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OXIDATIVE ADDITION REACTIONS OF PSEUDOHALOGENS TO (η^5-C_5Me_5)CoL_2 (L = CO OR C_2H_4)

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Summary

The oxidative addition of the pseudohalogens $(SCN)_2$ and $S(CN)_2$ to the complexes (η^5-C_5Me_5)CoL_2 (L = CO or C_2H_4) give the complexes (η^5-C_5Me_5)-Co(L)$(NCS)_2$ and (η^5-C_5Me_5)Co(L)(NCS)(CN), respectively. All of the compounds have been characterized by elemental analysis and IR, electronic and ^{1}H NMR spectroscopy.

Introduction

Following the previous study on oxidative addition reactions of pseudohalogenes to dicarbonylpentamethylcyclopentadienylcobalt, (η^5-C_5Me_5)$Co(CO)_2$ [1,2], we compare here the reactivity of this complex towards the pseudohalogens $(SCN)_2$ and $S(CN)_2$, with that for the di(ethylene)pentamethylcyclopentadienylcobalt, (η^5-C_5Me_5)$Co(C_2H_4)_2$, in order to study the influence of the metal–olefin bond on the reactivity. In all cases the oxidation of cobalt(I) to cobalt(III) and the elimination of a carbonyl or ethylene ligand, respectively, take place.

The complex (η^5-C_5Me_5)$Co(C_2H_4)_2$ has been synthesized recently and the ethylene ligands are more labile in displacement reactions with neutral ligands such as PPh_3, C_8H_8, C_8H_{12} and acetylenes (RC_2R') [3], than the carbonyl ones in (η^5-C_5Me_5)$Co(CO)_2$.

The reactions reported in this paper are the first reported oxidative additions involving (η^5-C_5Me_5)$Co(C_2H_4)_2$.

Results and discussion

The mixing of ethereal solutions of $(SCN)_2$ or $S(CN)_2$ and (η^5-C_5Me_5)CoL_2 (L = CO, C_2H_4) gives rise to the loss of CO and C_2H_4 respectively, and the precipitation of solids with the stoichiometry: (η^5-C_5Me_5)Co(L)X(NCS) (L = CO, C_2H_4; X = CN or NCS). The compounds are very hygroscopic and fairly soluble in

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TABLE 1 [a]

IR SPECTRAL DATA FOR THE COMPLEXES

$RCo(CO)_2$-$(NCS)_2$	$RCo(CO)$-$(CN)(NCS)$	$RCo(C_2H_4)$-$(NCS)_2$	$RCo(C_2H_4)$-$(CN)(NCS)$	Assignments
2140vs (1.9)	2149vs	2149s (2.0)	2148vs	$\nu(CN)$ of (CN) and (NCS)
		2097vs,sh		
2101vs (2.2)	2104vs (2.3)		2100s (2.1)	
		2069vs (2.1)		
2060vs	2064vs			$\nu(CO)$
		1480w	1490w	$\nu(C{=}C)\ (C_2H_4)$
474m	475m	475m	470m	$\nu(Co{-}C_2H_4)$
449w	456w		421vw	$\nu(Co{-}CO)$
	417w			$\nu(Co{-}CN)$
398vw		389vw	377w	$\delta(Co{-}CO)$
	355vw		360w	$\delta(Co{-}CN)$ and $\delta(NCS)$
321w	330m	323m	335w	ν(Co–ring)
277m	285m	273m	279m	$\nu(Co{-}NCS)$

[a] In cm^{-1}. $R = C_5Me_5$. The internal standard ratio determined by Bailey method is given in parentheses [6].

solvents such as CH_2Cl_2 and acetone. The ethylene compounds are more air-sensitive than the carbonyl ones.

In the IR spectra of the complexes (Table 1) the characteristic bands of the pentamethylcyclopentadiene ligand with C_{5v} symmetry can be observed [4,5]. The bands which correspond to terminal ν(CN) and the ν(CN) of NCS appear in the range 2149–2069 cm^{-1}. The determination of the internal standard ratio of ν(CN) of NCS bands by the Bailey method [6] indicates that in all the cases the NCS ligand is coordinated via the N atom. The range of stretching vibrations ν(CO) for $(\eta^5\text{-}C_5Me_5)Co(CO)X(NCS)$ (X = NCS or CN), is typical of terminal ligands [7].

In the spectrum of the complexes $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)X(NCS)$ (X = NCS or CN), a weak band is observed at 1480 and 1490 cm^{-1}, respectively, which can be assigned to the stretching vibration $\nu(C{=}C)$ of the ethylene, by comparison with other ethylene complexes [8,9]. This vibration, $\nu(C{=}C)$, in free ethylene appears at 1623 cm^{-1} (Raman). So, a shift to lower frequencies takes place as a result of the coordination to the metal. The vibrations $\delta(CH_2)$ and $\rho(CH_2)$ of the ethylene ligand are not observed because they are masked by the strong bands δ(CH) and γ(CH) of the pentamethylcyclopentadiene ring.

In all the complexes, the vibration ν(C–S) of the isothiocyanate ligands should be observed at ca. 800 cm^{-1} [10] but it also is masked by the strong band γ(CH) of the pentamethylcyclopentadiene ligand.

The bands which appear in the range 475–355 cm^{-1} correspond to ν(Co–CO), ν(Co–CN) and the deformations of these bands, together with the vibrations $\nu(Co{-}C_2H_4)$ [8] and δ(NCS) [10]. Finally, the vibration ν(Co–NCS) is observed in the range 285–273 cm^{-1}.

The electronic spectra of the complexes in dichlormethane solution are given in Table 2. Each spectrum displays a broad band in the range 16393–20242 cm^{-1} due to *d–d* transitions and a very intense peak in the vicinity of 30000 cm^{-1} due to

TABLE 2 [a]

ELECTRONIC SPECTRA OF THE COMPLEXES

$RCo(CO)(NCS)_2$	$RCo(CO)(CN)(NCS)$	$RCo(C_2H_4)(NCS)_2$	$RCo(C_2H_4)(CN)(NCS)$	Assignments
16501br	16611sh	16393br	16501br	*d–d*
16949sh		17064sh	17241sh	
	20242br			
29411	29585	30303	30674	Charge transfer
34246				

[a] In cm^{-1}; CH_2Cl_2 solution; R = C_5Me_5.

charge transfer transitions from the metal to the π^* orbital of CO, CN or NCS.

If we assume the complexes to be octahedral, the simultaneous presence of L (L = CO or C_2H_4), CN and NCS ligands reduces the symmetry to C_{2v} or C_s. In this way the triply-degenerate t_{2g} are split into the components e and b_2 and the double degenerate e_g orbitals are split into a_1 and b_1, as previously observed in the photoelectronic spectra of carbonylcyclopentadienyl complexes of C_{2v} symmetry [11,12]. For C_s symmetry a greater splitting can be expected, with the subsequent increase in the width of the absorption bands. This effect is reflected in the electronic spectra. In the complexes containing a cyanide and a thiocyanate ligand, *d–d* transitions occur at higher energies than in those containing two thiocyanate ligands, which is in agreement with the spectrochemical series: CN > NCS > SCN.

The ^1H NMR spectra of the complexes (η^5-C_5Me_5)Co(CO)X(NCS) (X = NCS or CN) display a single signal which can be attributed to the 15 equivalent protons of the 5 methyl groups substituted in the ring. This single signal is also observed in the spectra of the complexes (η^5-C_5Me_5)Co(C_2H_4)X(NCS) (X = NCS or CN) together with a multiplet, assignable to the protons of the ethylene ligand, in a range which is in accord with that observed in other cyclopentadienyl(olefin)metal complexes [3,13].

Experimental

All the reactions were carried out under oxygen-free N_2. The pentamethylcyclopentadiene [14], (η^5-C_5Me_5)Co$(CO)_2$ [15,16], (η^5-C_5Me_5)Co(C_2H_4) [3] and the pseudohalogens $(SCN)_2$ [17] and $S(CN)_2$ [18] 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). Cobalt was determined volumetrically.

The IR spectra were recorded in the range 4000–200 cm^{-1} on a Nicolet DX, using Nujol and Hostaflon mulls between CsI windows. ^1H NMR spectra were recorded on a Bruker WM-200-SY. The visible spectra were recorded on a Pye Unicam SP8-100 ultraviolet spectrophotometer.

Preparation of (η^5-C_5Me_5)Co(CO)$(NCS)_2$

In a 100 ml two-neck flask fitted with an N_2 inlet, magnetic stirrer and pressure-equalized dropping funnel, η^5-C_5Me_5Co$(CO)_2$ (1.5 g, 6 mmol) is dissolved in Et_2O (30 cm^3) saturated with oxygen-free N_2 and cooled to −20 °C. A solution of $(SCN)_2$ (0.70 g, 6 mmol), freshly obtained, in Et_2O (20 cm^3) is slowly added dropwise. A green solid immediately appears, and evolution of CO is observed. The solid is filtered off on a cooled sintered glass disc (−20 °C), washed several times with cooled Et_2O and dried in vacuum. The yield is 1.75 g (85%). Found: C, 45.78; H, 4.38; N, 8.33; Co, 17.47. $C_{13}H_{15}CoON_2S_2$ calcd.: C, 46.16; H, 4.43; N, 8.28; Co, 17.43%. ^1H NMR ($CDCl_3$): δ 1.52 (15H, C_5Me_5) ppm.

Preparation of (η^5-C_5Me_5)Co(CO)(CN)(NCS)

Following the procedure described above, solutions of η^5-$C_5Me_5Co(CO)_2$ (1.5 g, 6 mmol) in Et_2O (30 cm^3) and $S(CN)_2$ (0.52 g, 6 mmol) in Et_2O (25 cm^3) are mixed. A reddish solid is obtained. The yield is 1.39 g (75%). Found: C, 49.93; H, 4.98; N, 8.95; Co, 19.20. $C_{13}H_{15}CoON_2S$ calcd.: C, 50.99; H, 4.90; N, 9.15; Co, 19.26%. ^1H NMR ($CDCl_3$): δ 1.54 (15H, C_5Me_5) ppm.

Preparation of (η^5-C_5Me_5)Co(C_2H_4)$(NCS)_2$

Following the procedure described above for $C_5Me_5Co(CO)(NCS)_2$, solutions of $C_5Me_5Co(C_2H_4)$ (1.5 g, 6 mmol) in light petroleum (65–70 °C) (40 cm^3) and $(SCN)_2$ (0.69 g, 6 mmol) in Et_2O (20 cm^3) were mixed. A green solid is obtained and evolution of C_2H_4 is observed. The yield is 1.60 g (80%). Found: C, 48.93; H, 5.80; N, 8.12; Co, 17.39. $C_{14}H_{19}CoN_2S_2$ calcd.: C, 49.71; H, 5.62; N, 8.28; Co, 17.43%. ^1H NMR ($CDCl_3$): δ 1.59 (15H, C_5Me_5), 1.30 (4H, C_2H_4) ppm.

Preparation of (η^5-C_5Me_5)Co(C_2H_4)(CN)(NCS)

Following the procedure described above for $C_5Me_5Co(CO)(CN)(NCS)$, solutions of $C_5Me_5Co(C_2H_4)_2$ (1.5 g, 6 mmol) in light petroleum (65–70 °C) (40 cm^3) and $S(CN)_2$ (0.50 g, 6 mmol) in Et_2O (25 cm^3) are mixed. A deep green solid is obtained. The yield is 1.37 g (75%). Found: C, 54.01; H, 6.40; N, 9.05; Co, 19.29. $C_{14}H_{19}CoN_2S_2$ calcd.: C, 54.91; H, 6.21; N, 9.15; Co, 19.26%. ^1H NMR ($CDCl_3$): δ 1.55 (15H, C_5Me_5), 1.21 (4H, C_2H_4) ppm.

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