REATIONS OF MONOCYCLOPENTADIENYLCOBALT CATIONS WITH NUCLEOPHILES

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Summary

The reactions of [Co(η-C₅H₅)(PMe₃)₃][PF₆]₂ with the nucleophiles Y⁻ = CN⁻, N₃⁻, MeO⁻, H²⁺, NO₂⁻ have been investigated. Only for Y⁻ = CN⁻ or N₃⁻ were crystalline products [Co(η-C₅H₅)(PMe₃)₂Y][PF₆] (Y⁻ = CN⁻, N₃⁻) and Co(η-C₅H₅)(PMe₃)(CN)₂ isolated. MeO⁻ and H⁺ gave untractable products and with NO₂⁻ no reaction was observed. Reaction of Co(η-C₅H₅)(CO)I₂ with PE₃ in the stoichiometry 1 : 1, 1 : 2 or 1 : 3 gave the complexes Co(η-C₅H₅)(PE₃)I₂, [Co(η-C₅H₅)(PE₃)₂I]I and a mixture of Co(PE₃)₂(CO)I and Co(PE₃)₂I₂, respectively.

Introduction

Organotransition metal cations containing unsaturated hydrocarbon ligands undergo nucleophilic addition [1]. We were interested in nucleophilic addition to the cation [Co(η-C₅H₅)(PMe₃)₃]²⁺.

Results and discussion

The reaction of the salt [Co(η-C₅H₅)(PMe₃)₃][PF₆]₂ (I) [2], with an excess of KCN gave a crystalline yellow compound, which was characterised as the neutral compound Co(η-C₅H₅)(PMe₃)(CN)₂ (II). Similar cyanide complexes have been described previously [3]. When a stoichiometric amount of KCN is used the yellow crystalline salt [Co(η-C₅H₅)(PMe₃)₂CN][PF₆] (III) is obtained. In contrast, treatment of [Co(η-C₅H₅)(PMe₃)₃][PF₆]₂ (I) with an excess of KN₃ gave the monosubstituted species [Co(η-C₅H₅)(PMe₃)₂N₃][PF₆] (IV) as dark red crystals. It thus seems that treatment of [Co(η-C₅H₅)(PMe₃)₃][PF₆]₂ (I) with nucleophiles such as N₃⁻ and CN⁻ gives rise to ligand substitution, yielding mono- and di-substituted species of the types A and B. When an excess of Me⁻ is used, the disubstituted B species is obtained [4].
In an attempt to obtain the analogue of compound I by treatment of Co(η-C₅H₅)(CO)I₂ (V) [5], with PEr₃, we found that the reaction proceeded differently. Treatment of V with PEr₃ in the stoichiometries 1 : 1, 1 : 2 and 1 : 3 in fact gave the results shown below:

\[
\begin{align*}
1 : 1 \text{ PEr₃} & \rightarrow \text{Co(η-C₅H₅)(PEr₃)I₂} \\
(\text{VI}) \\
\text{Co(η-C₅H₅)(CO)I₂} & \rightarrow [\text{Co(η-C₅H₅)(PEr₃)₂}I] \\
(\text{V}) & \rightarrow [\text{Co(η-C₅H₅)(PEr₃)₂}I] \\
1 : 2 \text{ PEr₃} & \rightarrow \text{Co(PEr₃)₂I₂} + \text{Co(PEr₃)₃(CO)₂I} + [\text{PEr₃(C₅H₅)}]I \\
(\text{VII}) & \rightarrow (\text{VIII}) \\
1 : 3 \text{ PEr₃} & \rightarrow \text{Co(PEr₃)₂I₂} + \text{Co(PEr₃)₃(CO)₂I} + [\text{PEr₃(C₅H₅)}]I \\
(\text{VIII}) & \rightarrow (\text{IX}) \\
& \rightarrow (\text{X})
\end{align*}
\]

It is probable that the reactions proceeds through the sequence shown in Scheme 2.

The first mole of PEr₃ displaces the CO ligand, the second mole of PEr₃ displaces an iodo ligand to give the cationic species VII, while the third mole of PEr₃ adds nucleophilically the η-C₅H₅ ring to give the intermediate XI (which we were unable to isolate under the conditions employed), which decomposes to give the phosphonium salt which was isolated as the PF₆⁻ salt and a cobalt(I) moiety which in the presence of CO gives stable Co(PEr₃)₂(CO)₂I and partially disproportionates to Co(PEr₃)₂I₂ and a cobalt(0) residue not identified.
SCHEME 2

Experimental

All reactions and manipulations were carried out under nitrogen or in vacuum. All solvents were dried and distilled. The $^1$H NMR spectra (Table 1) were recorded using a Bruker (90 MHz) or a Varian (80 MHz) instrument. Microanalyses (Table 2) were determined with a Perkin-Elmer 240 B elemental analyser. Infrared spectra (Table 1) were recorded as KBr pellets on a Perkin-Elmer 589 infrared spectrophotometer.

<p>| TABLE 1 | SPECTROSCOPIC DATA |</p>
<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1$H NMR $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>II, Co(η-C₅H₅)(PMe₃)(CN)₂</td>
<td>d (J(3¹P−Me) 12.64), PMe₃; 8.18(9), d (J(3¹P−C₅H₅) 0.44), C₅H₅ $^b$</td>
</tr>
<tr>
<td>III, [Co(η-C₅H₅)(PMe₃)CN][PF₆]</td>
<td>8.38−8.05(18), s, PMe₃; 4.27(5), s, C₅H₅ $^b$</td>
</tr>
<tr>
<td>IV, [Co(η-C₅H₅)(PMe₃)₂N₃][PF₆]</td>
<td>8.33−8.10(18), q, PMe₃; 4.29(5), s, C₅H₅ $^b$</td>
</tr>
<tr>
<td>VI, Co(η-C₅H₅)(P(CH₂−CH₂−CH₃)₃)₂</td>
<td>8.76(9), d-t, CH₃; 7.85−7.48(6), s, CH₂ $^c$; 4.8(5), s, C₅H₅</td>
</tr>
<tr>
<td>XIX, [Co(η-C₅H₅)(P(CH₂−CH₃)₃)₂][PF₆]</td>
<td>8.9−8.6(18), s, CH₃; 7.8−7.55(12), s, CH₂ $^b$; 4.27(5), t(J(3¹P−C₅H₅) 0.6), C₅H₅</td>
</tr>
</tbody>
</table>

$^a$ Data presented as chemical shift ($ω$), relative intensity (in parentheses), multiplicity (J in Hz), assignment.
$^b$ In (CD₃)₂CO. $^c$ In CDCl₃. $^d$ ν(C−N) = 2120−2110 cm⁻¹. $^e$ ν(C−N) = 2120 cm⁻¹. $^f$ ν(N−N−N) = 2035 cm⁻¹.
TABLE 2
ANALYTICAL DATA

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Analysis found (calcd.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>II, Co(η-C₅H₅)(PMe₃)(CN)₂</td>
<td>Yellow</td>
<td>47.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(47.9)</td>
</tr>
<tr>
<td>III, [Co(η-C₅H₅)(PMe₃)₂CN][PF₆]</td>
<td>Yellow</td>
<td>32.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(32.9)</td>
</tr>
<tr>
<td>IV, [Co(η-C₅H₅)(PMe₃)₂N₃][PF₆]</td>
<td>Dark red</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(28.6)</td>
</tr>
<tr>
<td>VI, Co(η-C₅H₅)(PEt₃)I₂</td>
<td>Black</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(26.8)</td>
</tr>
<tr>
<td>VII, [Co(η-C₅H₅)(PEt₃)₂]I</td>
<td>Brown</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(33.35)</td>
</tr>
<tr>
<td>XII, [Co(η-C₅H₅)(PEt₃)₂][PF₆]</td>
<td>Brown</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(32.6)</td>
</tr>
</tbody>
</table>

_Cyano(η-cyclopentadienyl)bis(trimethylphosphine)cobalt hexafluorophosphate_

A suspension of [Co(η-C₅H₅)(PMe₃)₃][PF₆]₂ (0.34 g, 0.53 mmol) in tetrahydrofuran (20 cm³) was treated with KCN (0.036 g, 0.55 mmol) and then stirred for 30 min at room temperature. The mixture was stirred for 1 hour under reflux. The solvent was removed under reduced pressure and the yellow residue extracted with dichloromethane (5 × 20 cm³). The yellow extract was concentrated to give yellow crystals of [Co(η-C₅H₅)(PMe₃)₂(CN)][PF₆] (ca. 75%).

_Di(cyano)(η-cyclopentadienyl)(trimethylphosphine)cobalt_

A suspension of [Co(η-C₅H₅)(PMe₃)₃][PF₆]₂ (0.66 g, 1.03 mmol) in tetrahydrofuran was treated with KCN (0.15 g, 2.30 mmol) and then stirred for 12 hours at 60°C. The solution became light yellow. The solvent was removed under reduced pressure and the yellow residue was crystallised several times from ethanol/pentane and acetone/diethyl ether in order to remove K[PF₆]. Pure Co(η-C₅H₅)(PMe₃)(CN)₂ was finally obtained as yellow crystals (ca. 75%).

(Azido)(η-cyclopentadienyl)bis(trimethylphosphine)cobalt hexafluorophosphate

A suspension of [Co(η-C₅H₅)(PMe₃)₃][PF₆]₂ (0.55 g, 0.84 mmol) in tetrahydrofuran (30 cm³) was treated with NaN₃ (0.15 g, 2.70 mmol) and then stirred for 48 hours under reflux. The solution became brown. The solvent was removed under reduced pressure and the residue was washed with water and extracted with dichloromethane. Slow removal of dichloromethane under reduced pressure gave red-brown crystals of [Co(η-C₅H₅)(PMe₃)₂N₃][PF₆] (ca. 30%).

_Reaction of Co(η-C₅H₅)(CO)I₂ with PEt₃, 1 : 1_

A solution of Co(η-C₅H₅)(CO)I₂ (2.20 g, 5.40 mmol) in toluene (300 cm³) was treated with PEt₃ (0.80 cm³, 0.54 mmol). Gas evolution was observed. The
solvent was partly removed under reduced pressure. Evaporation gave black crystals of Co(η-C₅H₅)(PEt₃)I₂ (ca. 60%).

Reaction of Co(η-C₅H₅)(CO)I₂ with PEt₃ 1 : 2

A solution of Co(η-C₅H₅)(CO)I₂ (1.62 g, 4.00 mmol) in toluene (200 cm³) was cooled to ca. −20°C and then treated with PEt₃ (1.20, cm³, 0.96 g, 8.13 mmol) with stirring. Gas evolution was observed. A brown precipitate formed and the solution became yellow. The brown precipitate was filtered off, washed with toluene (4 × 20 cm³), and extracted with water (ca. 100 cm³) to give a yellow solution. Addition of [NH₄][PF₆] (1.50 g in 10 cm³) gave a yellow-brown precipitate. This was crystallised from acetone/diethyl ether to give black crystals of [Co(η-C₅H₅)(PEt₃)₂I][PF₆] (ca. 60%).

Reaction of Co(η-C₅H₅)(CO)I₂ with PEt₃, 1 : 3

A solution of Co(η-C₅H₅)(CO)I₂ (1.30 g, 3.20 mmol) in toluene (200 cm³) was treated with PEt₃ (2.50 cm³, 2.00 g, 16.9 mmol). The colour of the solution changed from the dark purple to yellow, and a pale yellow precipitate immediately separated. This was filtered off, and washed with toluene (3 × 20 cm³) becoming paler. The pale yellow precipitate was extracted with water, and addition of [NH₄][PF₆] (0.50 g in cm³) to the solution gave a white precipitate. This was crystallised from acetone/water to give white crystals and comparison of their analytical data, ¹H NMR, and IR spectra with those of an authentic sample showed them to be [(PEt₃)(C₅H₅)][PF₆] (ca. 35%). The yellow toluene solution was concentrated in vacuum to ca. 2 cm³ and water was added. A yellow crystalline compound was formed and was filtered off and recrystallised from light petroleum to give yellow needles. Comparison of the analytical data and IR spectrum of the product with that of an authentic sample showed it to be Co(PEt₃)₂(CO)I (ca. 70%).

The colourless water solution was evaporated under reduced pressure to give a blue residue. This was crystallized from toluene/petroleum ether (b.p. 50–70°C) to give turquoise blue crystals. These were identified as Co(PEt₃)₂I₂ by comparison of their analytical data, m.p. and IR spectra with that of an authentic sample (ca. 18%).

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References
