Co-operative Electronic Ligand Effects in Square-planar Complexes Containing the Selenocyanate Ion

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Summary The complex *trans*-[$Rh(PPh_3)_2(CO)NCSe$], when compared with *trans*-[$Pd(PPh_3)_2(SeCN)_2$], has provided the first example of co-operative electronic ligand control of the bonding mode of the selenocyanate ion in square-planar complexes.

SINCE the first discovery[1] of co-operative ligand control of the bonding mode of the thiocyanate ion in square-planar palladium(II) and platinum(II) complexes, numerous additional examples[2] have been reported. These have involved both square-planar and octahedral thiocyanate complexes of a variety of metal ions, and have been attributed to steric and/or electronic effects. Although steric control of the bonding mode of the selenocyanate ion in square-planar palladium(II) complexes has been firmly established,[3] co-operative electronic ligand control of the ion's bonding mode in square-planar complexes has not previously been observed, *i.e.*, only *Se*-bonding has been found to occur in the sterically unhindered complexes of palladium(II),[4,5] platinum(II),[4,6] and gold(III).[7]

If the π-bonding hypothesis originally put forward by Turco and Pecile[1] to account for the co-operative electronic ligand control of the thiocyanate's bonding mode is correct, one would expect that this effect would become most important in complexes containing CO or PF_3. Accordingly, we have synthesized the complex *trans*-[$Rh(PPh_3)_2(CO)NCSe$] by reaction of the corresponding chloro-complex (0·25 mmole) with NaSeCN (0·25 mmole) in 205 ml of Spectrograde acetone. After stirring for 15 min at room temperature, the precipitated sodium chloride was removed by filtration, the filtrate was evaporated to dryness in the cold under reduced pressure, and the residue extracted with 25 ml of chloroform. The product was precipitated by pouring the filtered extract into 200 ml of 95% ethanol. After the mixture had been stirred for 1 h, the product was isolated by filtration, washed with diethyl ether, and dried *in vacuo* over calcium sulphate. Yield, 58%; m.p. 125—127° (dec.).

The fact that the selenocyanate group is *N*-bonded, both in the solid state and in chloroform solution, is clearly indicated[2] by its enhanced (relative to the free ion values) ν_{CSe} frequency (565 cm^{-1}, Nujol mull) and ν_{CN} integrated absorption intensity ($9{\cdot}0 \times 10^4$ M^{-1} cm^{-2}, chloroform solution, ν_{CN} at 2096 cm^{-1}). When compared to the *Se*-bonding found[5] in the sterically similar *trans*-[$Pd(PPh_3)_2(SeCN)_2$] complex, it is clear that the *N*-bonding found in the rhodium(I) complex may be ascribed to the presence of the CO group.

When the same procedure was used in an attempt to synthesize the iridium(I) analogue, the complex decomposed before it could be isolated. Consequently, it was isolated rapidly and directly from the acetone solution by reducing the volume of the solution in the cold (but not to dryness). The product, [$Ir(PPh_3)_2$(acetone)(CO)NCSe], was found to contain one mole of acetone, as well as an *N*-bonded selenocyanate group (ν_{CSe} 560 cm^{-1}, Nujol mull; ν_{CN} 2094 cm^{-1}, $A_{\text{integr}} = 7 \times 10^4$ M^{-1} cm^{-2}, chloroform solution). Yield, 40%; m.p. 123—126° dec.).

Formulation of the product as a five-co-ordinate complex is based on the fact that no acetone is lost upon heating the complex for 8 h at 40° *in vacuo*, and the appearance of an extra absorption band in the visible region of the spectrum (compared with the spectra of the corresponding four-co-ordinate chloro-, isocyanato-, and isothiocyanato-complexes).

By way of contrast, the corresponding cyanate[8-10] and thiocyanate[2,9,11] complexes of rhodium(I) and iridium(I), as well as those of palladium(II) and platinum(II), all contain only *N*-bonded pseudohalides, emphasizing the previously noted[12] tendency of palladium(II) to favour bonding to selenium, as opposed to sulphur (and, of course, oxygen).

Although the anti-symbiotic[13] switch to *N*-bonding in the complex [$Rh(PPh_3)_2(CO)NCSe$] is in accord with Turco and Pecile's hypothesis,[1] an opposing symbiotic[13] trend is apparently operative when metal ions of the first transition series are involved. Thus, [$Fe(NCSe)_4$]$^{2-}$ contains, as expected, *N*-bonded groups,[4] whereas [$C_5H_5Fe(CO)_2SeCN$] contains an *Se*-bonded selenocyanate.[14] This class *a* (symbiotic)–class *b* (anti-symbiotic) disparity in behaviour has been frequently observed for thiocyanate complexes,[2] [$Co(NH_3)_5NCS$]$^{2+}$ [15] and [$Co(CN)_5SCN$]$^{3-}$ [16] being typical examples of the former case. A satisfactory explanation for the existence of the opposing trends has yet to be presented.

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