Bonding Mode of Thiocyanate in Palladium(II) Phosphite Complexes: *X*-Ray Structure of *trans*-Dithiocyanatobis(triphenyl phosphite)palladium(II)

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Summary In contrast to the presence of *N*-bonded thiocyanate groups in *trans*-Pd(NCS)$_2$(PPh$_3$)$_2$ the phosphite compound *trans*-Pd(SCN)$_2$[P(OPh)$_3$]$_2$ contains *S*-bonded thiocyanates as shown by *X*-ray crystallographic structure determination: antisymbiosis in the phosphine complexes appears primarily to result from steric inhibition of *S*-bonding rather than electronic effects.

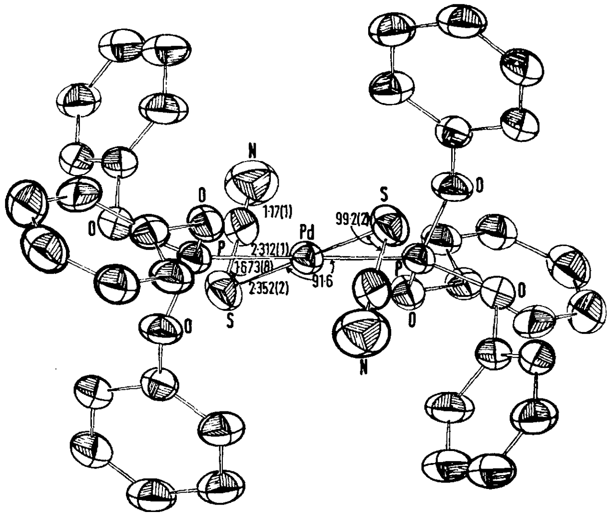

FIGURE. Molecular structure of *trans*-Pd(SCN)$_2$[P(OPh)$_3$]$_2$ showing some pertinent bond lengths and angles.

ONE of the classical and widely quoted[1] examples of antisymbiosis is the presence of M–NCS bonding in *trans*-Pd(NCS)$_2$(PR$_3$)$_2$ and *cis*-Pt(NCS)$_2$(PR$_3$)$_2$ (R = Et, Ph). This inversion of the preference of a soft ion for S over N donors has most frequently been rationalised in terms of π-bonding,[2] although alternative explanations have been proposed.[1a,1d,2b,3,4] In contrast to electronic arguments there is evidence[5] of a major role for steric effects in dictating M–NCS or M–SCN bonding in phosphine complexes. The key position of the compounds M(NCS)$_2$(PR$_3$)$_2$ in co-ordination chemistry justified a study of analogous P(OR)$_3$ derivatives since phopshites have different *trans*-influences than phosphines,[6] smaller steric angles,[7] and, when π-bonding is important, are better π-acceptors. Thus the interplay of steric and electronic factors modifying symbiosis in CNS$^-$ complexes could be investigated.

The compound *trans*-Pd(SCN)$_2$[P(OR)$_3$]$_2$ (I) prepared from the chloride[8] by metathesis has a solid state i.r. spectrum [ν(C$\equiv$N) 2117 s, sp cm^{-1} (s = strong, sp = sharp)] characteristic of *S*- bonded thiocyanate. The complex did not isomerise on heating to 95° for 4 h nor on recrystallisation from CH$_2$Cl$_2$–EtOH. Crystals (from MeCN) are monoclinic, $a = 9{\cdot}922(4)$, $b = 10{\cdot}096(8)$, $c = 19{\cdot}334(14)$ Å, $\beta = 108{\cdot}46(5)°$; space group $P2_1/c$, $Z = 4$, $D_m = 1{\cdot}54$ g cm^{-3}, $D_c = 1{\cdot}524$ g cm^{-3}. The structure was solved by the heavy-atom method using 3089 observed diffractometer data ($2\theta \leqslant 60°$) measured on a G.E. XRD6 diffractometer with Mo-K_α radiation and refined to the present R value of 0·063. The palladium atom is co-ordinated in square-planar fashion to the phosphorus atoms of two P(OPh)$_3$ molecules and the sulphur atoms of two thiocyanate groups (Figure). The shortening of the Pd–P bonds [2·312(1) Å] in (I) compared to *trans*-Pd(SCN)$_2$(Ph$_2$PC$\equiv$CBu^t)$_2$ [2·326(3) Å] consistent with either the increased π-acceptor ability of the phosphite relative to the phosphine, reduced steric demand by the smaller phosphite, or a lower *trans* influence for the phosphite, is accompanied by a significant lengthening of the Pd–S bonds [2·352(2) Å in (I) *vs.* 2·336(3) Å in *trans*-Pd(SCN)$_2$(Ph$_2$PC$\equiv$CBu^t)$_2$] perhaps indicating a mechanism for retaining the same electron density at the metal atom or the same non-bonded repulsions in the co-ordination sphere. The contrast in solid-state structures of *trans*-Pd(NCS)$_2$(PPh$_3$)$_2$ and *trans*-Pd(SCN)$_2$[P(OPh)$_3$]$_2$ is notable. Solution i.r. spectra of *trans*-Pd(NCS)$_2$(PPh$_3$)$_2$ in benzene, CHCl$_3$, and CH$_2$Cl$_2$ showed little if any evidence for *S*-bonded thiocyanate while for (I) *S*-bonded species were major components in all solutions. The tendency to increased *S*-bonding evident for phosphite complexes in the solid state was confirmed by the characterisation of the mixed species Pd(SCN)(NCS)[P(OMe)$_3$]$_2$ [ν(C$\equiv$N) 2125 s, sp; 2088 s, br cm^{-1}], *cis*-Pt(SCN)(NCS)-[P(OPh)$_3$]$_2$ [ν(C$\equiv$N) 2132 s, sp; 2088 s, br cm^{-1}] and *cis* Pt(SCN)(NCS)[P(OMe)$_3$]$_2$[ν(C$\equiv$N) 2132 s, sp; 2097 s, br cm^{-1}] having both *N*- and *S*-bonded groups. Although we were able to isolate *cis*-Pd(NCS)$_2$[P(OMe)$_3$]$_2$ [ν(C$\equiv$N) 2082 s, br; 2103 s, br cm^{-1}] and Pt(NCS)$_2$[P(OPh)$_3$]$_2$

[ν(C$\equiv$N) 2099 s, br cm^{-1}] from one solvent system (DMF–Et$_2$O),[9]† solution spectra in other solvents gave no evidence for *complete* isomerisation of Pd(SCN)$_2$[P(OPh)$_3$]$_2$, Pd(SCN)(NCS)[P(OMe)$_3$]$_2$, or Pt(NCS)(SCN)[P(OR)$_3$]$_2$ (R = Me, Ph) to *N*-bonded species.

The presence of M–SCN bonds in the phosphite complexes is incompatible with the π-bonding hypothesis. The results also appear at variance with recent data for Au^{I} complexes.[10]‡ The greater tendency to *S*-bonding in the P(OR)$_3$ complexes of Pd^{II} may be due to a reduced steric inhibition to sulphur co-ordination on replacing a phosphine by a smaller phosphite. Conversely the presence of M–NCS bonds in M(NCS)$_2$(PR$_3$)$_2$ (R = Et, Ph) may be steric rather than electronic in origin.

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† Single crystals of these complexes contain DMF of crystallisation. It is uncertain to what extent this influences the solid state structures.

‡ For Au^{I}, a higher ratio of *N*- to *S*-bonded CNS$^-$ was found for P(OPh)$_3$ than PPh$_3$, despite the fact that phosphites P(OR)$_3$ have a lower *trans*-influence than the corresponding phosphines PR$_3$.

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[9] Compare with J. L. Burmeister and H. J. Gysling, *Inorg. Chim. Acta.*, 1967, **1**, 100.

[10] J. L. Burmeister and J. B. Melpolder, *J.C.S. Chem. Comm.*, 1973, 613.