Reactions of (η-C₅H₅)Co(CO)₂ and (η-EtMe₄C₅)Co(CO)₂ with Iodine and Cyanogen Halides, XCN (X = Br OR I)

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Cyanogen Halides

The title compounds react with iodine to give the iodinecarbonyl complexes (η-C₅H₅)Co(CO)ICO₂ and (η-EtMe₄C₅)Co(CO)ICO₂. The reactions of the same compounds with the cyanogen halides XCN (X = Br or I) give rise to the formation of mixed cyanocarbonylhalogenated complexes (η-C₅H₅)Co(CO)(CN)ICO₂ and (η-EtMe₄C₅)Co(CO)(CN)ICO₂ (X = Br or I) respectively. The compounds have been characterized by elemental analyses and IR and HNMR spectra.

Introduction

We have recently showed that the oxidative addition of pseudohalogen to coordinatively unsaturated organometallic compounds gives rise to the formation of the corresponding pseudohalogen derivatives with excellent yields. In other similar reactions with organometallic carbonyls, the pseudohalogen ligands rapidly displace the carbonyl groups [1, 2]. Having these facts in mind, we have studied the reactions of (η-C₅H₅)Co(CO)ICO₂ and the analogous ethyltetramethylcyclopentadiene complex with I₂ and the cyanogen halides XCN (X = Br or I).

The study of the reactions of the complexes of the substituted cyclopentadienyls is currently receiving considerable attention [3, 4], due in part to the fact that these complexes are generally more soluble than their unsubstituted analogs, and also because the electron-donating power of five alkyl groups to the cyclopentadienyl ring can cause interesting differences between the properties of the metal peralkylcyclopentadienyls and those of their non-substituted analogs.

Results and Discussion

The mixed cyanocarbonylhalogenated complexes (η-C₅H₅)Co(CO)(CN)ICO₂ (X = Br or I) are easily obtained by mixing ethereal solutions of XCN (X = Br or I) and cyclopentadienylidicarbonylcobalt. These complexes are related to the dihalogenocarbonyls, (η-C₅H₅)Co(CO)ICO₂ (X = Cl, Br and I) described by Heck [5] and King [6]. The reactions of (η-EtMe₄C₅)Co(CO)ICO₂ with I₂ in ether occurs in a similar way to the one previously described for the analogue (η-Me₅C₅)Co(CO)ICO₂ [7], giving black crystals of the new (η-EtMe₄C₅)Co(CO)ICO₂.

The mixed complexes (η-EtMe₄C₅)Co(CO)(CN)ICO₂ (X = Br or I) are obtained in the reactions of (η-EtMe₄C₅)Co(CO)ICO₂ with XCN (X = Br or I) in a similar way to the one already described for the compounds of non-substituted cyclopentadienyl.

The solubility of the synthesized complexes of ethyltetramethylcyclopentadiene is higher than that of the similar compounds of non-substituted cyclopentadienyl in solvents such as chloroform, acetone or nitrobenzene, but they are only slightly soluble in ether or saturated hydrocarbons. The monomeric nature of the complexes has been confirmed by the molecular weight in nitrobenzene.

In the IR spectra of the complexes the characteristic bands of the cyclopentadienyl ligands (see Experimental) with Cᵥ symmetry [8, 9] appear. In Table I the bands corresponding to the cyanide and carbonyl ligands are reported and also those which correspond to the metal-ligand bonds. The range of the stretching vibrations v(CN) and v(CO) is characteristic of terminal ligands [10]. The electron-donating capacity of the ligand ethyltetramethylcyclopentadienyl is reflected in the values of v(CO) which are smaller than in the corresponding complexes of non-substituted cyclopentadienyl as in shown in Table I. For both η-C₅H₅ and η-EtMe₄C₅ complexes it is observed that the frequency of v(CO) increases going from η-C₅H₅Co(CO)ICO₂ to η-C₅H₅Co(CO)(CN)ICO₂ (X = Br or I), which can be explained due to the decreasing of the symmetry or to the π-acceptor ability of the cyanide. In the range

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Table I. ν(CN), ν(CO) and far IR spectra of the complexes.

<table>
<thead>
<tr>
<th>RCo(CO)I₂</th>
<th>RCo(CO)(CN)I</th>
<th>RCo(CO)(CN)Br</th>
<th>R'Co(CO)I₂</th>
<th>R'Co(CO)(CN)I</th>
<th>R'Co(CO)(CN)Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>2120 vs b</td>
<td>2128 vs b</td>
<td>2130 s b</td>
<td>2132 vs b</td>
<td>2135 s b</td>
<td>2130 vs b</td>
</tr>
<tr>
<td>(2115 vs)c</td>
<td>(2125 vs)c</td>
<td></td>
<td></td>
<td>(2125 vs)c</td>
<td></td>
</tr>
<tr>
<td>2062 vs b</td>
<td>2095 s b</td>
<td>2093 s b</td>
<td>2036 vs b</td>
<td>2052 vs b</td>
<td>2050 vs b</td>
</tr>
<tr>
<td>(2060 vs)c</td>
<td>(2088 s)c</td>
<td></td>
<td></td>
<td>(2088 s)c</td>
<td></td>
</tr>
<tr>
<td>575 w</td>
<td>578 w</td>
<td>578 w</td>
<td>510 s</td>
<td>515 w</td>
<td>510 w</td>
</tr>
<tr>
<td>492 s</td>
<td>470 w</td>
<td>485 w</td>
<td>510 s</td>
<td>494 w</td>
<td>490 s</td>
</tr>
<tr>
<td>463 s</td>
<td>442 m</td>
<td>460 m</td>
<td>440 w</td>
<td>438 m</td>
<td>462 s</td>
</tr>
<tr>
<td>350 m</td>
<td>365 m</td>
<td>360 m</td>
<td>346 m</td>
<td>330 m</td>
<td>415 w</td>
</tr>
<tr>
<td>192 m</td>
<td>170 m</td>
<td></td>
<td>187 m</td>
<td>168 m</td>
<td>252 m</td>
</tr>
<tr>
<td>176 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a R = η-CsH₅; R' = η-EtMe₄C₅; b in Nujol; c in CH₂Cl₂.

500–400 cm⁻¹ appear the bands corresponding to ν(CoCN) and ν(CoCO) and also those of the deformation vibrations of these bonds [10].

The bands corresponding to ν(CoI) appear in the range of 190–170 cm⁻¹ and ν(CoBr) in 250–240 cm⁻¹ in good agreement with the known relation ν(MI)/ν(MBr) = 0.83 [12] for terminal metal-halogen bonds.

All the synthesized compounds are diamagnetic.

The ¹H NMR spectra of the complexes η-CsH₅Co(CO)(CN)X (X = Br or I) consists of only one signal in the vicinity of 5 δ, which corresponds to the five equivalent protons of the cyclopentadienyl ring. This shift is in agreement with the one observed for other cyclopentadienyl cyanide cobalt(III) complexes [13]. However, the ¹H NMR spectra of the η-EtMe₄C₅ complexes are much more complicated, due to the lower symmetry of this ligand in comparison with η-CsH₅. If we assume that these molecules have the “piano stool” symmetry, adopted by the complexes which have only one aromatic ligand bonded in “sandwich” form [14], in the compounds with two equivalent ligands the molecule will have a symmetry plane. Hence the methylene protons of the ethyl group will be equivalent methyl groups, as is observed in the spectrum of (η-EtMe₄C₅)Co(CO)I₂ (Table II). In contrast, for molecules with no symmetry plane the spectrum will be more complicated, as in the case of complexes (η-EtMe₄C₅)Co(CO)(CN)X (X = Br or I) where it is seen that there are four non equivalent methyl substituents in the rings, and also the methylene protons (C(H₃), H₅) are not equivalent.

Experimental

All reactions were carried under oxygen-free N₂. Ethyltetramethylcyclopentadiene [15], η-CsH₅Co(CO)₂ [16], η-EtMe₄Co(CO)(CN)Br [3] and the cyanogen halides XCO (X = Br or I) [17] were prepared by the published procedures. Micro-

Table II. ¹H NMR spectra of the complexes.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>δ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>η-CsH₅Co(CO)I₂</td>
<td>5.65 s</td>
</tr>
<tr>
<td>η-CsH₅Co(CO)(CN)I</td>
<td>5.87 s</td>
</tr>
<tr>
<td>η-CsH₅Co(CO)(CN)Br</td>
<td>5.86 s</td>
</tr>
<tr>
<td>η-EtMe₄C₅Co(CO)I₂</td>
<td>CH₂–CH₃ 1.12 t (3H) (J = 6.8 Hz)</td>
</tr>
<tr>
<td>η-EtMe₄C₅Co(CO)(CN)I</td>
<td>CH₂–CH₃ 1.05 t (3H) (J = 7.2 Hz)</td>
</tr>
<tr>
<td>η-EtMe₄C₅Co(CO)(CN)Br</td>
<td>CH₂–CH₃ 1.05 t (3H) (J = 7.2 Hz)</td>
</tr>
</tbody>
</table>

a In CDCl₃.
analyses were performed by the Centro Nacional de Química Orgánica (Madrid-Spain). The cobalt was determined gravimetrically. The IR spectra were recorded in the range 4000-140 cm⁻¹ on a Perkin-Elmer model 180, using Nujol and Hostafon mulls between CsI and polyethylene windows. ¹H NMR spectra were recorded on a Varian Model XL-100/15.

Preparation of \( \eta^5\)-C\(_5\)H\(_5\)Co(CO)\(_2\)Br

This compound was prepared by the published procedure [6]. (Found: C 16.9; H 1.0; Co 13.8; M (cryoscopically in nitrobenzene): 230. C\(_{13}\)H\(_{17}\)NOICo Calcd.: C 32.5; H 1.9; N 5.4; Co 22.0; M 406.)

Preparation of \( \eta^5\)-C\(_5\)H\(_5\)Co(CO)\(_2\)I

In a two-neck flask (100 cm³) fitted with N\(_2\) inlet, magnetic stirrer and pressure equalized dropping funnel, \( \eta^5\)-C\(_5\)H\(_5\)Co(CO)\(_2\) (1.8 g, 10 mmole) was dissolved in Et\(_2\)O (30 cm³) saturated with oxygen-free N\(_2\). A solution of BrCN (1 g, 10 mmole) in Et\(_2\)O (10 cm³) was slowly added dropwise. A brown solid immediately appeared, and evolution of CO was observed. The solid was filtered off, washed several times with Et\(_2\)O and dried in vacuum. The yield is 2.5 g (97%). (Found: C 31.9; H 1.7; N 5.0; Co 22.0; M (cryoscopically in nitrobenzene): 230. C\(_{13}\)H\(_{17}\)NOBrCo Calcd.: C 32.5; H 1.9; N 5.4; Co 22.8%; M 256.)

Preparation of \( \eta^5\)-C\(_5\)H\(_5\)Co(CO)(CN)I

Following the procedure described above, solutions of \( \eta^5\)-C\(_5\)H\(_5\)Co(CO)\(_2\) (1.8 g, 10 mmole) in Et\(_2\)O (30 cm³) and ICN (1.5 g, 10 mmole) in Et\(_2\)O (10 cm³) were mixed. A brown solid was obtained. The yield is 3.3 g (97%). (Found: C 26.8; H 1.2; N 4.1; Co 18.9; M (cryoscopically in nitrobenzene): 278. C\(_{13}\)H\(_{17}\)NOICO: C 27.5; H 1.6; N 4.5; Co 19.3%; M 305.)

Preparation of \( \eta^5\)-EtMe\(_4\)C\(_5\)Co(CO)I\(_2\)

A similar procedure was used with \( \eta^5\)-EtMe\(_4\)C\(_5\)Co(CO)\(_2\) (2.6 g, 10 mmole) in Et\(_2\)O (30 cm³) and I\(_2\) (2.5 g, 10 mmole) in Et\(_2\)O (20 cm³). A black crystalline solid appeared immediately. The yield is 4.8 g (98%). (Found: C 28.7; H 3.0; Co 11.7; M (cryoscopically in nitrobenzene): 460. C\(_{12}\)H\(_{17}\)OICo Calcd.: C 29.4; H 3.4; Co 12.0%; M 490.)

Preparation of \( \eta^5\)-EtMe\(_4\)C\(_5\)Co(CO)(CN)I

Using BrCN (1.1 g, 10 mmole) in Et\(_2\)O (10 cm³) and \( \eta^5\)-EtMe\(_4\)C\(_5\)Co(CO)\(_2\) (2.6 g, 10 mmole) in Et\(_2\)O (30 cm³) a green solid immediately precipitated with quantitative yield. (Found: C 44.8; H 4.3; N 3.8; Co 16.8; M (cryoscopically in nitrobenzene): 310. C\(_{12}\)H\(_{17}\)NOBrCo Calcd.: C 45.6; H 4.9; N 4.1; Co 17.2; M 342.)

Preparation of \( \eta^5\)-EtMe\(_4\)C\(_5\)Co(CO)(CN)I

Similarly ICN (1.5 g, 10 mmole) in Et\(_2\)O (10 cm³) and \( \eta^5\)-EtMe\(_4\)C\(_5\)Co(CO)\(_2\) (2.6 g, 10 mmole) in Et\(_2\)O (30 cm³) five a brown solid with quantitative yield. (Found: C 39.5; H 4.0; N 3.1; Co 14.8; M (cryoscopically in nitrobenzene): 368. C\(_{12}\)H\(_{17}\)NOICO Calcd.: C 40.1; H 4.3; N 3.6; Co 15.1%; M 389.)

We thank Dr. Jay A. Labinger the helpful discussions.