental

All the isolated complexes are hygroscopic. The reactions were carried out under oxygen-free N_2. The $Cp'Co(CO)_2$ [14], $Cp'Co(CO)PPh_3$ [13], and the pseudohalogens XCN (X = Br, I) [15] were prepared by published procedures.

The cobalt was determined by titration of the Co-EDTA complex in the presence of Eriochrome Black T as indicator. The C, H and N analyses were performed with a conventional microanalyzer.

The IR spectra were recorded in the range 4000–200 cm^{-1} on a Nicolet 5 DX spectrometer using Nujol and hexachlorobutadiene mulls between CsI windows. ^1H NMR spectra were recorded on a Bruker WM-200-SY spectrometer.

Preparation of Cp′Co(CO)(CN)Br

The complex $Cp'Co(CO)_2$ (1 g, 5.2 mmol) was dissolved in Et_2O (30 cm^3) saturated with oxygen-free N_2 contained in a 100 ml two-neck flask fitted with an N_2 inlet, magnetic stirrer and pressure-equalizing dropping funnel. A solution of BrCN (0.55 g, 5.2 mmol) in Et_2O (10 cm^3) was slowly added dropwise. A dark green solid inmediately appeared, and CO was evolved. The solid was filtered off, washed with Et_2O, and dried in vacuum. The yield was 1.25 g (90%). (Found: C, 37.50; H, 2.65;

N, 5.02; Co, 21.55; Br, 28.98. $C_8H_7CoNOBr$ calcd.: C, 37.89; H, 2.57; N, 5.15; Co, 21.67; Br, 29.39%). ^1H NMR ($CDCl_3$): δ 1.6 (s, CH_3); 3.9 (m, AA′ of AA′BB′); 5.35 (m, BB′ of AA′BB′) ppm.

Preparation of Cp′Co(CO)(CN)I

The procedure described above was used but starting with solutions of $Cp'Co(CO)_2$ (1 g, 5.2 mmol) in Et_2O (30 cm^3) and ICN (0.78 g, 5.2 mmol) in Et_2O (10 cm^3). A dark brown solid was obtained. The yield was 1.55 g (95%). (Found: C, 29.85; H, 2.30; N, 4.30; Co, 18.40; I, 39.20. C_8H_7CoNOI calcd.: C, 30.11; H, 2.19; N, 4.39; Co, 18.48; I, 39.80%).

Preparation of Cp′Co(PPh$_3$)(CN)Br

On mixing solutions of $Cp'Co(CO)PPh_3$ (1 g, 2.3 mmol) in Et_2O (40 cm^3) and BrCN (0.25 g, 2.3 mmol) in Et_2O (5 cm^3) a dark green solid was obtained. The yield was 1.05 g (90%). (Found: C, 58.60; H, 4.42; N, 2.68; Co, 11.50; Br, 15.30. $C_{25}H_{22}CoNPBr$ calcd.: C, 59.32; H, 4.34; N, 2.76; Co, 11.65; Br, 15.79%). ^1H NMR ($CDCl_3$): δ 2.17 (d, CH_3); 4.15 (m, AA′ of AA′BB′); 4.92 (m, BB′ of AA′BB′); 7.46 (m, *m*- and *p*-H in C_6H_5); 7.97 (m, *o*-H of C_6H_5) ppm.

Preparation of Cp′Co(PPh$_3$)(CN)I

A similar procedure starting from $Cp'Co(CO)PPh_3$ (1 g, 2.3 mmol) and ICN (0.35 g, 2.3 mmol) in Et_2O gave a dark brown solid. The yield was 1.15 g (90%). (Found: C, 53.40; H, 4.10; N, 2.45; Co, 10.58; I, 22.20. $C_{25}H_{22}CoNPI$ calcd.: C, 54.25; H, 3.97; N, 2.53; Co, 10.65; I, 22.95%). ^1H NMR ($CDCl_3$): δ 1.95 (m, CH_3); 4.13–5.4 (m, br, AA′BB′); 7.40 (m, *m*- and *p*-H in C_6H_5); 7.58 (m, *o*-H of C_6H_5) ppm.

Preparation of Cp′Co(CO)TCNE

On mixing solutions of $Cp'Co(CO)_2$ (1 g, 5.2 mmol) in benzene (20 cm^3) and tetracyanoethylene (0.62 g, 5.5 mmol) in the same solvent (25 cm^3) a brown-reddish solid immediately separated and CO was evolved. The solid was filtered off, washed with hexane, and dried in vacuum. The yield was 1.35 g (90%). (Found: C, 54.85; H, 2.50; N, 18.95; Co, 19.98. $C_{13}H_7CoON_4$ calcd.: C, 53.07; H, 2.38; N, 19.05; Co, 20.04%). ^1H NMR ($CDCl_3$): δ 1.68 (d, CH_3); 4.2 (m, AA′ of AA′BB′); 4.7 (m, BB′ of AA′BB′) ppm.

Preparation of Cp′Co(PPh$_3$)TCNE

A similar procedure starting from $Cp'Co(CO)(PPh_3)$ (1 g, 2.3 mmol) and tetracyanoethylene (0.28 g, 2.5 mmol) in benzene solution gave a brown solid. The yield was 1.10 g (90%). (Found: C, 67.35; H, 4.22; N, 10.45; Co, 11.08. $C_{30}H_{22}CoON_4P$ calcd.: C, 68.19; H, 4.16; N, 10.6; Co, 11.16%). ^1H NMR ($CDCl_3$): δ 2.05 (d,CH_3); 4.0–5.2 (m,br, AA′BB′); 7.36 (m, *m*- and *p*-H in C_6H_5); 7.55 (m, *o*-H of C_6H_5) ppm.

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