Oxidative Addition of Pseudohalogen to [P(OPh)₃]₄Ni

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The title compound reacts with cyanogen halides, XCN (X = Br or I) to give the complexes L₂(X)(CN)Ni (L = P(OPh)₃, X = Br or I). The oxidative addition of (SCN)₂ and (SeCN)₂ to the same compound results in the formation of L₂Ni(XCN)₂ (X = S or Se).

All the complexes have been characterized by elemental analysis, and IR, ¹H NMR and electronic spectra.

Introduction

Until now there are very few well studied oxidative additions of pseudohalogens to compounds of Ni(O); in the literature some of these reactions with HCN and (CN)₂ are reported [1]. Here we describe the oxidative addition reactions of thiocyanogen, selenocyanogen and cyanogen halides XCN (X = Br or I) to Ni[P(OPh)₃]₄.

Results and Discussion

The mixed halocyanide complexes L₂Ni(CN)(X) [L = P(OPh)₃; X = Br, I] are easily obtained as solids of yellow-brown colour by mixing solutions of XCN (X = Br or I) and L₂Ni (L = P(OPh)₃). The reactions between solutions of L₂Ni and (XCN)₂ (X = S or Se) lead to the formation of brown solids of the composition L₂Ni(XCN)₂ (X = S or Se). The diamagnetism observed in these complexes and also the visible spectra seem to indicate that the complexes have square-planar symmetry.

The IR spectra present the characteristic bands of the ligand P(OPh)₃; ν(C–C(Ph)) appearing in the range 1260–1160 cm⁻¹ and ν(P–O) at 1040–1000 cm⁻¹ [2, 3]. In Table 1 the bands corresponding to the cyanide and XCN (X = S or Se) ligands are reported and also those which correspond to the metal-ligand bond. The range of the stretching vibrations v(CN) is characteristic for terminal ligands and is similar to the one found in other nickel cyanide phosphine complexes [4].

The bands which correspond to ν(CN) of XCN (X = S or Se) appear near 2130 cm⁻¹. The determination of the internal standard ratio of these bands by the Bailey method [6] indicate that in all cases the NCX ligand is coordinated via the S or Se atom. ν(SeC) appears at 520 cm⁻¹ and ν(S) at 760 cm⁻¹ as found for other M–XCN complexes (X = S or Se) [5]. The presence of only one band corresponding to ν(CN) in the solid and also in CH₂Cl₂ solution indicate that the two groups XCN (X = S or Se) are in trans positions.

The assignment of the bands corresponding to ν(NiP) has been the object of a considerable controversy [7, 8]. However, Nakamoto has recently proposed [9] a new assignment of those bands on the basis of the isotopic substitution of the metal and he ascribes the ν(NiP) vibrations in the trans square-planar complexes Ni₄L₄X₄ (L = phosphine, X = halogen) to the range 270–200 cm⁻¹. In the case of the cis-isomers he found that ν(NiP) appears in the range 370–350 cm⁻¹, because in these isomers, the Ni–P bond is influenced by the trans-effect of the halogen ligands. In the tetrahedral isomers ν(Ni–P) appears below 200 cm⁻¹ [9].

In our complexes (Table 1) only one band appears in the range 290–220 cm⁻¹ which can be assigned to ν(NiP), in agreement with trans square-planar symmetry. We obtained the same result with the visible spectra as we will discuss later.

In the L₂Ni(CN)X complexes the bands which appear at 335 and 282 cm⁻¹ are assigned to ν(NiBr) and ν(NiI) [9]; the relation ν(NiI)/ν(NiBr) = 0.84 is in good agreement with the one found in many tetra-coordinated complexes [10]. The bands corresponding to ν(NiC) might appear in the range 500–450 cm⁻¹ [11] and are masked by the strong absorption of the triphenylphosphine ligands.

In the IR spectra of the complexes L₂Ni(XCN)₂ (X = S or Se) the bands corresponding to ν(NiS) appear at 300 cm⁻¹, and ν(Ni–Se) at 255 cm⁻¹ in agreement with the results in other nickel complexes [12, 13].
Table I. IR characteristic bands of the complexesa.

<table>
<thead>
<tr>
<th>L₂NiI(CN)</th>
<th>L₂NiBr(CN)</th>
<th>L₂Ni(SeCN)₂</th>
<th>L₂Ni(SCN)₂</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2120 vs (2120)c</td>
<td>2122 vs (2120)c</td>
<td>2135 vs (0,5)b</td>
<td>2128 vs (0,5)b</td>
<td>ν(CN)</td>
</tr>
<tr>
<td>2120 vs (2120)c</td>
<td>2135 vs (0,5)b</td>
<td>520 w</td>
<td>412 w</td>
<td>ν(CS)</td>
</tr>
<tr>
<td></td>
<td>760 s</td>
<td></td>
<td></td>
<td>ν(CSe)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ν(NiBr)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ν(NiI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ν(NiSe)</td>
</tr>
<tr>
<td>335 m</td>
<td></td>
<td></td>
<td></td>
<td>ν(Ni-P)</td>
</tr>
<tr>
<td>282 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 m</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

a Data in cm⁻¹, L = P(OPh)₃; b integrate intensity; c in CH₂Cl₂ solution; d obscured by phenyl absorption.

Table II. Visible and ultraviolet spectra of the complexesa.

<table>
<thead>
<tr>
<th>L₂NiI(CN)</th>
<th>L₂NiBr(CN)</th>
<th>L₂Ni(SeCN)₂</th>
<th>L₂Ni(SCN)₂</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nujol CH₂Cl₂</td>
<td>Nujol CH₂Cl₂</td>
<td>Nujol CH₂Cl₂</td>
<td>Nujol CH₂Cl₂</td>
<td>pX¹ - dNi</td>
</tr>
<tr>
<td>27,000</td>
<td>27,400</td>
<td>28,400</td>
<td>28,500</td>
<td>22,470</td>
</tr>
<tr>
<td>33,300</td>
<td>34,300</td>
<td>33,600</td>
<td>33,300</td>
<td>26,700</td>
</tr>
<tr>
<td>37,700</td>
<td>38,000</td>
<td>39,000</td>
<td>39,100</td>
<td>30,400</td>
</tr>
</tbody>
</table>

a In cm⁻¹; L = P(OPh)₃.

The variation which is produced in ν(NiP) (Table I) is practically independent of the other ligands because the two Ni–P bonds are in trans-positions, as already indicated. The small variation observed in the position of this band is due to the different nature of the ligand which is in cis-position to the Ni–P bond. However, this cis-effect is of a much smaller magnitude than the trans-effect, as was shown for other square-planar complexes [14].

In Table II the wavenumbers of the bands observed in the electronic spectra of the synthesized complexes are reported. As CN, SCN and SeCN are strong-field ligands, the bands corresponding to d–d transitions appear in the same range as the charge-transfer bands heading to overlap; in some cases it was necessary to resolve the bands by using a program BIGAUSS.

The spectra are typical of Ni(II) square-planar complexes, no band appearing in the range 10,000–16,000 cm⁻¹ [15] (which would indicate the existence of tetrahedral isomers) and are in agreement with the IR spectra previously discussed and also with the diamagnetism observed for the complexes. The assignments of the d–d transitions are in accord with the order of the d orbitals for square-planar complexes proposed by Gray [16]: dx² < dy², dyz < dxz < dxy for strong π-acceptor ligands.

In L₂Ni(XCN)₂ (L = P(OPh)₃, X = S or Se) ν₁ varies with SCN⁻ > SeCN⁻ (Table II), which is in agreement with the position of these ligands in the spectrochemical series when they coordinate by the sulphur or selenium atoms [17]. This result confirms those obtained by the IR spectra.

In the spectra of L₂NiX(CN) (X = Br or I) ν₂ varies with Br⁻ > I⁻ (Table II) which also agrees with the spectrochemical series. The other observed bands are assigned to charge-transfer transitions. Thus in L₂Ni(XCN) (X = S or Se) the bands which appear at 30,000 cm⁻¹ are assigned to the transition π(XCN) → dNi by analogy with other thiocyanate or selenocyanate complexes [15, 18].

In L₂NiX(CN) (X = Br or I) the bands which appear at 33,000 cm⁻¹ can be assigned to the transition dNi → π*(CN) in agreement with the bands observed in other nickel cyanide complexes [19, 20], while the bands which appear at 37,000 and 39,000 cm⁻¹ can be assigned to the transitions p⁻ → dNi and pBr⁻ → dNi, which is in agreement with the different ability of donation pσ or pπ of these halide ligands.
Experimental

All the reactions were carried out under oxygen-free N₂. [NiP(OPh)₃]₄ [21], XCN [22], (SCN)₂ [22] and (SeCN)₂ [23] were prepared by literature methods. Nickel was determined by atomic absorption. Microanalyses were performed by Centro Nacional de Quimica Organica (Madrid).

The IR spectra were recorded at 4000–200 cm⁻¹ on a Perkin-Elmer model 580-B, using nujol and hostafon mulls between CsI windows.

The UV-visible spectra were recorded on a Cary model 17. The ¹H NMR spectra were recorded on a Varian model XL-100/15.

Preparation of [P(OPh)₃]₄Ni(SCN)₂

In a 100 ml two-neck flask fitted with N₂-inlet, magnetic stirrer and pressure-equalized dropping funnel, [NiP(OPh)₃]₄ (1.5 g, 1.15 mmol) was placed, dissolved in CH₂Cl₂/n-pentane 1:1 (40 cm³). The flask was cooled to −20 °C and a (SCN)₂-solution previously obtained from Br₂ (0.6 g, 3.7 mmol) and (SCN)₂/P₃0 (1.3 g, 4 mmol) in CH₂Cl₂/n-pentane 1:1 (20 cm³), was added dropwise through the funnel. A brown-yellow solid appeared immediately and the solution turned orange. The solid was filtered off, washed several times with cold CH₂Cl₂/n-pentane and dried in vacuo. The yield was 40%.

C₃₈H₃₀N₆O₃S₂P₂Ni
Calcd C 57.3 H 3.7 N 3.5 Ni 7.3.
Found C 56.9 H 3.6 N 3.3 Ni 6.9.
¹H NMR (acetone-d₆): 2.95 r.

Preparation of [P(OPh)₃]₄Ni(SeCN)₂

Following the above procedure solutions of [NiP(OPh)₃]₄ (2 g, 1.5 mmol) in CH₂Cl₂/n-pentane (40 cm³) and (SeCN)₂ previously obtained from I₂ (1 g, 3.9 mmol) and AgSeCN (2.14 g, 10 mmol) in CH₂Cl₂/n-pentane (20 cm³), were mixed. A red-brown solid was obtained in 45% yield.

C₃₈H₃₀N₆O₃Se₂P₂Ni
Calcd C 51.3 H 3.3 N 3.1 Ni 6.6.
Found C 50.1 H 3.2 N 2.9 Ni 6.1.
¹H NMR (acetone-d₆): 2.90 r.

Preparation of [P(OPh)₃]₄NiI(CN)

A similar procedure was used with [NiP(OPh)₃]₄ (2 g, 1.53 mmol) in CH₂Cl₂/n-pentane 1:1 (40 cm³) and ICN (0.3 g, 1.9 mmol) in CH₂Cl₂/n-pentane (20 cm³). Immediately a brown solid appeared. The yield was 70%.

C₃₈H₃₀O₃NP₂I Ni
Calcd C 53.4 H 3.6 N 1.7 Ni 7.1.
Found C 52.9 H 3.4 N 1.5 Ni 7.0.
¹H NMR (acetone-d₆): 2.90 r.

Preparation of [P(OPh)₃]₄NiBr(CN)

Similarly [NiP(OPh)₃]₄ (2 g, 1.53 mmol) in CH₂Cl₂/n-pentane 1:1 (40 cm³) and BrCN (0.2 g, 1.8 mmol) in CH₂Cl₂/n-pentane (20 cm³) gave a brown solid with 60% yield.

C₃₈H₃₀O₃NP₂Br Ni
Calcd C 56.6 H 3.8 N 1.7 Ni 7.7.
Found C 55.8 H 3.6 N 1.6 Ni 7.2.
¹H NMR (acetone-d₆): 2.90 r.