Oxidative Addition Reactions of P(CN)₃, P(NCO)₃ and P(NCS)₃ to (η⁵-C₅Me₅)Co(CO)₂

Mª S. Delgado*, Mª J. Macazaga, and J. R. Masaguer
Departamento de Química Inorgánica, Universidad Autónoma de Madrid, Cantoblanco, Madrid-34, Spain.
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Phosphorus Pseudohalogen Reactions, Cobalt

The phosphorus pseudohalogen P(CN)₃, P(NCO)₃, and P(NCS)₃, react with (η⁵-C₅Me₅)Co(CO)₂ to give the complexes (η⁵-C₅Me₅)Co(CO)XPX₂ (X = CN, NCO, NCS). All the compounds are characterized by elemental analysis, IR, electronic and ¹H NMR spectra.

Introduction
The oxidative addition of pseudohalogen to coordinately unsaturated organometallic compounds gives rise, to the formation of the corresponding pseudohalogen derivatives. Thus oxidative additions to (η⁵-C₅H₅)Co(CO)₂, (η⁵-C₅EtMe₅)Co(CO)₂ [1] and (η⁵-C₅Me₅)Co(CO)₂ [2] have been studied. In all cases the elimination of a carbonyl-group and the oxidation of Co(I) to Co(III) takes place.

In the present work we employ the phosphorus pseudohalogen P(CN)₃, P(NCO)₃ and P(NCS)₃, the reactivity of which has been studied with volatile halides of transition metals such as TiCl₄ and ZrCl₄ [3], but which are utilized in oxidative addition reactions for the first time.

Results and Discussion
The addition of P(CN)₃, P(NCO)₃ and P(NCS)₃ solutions in benzene to ether solutions of (η⁵-C₅Me₅)Co(CO)₂, in an N₂ atmosphere, gives rise to the release of CO and precipitation of solids with the following stoichiometry: (η⁵-C₅Me₅)Co(CO)XPX₂ (X = CN, NCO, NCS). These compounds are hygroscopic and sparingly soluble in solvents such as benzene, nitrobenzene, or dichloromethane.

IR spectra of the compounds display, in the range of stretching vibration ν(CO) for the cyanate complex the determination of the internal standard ratio of ν(CN) to the N atom [7]. For the thiocyanate complex the determination of the internal standard ratio of ν(CN) of the SCN band by the Bailey method [8] indicates that the coordination is via the N atom.

In the range 595–550 cm⁻¹ appear the bands corresponding to ν(P–C) for the complex (η⁵-C₅Me₅)Co(CO)(CN)P(CN)₂ [9], and those corresponding to the vibrations δ(NCO), δ(P–NCO) and δ(P–NCS) for the complexes (η⁵-C₅Me₅)Co(CO)(NCX)P(NCX)₂ (X = O, S) [10, 11].

In the range 490–418 cm⁻¹ appear the bands corresponding to ν(CO–CN) and ν(CO–CO) together with those of the deformation vibrations of these bonds [6]. The vibrations δ(P–CN) and δ(NCS) are also observed.

In the complex RCo(CO)(NCX)P(NCX)₂, the vibrations ν(CO–ring), δ(P–NCS) and ν(CO–N) are expected to be involved in the intense broad band observed at 320 cm⁻¹.

The electronic spectra of the complexes in dichloromethane solution are set out in Table II.
Table Ia. IR spectral data for the complexes.b.

<table>
<thead>
<tr>
<th>RCo(CO)(CN)P(CN)₂</th>
<th>RCo(CO)(NCO)P(NCO)₂</th>
<th>RCo(CO)(NCS)P(NCS)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.170 m</td>
<td>v(CN)</td>
<td>v(CN) of NCO and P(NCO)₂</td>
</tr>
<tr>
<td>2.150 m</td>
<td>of</td>
<td>(2.2)</td>
</tr>
<tr>
<td>2.130 w, sh</td>
<td>(CN) and P(CN)₂</td>
<td>2.110 s</td>
</tr>
<tr>
<td>2.060 m</td>
<td>v(CO)</td>
<td>v(CO)</td>
</tr>
<tr>
<td>2.040 m</td>
<td>v(CO)</td>
<td>2.045 s</td>
</tr>
<tr>
<td>1.320 w</td>
<td>v(CO) of (NCO)</td>
<td>1.950 m. br.</td>
</tr>
<tr>
<td>590 v. s.</td>
<td>v(P—C)</td>
<td>v(CN) of (NCS)</td>
</tr>
<tr>
<td>580 s</td>
<td></td>
<td>v(CN) of (NCS)</td>
</tr>
<tr>
<td>490 sh, w</td>
<td>δ(P—CN)</td>
<td>470 m</td>
</tr>
<tr>
<td>470 m</td>
<td>δ(Co—CO)</td>
<td>450 m, sh</td>
</tr>
<tr>
<td>465 w, sh</td>
<td>δ(Co—CO)</td>
<td>v(Co—CO) and</td>
</tr>
<tr>
<td>435 w</td>
<td>v(Co—CO) and</td>
<td>v(Co—CO)</td>
</tr>
<tr>
<td>418 w</td>
<td>δ(Co—CN)</td>
<td>440 w</td>
</tr>
<tr>
<td>340 w</td>
<td>v(Co—ring)</td>
<td>320 v. s., br</td>
</tr>
<tr>
<td>315 v. w</td>
<td></td>
<td>v(Co—N)</td>
</tr>
<tr>
<td>280 w</td>
<td>v(Co—N)</td>
<td></td>
</tr>
</tbody>
</table>

a In cm⁻¹; b R = η⁵-C₅Me₅; in parenthesis, the internal standard ratio determined by Bailey method [8].

Table II. Electronic spectra of the complexes.a.

<table>
<thead>
<tr>
<th>RCo(CO)(CN)P(CN)₂</th>
<th>RCo(CO)(NCO)P(NCO)₂</th>
<th>RCo(CO)(NCS)P(NCS)₂</th>
<th>Assignation</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.161 sh, br</td>
<td>16.393</td>
<td>16.501 sh, br</td>
<td>d—d</td>
</tr>
<tr>
<td>27.322</td>
<td>27.800</td>
<td>27.777</td>
<td>charge transfer</td>
</tr>
</tbody>
</table>

a In cm⁻¹, CH₂Cl₂ solution, R = η⁵-C₅Me₅.

If we assume the complexes to be octahedral, the simultaneous presence of CO, X (X = CN, NCO or NCS) and PX₂ ligands reduces the symmetry to Cs. In this way the triply degenerate t₂g are split into the components e and b₁, and the doubly degenerate eg orbitals are split into a₁ and b₁, as previously observed in the photoelectronic spectra of carbonylcyclopentadienyl complexes of C₂ᵥ symmetry [12, 13]. For Cs 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 which display wide bands, of poor resolution, in the 16000–20000 cm⁻¹ range, due to d—d transitions, and an intense band near 28000 cm⁻¹ brought about by the charge transfer from the metal to the π* orbital of CN, CO or NCX.

¹H NMR spectra display a single signal that can be attributed to the 15 equivalent protons of the 5 methylsubstituents of the ring.

Experimental

All reactions were carried under oxygen-free N₂. The pentamethycyclopentadiene [14], (η⁵-C₅Me₅)Co(CO)₂ [15] and the reactants P(CN)₃ [9], P(NCO)₃ [10], P(NCS)₃ [11] were prepared by the published procedures.

The cobalt was determined by titration of the Co-EDTA complex in presence of NET as indicator. The phosphorus was determined gravimetrically as Mg₂P₂O₇ [16].

The IR spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer model 325, using Nujol and Hostaflon mulls between CsI windows. ¹H NMR spectra were recorded on a Varian model XL-100/15.

The visible spectra were recorded on a Pye Unicam SP8–100 ultraviolet spectrophotometer.

Preparation on (η⁵-C₅Me₅)Co(CO)(CN)P(CN)₂

In a two-neck flask (100 cm³) fitted with N₂ inlet, magnetic stirrer and pressure equalized dropping
funnel, $\eta^5$-C$_5$Me$_5$Co(CO)$_2$ (1.5 g, 6 mmole) was dissolved in Et$_2$O (30 cm$^3$) saturated with oxygen-free N$_2$. A solution of P(CN)$_3$ (0.75 g, 6.9 mmole) in benzene (20 cm$^3$), freshly obtained, was slowly added dropwise. A dark brown solid immediately appeared, and evolution of CO was observed. The solid was filtered off, washed with Et$_2$O and dried in vacuum. The yield is 1.5 g (75%).

C$_{14}$H$_{15}$N$_3$OPCo
Calcd C 50.7 H 4.5 N 12.7 P 9.3 Co 17.8,
Found C 49.5 H 4.6 N 11.8 P 8.2 Co 17.1.  
$^1$H NMR (CDCl$_3$): 1.65 d.

Preparation of ($\eta^5$-C$_5$Me$_5$)Co(CO)(NCS)P(NCS)$_2$
A similar procedure was used with $\eta^5$-C$_5$Me$_5$Co(CO)$_2$ (1.5 g, 6 mmole) in Et$_2$O (30 cm$^3$) and P(NCS)$_3$ (1.4 g, 6.8 mmole) in benzene (20 cm$^3$). A brown solid appeared immediately. The yield is 1.9 g (75%).

C$_{14}$H$_{13}$N$_3$OPS$_3$Co
Calcd C 44.3 H 3.9 N 9.8 P 7.2 Co 13.8,
Found C 43.5 H 4.4 N 12.2 P 6.3 Co 13.4.  
$^1$H NMR (CDCl$_3$): 1.55 d.

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