Comparison of the Molecular Structures of *trans*-Di(isothiocyanato)bis(triphenylphosphine)palladium(II) and *trans*-Di(thiocyanato)bis(triphenyl phosphite)palladium(II)

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The molecular structures of *trans*-[Pd(NCS)$_2$(PPh$_3$)$_2$] (I) and *trans*-[Pd(SCN)$_2${P(OPh)$_3$}$_2$] (II) have been determined by single-crystal *X*-ray diffractometry to investigate the roles of π-bonding and steric effects on the thiocyanate bonding mode. Crystals of (I) are triclinic, space group $P\bar{1}$ with unit-cell dimensions a = 7.912(6), b = 11.659(7), c = 10.532(9) Å, α = 111.00(5), β = 87.51(8), γ = 106.36(6)°, Z = 1. Crystals of (II) are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 9.922(4), b = 10.096(8), c = 19.334(14) Å, β = 108.46(5)°, Z = 2. The structures were solved by heavy-atom methods and refined to R 0.036 [(I), 2 513 reflections] and 0.060 [(II), 3 089 reflections].

The thiocyanate ion is *N*-bonded in (I) and *S*-bonded in (II). Pd–P bond lengths are 2.3404(9) in (I) and 2.312(2) Å in (II), the significantly shorter length in the latter being attributed to decreased steric bulk and a lower σ-*trans* influence for the phosphite ligands. The Pd–S bond length [2.352(2) Å] in (II) appears to be anomalously long and inconsistent with a strong π-component to the bond. The presence of *N*-bonded thiocyanates in (I) is probably a result of intramolecular steric crowding rather than Pd–P π-bonding.

ONE of the most controversial aspects of the chemistry of the platinum triad elements concerns the role of metal–phosphorus π-bonding in square-planar bis(phosphine) complexes [MX$_2$(PR$_3$)$_2$].[1] The extent of retrodative M–P d_π–d_π bonding is fundamental to an understanding of the metal–phosphorus bond and has far reaching ramifications in synthetic, mechanistic, and structural inorganic chemistry. Recently, interpretation of metal–phosphorus n.m.r. coupling-constant data for platinum(II) complexes has shifted the consensus away from an implicit belief in strong M–P π-bonding in square-planar complexes.[2] This viewpoint has been reinforced by the observation that nickel–phosphorus π-bonding plays an insignificant role in determining the stability of NiL$_4$ complexes (L = tertiary phosphine) or the extent of substitution of CO by L in [Ni(CO)$_4$].[3] Nevertheless M–P π-bonding remains a popular *ad hoc* explanation for a variety of experimental observations. Thus the classic example of antisymbiotic behaviour of palladium(II) in binding the nitrogen site of the thiocyanate ion in the complexes *trans*-[Pd(NCS)$_2$(PR$_3$)$_2$] [4] has been frequently

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[1] L. M. Venanzi, *Chem. in Britain*, 1968, **4**, 162.

[2] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 346.

[3] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[4] J. L. Burmeister and F. Basolo, *Inorg. Chem.*, 1964, **4**, 1587.

attributed to strong Pd–P π-bonding,[5] despite the fact that alternative explanations were recognised.[4] A number of papers in the post-1965 literature rationalising the bonding of thiocyanate ion and related ambidentate ligands rely heavily on π-bonding arguments.[6] In sharp contrast it has recently been unambiguously demonstrated that in *cis*-$[Pd(CNS)_2\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1$—3) the mode of bonding is dominated by steric constraints imposed by the diphosphines.[7] The characterisation of the *S*-bonded complex *trans*-$[Pd(SCN)_2(Ph_2P{\cdot}C{:}C{\cdot}CMe_3)_2]$ [8] and the implication that reduced steric demand by the phosphino-acetylene compared to triphenylphosphine, was in part responsible for the presence of only Pd–SCN bonding suggested a reassessment of factors influencing thiocyanate bonding in square-planar $[M(CNS)_2L_2]$ (M = Pd or Pt; L = unidentate phosphorus donor) complexes. Accordingly a programme of structural studies designed to delineate the roles of M–P π-bonding and steric effects in dictating solid-state structure was initiated. Parallel studies of solution equilibria utilising Fourier transform ^{31}P n.m.r. spectra are in progress.

For the purpose of assessing the relative effects of Pd–P π-bonding and intramolecular steric hindrance on palladium–thiocyanate bonding a comparison of *trans*-$[Pd(CNS)_2(PPh_3)_2]$, thought to contain Pd–NCS linkages with a corresponding triphenyl phosphite derivative, seemed important for the following reasons. (*a*) Triphenyl phosphite has a smaller cone angle (121°) than triphenylphosphine (145°) and should therefore be less sterically demanding.[3] (*b*) Triphenylphosphine is more basic than triphenyl phosphite but the latter has a greater π-acceptor ability. (*c*) Extensive ^{31}P n.m.r. studies have demonstrated a higher *trans*-influence for phosphines than phosphites.[9] We now compare the molecular structures of *trans*-$[Pd(NCS)_2(PPh_3)_2]$ (I) and *trans*-$[Pd(SCN)_2\{P(OPh)_3\}_2]$ (II) as determined by single-crystal *X*-ray diffraction. The synthesis, i.r., and ^{31}P n.m.r. spectra of these compounds and their platinum analogues will be reported elsewhere.

EXPERIMENTAL

The synthesis of (I) from *trans*-$[PdCl_2(PPh_3)_2]$ has been described.[4] Crystals used in the structure determination were prepared *via* the reaction of $K_2[Pd(SCN)_4]$ in hot acetonitrile with the stoicheiometric quantity of triphenylphosphine. Rhombic yellow single crystals were obtained on recrystallisation from dichloromethane. Orange-yellow prisms of *trans*-$[Pd(SCN)_2\{P(OPh)_3\}_2]$ [10] were grown from anhydrous acetonitrile. Relevant crystal data are listed in Table 1.

trans-$[Pd(NCS)_2(PPh_3)_2]$, (I).—Preliminary Weissenberg and precession photographs showed the crystals to be triclinic. An equidimensional crystal mounted on a glass fibre was aligned with the reciprocal cell axis a^* parallel to the ϕ axis of a General Electric XRD 6 diffractometer. Unit-cell dimensions were refined from a least-squares fit of 2θ values for 21 reflections. The intensities of all reflections in the hemisphere for which $2.5° < 2\theta \leqslant 50°$ were measured with zirconium-filtered Mo-K_α radiation ($\lambda = 0.710\,69$ Å), with scan rate 2° min^{-1}. Background counts of 10 s were made before and after each scan. The intensities of three standard reflections measured every 100 observations changed by $\leqslant 3\%$ during data collection. 2 513 Reflections with intensity $I \geqslant 3\sigma(I)$ were used in the structure analysis. Data were reduced to a set of structure amplitudes in the usual manner.

TABLE 1

Crystal data for $[Pd(NCS)_2(PPh_3)_2]$ (I) and $[Pd(SCN)_2\{P(OPh)_3\}_2]$ (II)

	(I)	(II)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	7.912(6)	9.922(4)
b/Å	11.659(7)	10.096(8)
c/Å	10.532(9)	19.334(14)
α/°	111.00(5)	
β/°	87.51(8)	108.46(5)
γ/°	106.36(6)	
μ/Å^3	868.49	1 837.4
M	747.09	843.15
Z	1	2
D_m/g cm^{-3}	1.43	1.54
D_c/g cm^{-3}	1.428	1.524
Crystal size/mm	0.20 × 0.22 × 0.25	0.10 × 0.15 × 0.18
μ(Mo-K_α)/cm^{-1}	7.63	7.44
Scan range in 2θ/°	2.5—50	2.5—60
Measured reflections	3 054	6 138
Obs. reflections	2 513	3 089

trans-$[Pd(SCN)_2\{P(OPh)_3\}_2]$, (II).—The systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated space group $P2_1/c$ (C^5_{2h}; No. 14). Accurate unit cell data were obtained as before, and intensity data were collected in the same way as for (I). The intensity variation of the three standards reflections was $\leqslant 7\%$.

3 089 Reflections with $I \geqslant 3\sigma(I)$ were used in the analysis. Lorentz and polarisation corrections were applied to the derivation of structure-factor amplitudes. No absorption correction was made.

Structure Solution and Refinement.—(*a*) (I). The structure was solved from a Fourier synthesis calculated with the heavy atom in the special position ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). This map unambiguously revealed the positions of all 22 non-hydrogen atoms, confirming the choice of $P\bar{1}$ as the space group. Least-squares refinement (2 cycles) of atomic positional co-ordinates gave R 0.112. Inclusion of isotropic temperature factors and two further cycles of least-squares refinement reduced R to 0.078. Conversion to anisotropic thermal parameters followed by two cycles of refinement gave R 0.045. At this stage a difference-Fourier synthesis

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[5] See *e.g.* (*a*) A. Turco and C. Pecile, *Nature*, 1961, **191**, 66; (*b*) J. L. Burmeister, *Co-ordination Chem. Rev.*, 1968, **3**, 225; (*c*) S. Ahrland, *Structure and Bonding*, 1966, **1**, 207; (*d*) F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 296; (*e*) A. H. Norbury, *J. Chem. Soc.* (*A*), 1971, 1089.

[6] For reviews see A. H. Norbury and A. I. P. Sinha, *Quart. Rev.*, 1970, **24**, 69; D. W. Meek, P. E. Nipcon, and V. I. Meek, *J. Amer. Chem. Soc.*, 1970, **92**, 5351.

[7] G. J. Palenik, M. Mathew, W. L. Steffen, and G. Beran, *J. Amer. Chem. Soc.*, 1975, **97**, 1059; G. J. Palenik, W. L. Steffen, M. Mathew, M. Li, and D. W. Meek, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 125.

[8] G. Beran, A. J. Carty, P. C. Chieh, and H. A. Patel, *J.C.S. Dalton*, 1973, 488.

[9] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

[10] S. E. Jacobson, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1974, 520.

revealed the locations of all 15 hydrogen atoms. In subsequent least-squares calculations (2 cycles) hydrogen atoms were assigned isotropic temperature factors and refined. Introduction of a weighting scheme, derived from the programme Ranger, of the form, $w^{-1} = 0.476\,99 - 0.007\,08|F_o| + 0.000\,54|F_o|^2$ and a final cycle of refinement with all atoms included gave convergence at R 0.036 and R' $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ of 0.045. In the final cycle no non-hydrogen atom parameter was observed to shift by $>0.25\sigma$. Full-matrix least-squares refinement methods were used. A final difference Fourier synthesis showed no peaks of intensity >0.25 eÅ^{-3} other than in the region of the heavy-atom ripple where the maximum peak height was 0.7 eÅ^{-3}. Atom scattering factors for non-hydrogen atoms and dispersion corrections used in structure factor calculations were obtained from ref. 11(*a*); both real and imaginary dispersion corrections were used for palladium. Hydrogen atom scattering factors were taken from ref. 11(*b*).

Final atomic co-ordinates with estimated standard deviations and hydrogen atom isotropic temperature factors are given in Table 2. Thermal parameters for non-hydrogen atoms and observed and calculated structure factors for (I) and (II) are listed in Supplementary Publication No. SUP 21582 (34 pp., 1 microfiche).*

TABLE 2

Final atomic co-ordinates (fractional $\times 10^4$) and hydrogen-atom thermal parameters ($B_{iso}/\text{Å}^2$) for [Pd(NCS)$_2$-(PPh$_3$)$_2$] (I)

	x	*y*	*z*	
Pd	5 000	5 000	5 000	
S	3 507(2)	2 720(2)	7 984(2)	
P	4 209(1)	6 830(1)	6 357(1)	
N	4 292(5)	4 166(3)	6 344(2)	
C(1)	3 978(5)	3 562(4)	7 013(4)	
C(11)	2 725(5)	6 680(3)	7 687(4)	
C(12)	3 309(6)	6 451(4)	8 785(4)	
C(13)	2 200(7)	6 350(5)	9 813(5)	
C(14)	517(7)	6 461(4)	9 753(5)	
C(15)	−79(6)	6 661(4)	8 660(5)	
C(16)	1 020(5)	6 775(4)	7 631(4)	
C(21)	3 089(5)	7 387(4)	5 326(4)	
C(22)	3 420(6)	8 669(4)	5 514(5)	
C(23)	2 422(7)	9 017(5)	4 710(6)	
C(24)	1 124(7)	8 107(6)	3 767(6)	
C(25)	789(7)	6 831(5)	3 579(5)	
C(26)	1 796(6)	6 468(4)	4 338(4)	
C(31)	6 152(5)	8 137(3)	7 235(4)	
C(32)	6 070(7)	9 070(5)	8 463(6)	
C(33)	7 568(8)	57(6)	9 082(6)	
C(34)	9 125(6)	130(4)	8 512(5)	
C(35)	9 231(6)	9 221(4)	7 298(5)	
C(36)	7 747(5)	8 221(4)	6 662(5)	
H(12)	450(5)	643(4)	889(4)	3.6(9)
H(13)	259(8)	625(6)	58(6)	7.7(15)
H(14)	−26(6)	641(5)	47(5)	5.2(11)
H(15)	−132(6)	667(4)	854(4)	4.3(9)
H(16)	61(5)	696(4)	687(4)	3.8(9)
H(22)	433(6)	930(4)	617(4)	3.8(9)
H(23)	275(7)	0(5)	493(5)	5.9(12)
H(24)	37(7)	834(5)	327(5)	5.5(12)
H(25)	−21(7)	623(5)	291(5)	5.7(12)
H(26)	145(6)	554(4)	426(4)	4.5(10)
H(32)	497(8)	895(7)	895(6)	7.2(15)
H(33)	751(9)	61(7)	986(7)	10.3(20)
H(34)	29(7)	86(5)	890(5)	5.8(12)
H(35)	33(7)	926(5)	688(5)	5.4(12)
H(36)	782(6)	766(5)	588(5)	5.3(12)

(*b*) (II). With $Z = 2$, space group $P2_1/c$, the palladium atoms are required to occupy sites of $\bar{1}$ symmetry. The co-ordinates of the sulphur and phosphorus atoms were determined from an unsharpened Patterson synthesis. A Fourier synthesis phased on the positions of palladium, sulphur, and phosphorus revealed the locations of all other non-hydrogen atoms. With all non-hydrogen atoms having isotropic temperature factors, least-squares refinement yielded R 0.12. Anisotropic refinement gave R 0.066. In the final refinement the reflections were weighted according to the scheme $w = (0.674\,7 - 0.014\,47|F_o| + 0.001\,04|F|^2)^{-1}$ and the function minimised was $\Sigma w\Delta^2$ where $\Delta = |F_o| - |F_c|$. A difference-Fourier computed at this stage showed the positions of hydrogen atoms. In a final cycle of refinement, positions and isotropic temperature factors for hydrogens were allowed to vary. Final discrepancy indices R of 0.060 and R' of 0.081 were obtained. Scattering factors were those used for (I). Computer programmes used in the structure determinations have been listed elsewhere.[12,13] Final atomic co-ordinates with estimated standard deviations are given in Table 3.

TABLE 3

Final atomic co-ordinates (fractional $\times 10^4$) and hydrogen-atom thermal parameters ($B_{iso}/\text{Å}^2$) for [Pd(SCN)$_2$-{P(OPh)$_3$}$_2$] (II)

	x	*y*	*z*	
Pd	0	0	0	
S	2 133(2)	675(2)	−180(1)	
P	848(1)	548(2)	1 229(1)	
O(1)	540(5)	−494(5)	1 771(2)	
O(2)	2 495(4)	851(5)	1 534(2)	
O(3)	208(4)	1 860(5)	1 456(2)	
N	2 241(10)	3 358(8)	273(5)	
C(1)	2 171(7)	2 250(8)	94(4)	
C(11)	716(6)	−1 862(2)	1 681(3)	
C(12)	1 890(8)	−2 374(7)	1 532(4)	
C(13)	1 998(9)	−3 712(8)	1 454(5)	
C(14)	939(9)	−4 571(8)	1 524(5)	
C(15)	−222(8)	−4 036(8)	1 671(4)	
C(16)	−360(7)	−2 683(7)	1 748(3)	
C(21)	3 138(6)	1 492(7)	2 222(3)	
C(22)	3 435(7)	773(8)	2 857(4)	
C(23)	4 070(9)	1 432(10)	3 513(4)	
C(24)	4 406(8)	2 756(10)	3 524(4)	
C(25)	4 142(8)	3 443(9)	2 874(5)	
C(26)	3 495(7)	2 824(8)	2 199(4)	
C(31)	−1 253(6)	2 206(6)	1 150(3)	
C(32)	−1 589(8)	3 063(8)	583(4)	
C(33)	−3 026(9)	3 502(9)	280(5)	
C(34)	−3 998(8)	3 023(9)	625(6)	
C(35)	−3 617(8)	2 153(10)	1 187(5)	
C(36)	−2 203(7)	1 735(8)	1 480(4)	
H(12)	281(12)	−180(11)	152(6)	9(3)
H(13)	248(12)	−413(12)	125(6)	8(3)
H(14)	114(11)	−559(11)	139(5)	7(2)
H(15)	−99(12)	−463(11)	159(6)	10(3)
H(16)	−123(10)	−220(9)	179(5)	6(2)
H(22)	318(9)	−8(7)	286(4)	4(2)
H(23)	425(11)	88(11)	396(6)	8(2)
H(24)	492(11)	346(10)	396(6)	8(2)
H(25)	425(11)	419(11)	289(6)	8(3)
H(26)	320(9)	320(9)	173(5)	5(2)
H(32)	−97(10)	338(9)	32(5)	7(2)
H(33)	−340(10)	392(9)	−15(5)	6(2)
H(34)	−486(14)	333(13)	39(8)	18(4)
H(35)	−426(13)	174(11)	144(7)	12(3)
H(36)	−196(11)	131(10)	181(6)	7(3)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[11] (*a*) 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, pp. 201—227; (*b*) R. F. Stewart, G. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[12] N. J. Taylor, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J.C.S. Dalton*, 1975, 438.

[13] N. J. Taylor, S. E. Jacobson, and A. J. Carty, *Inorg. Chem.*, 1975, **14**, 2648.

DISCUSSION

Bond lengths and angles for (I) are given in Table 4 and for (II) in Table 5. Figures 1 and 2 are perspec-

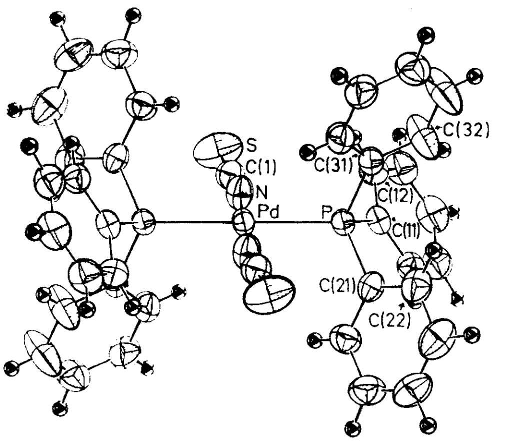

FIGURE 1 A perspective view of the structure of *trans*-$[Pd(NCS)_2(PPh_3)_2]$ (I) showing the atom numbering system used. Hydrogen atoms are numbered according to the carbon atoms to which they are attached

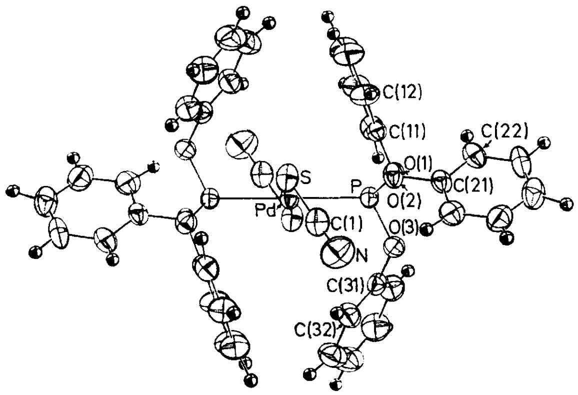

FIGURE 2 A view of the molecular structure of *trans*-$[Pd(SCN)_2\{P(OPh)_3\}_2]$ (II) similar to that of (I) in Figure 1

TABLE 4

Intramolecular bond lengths (Å) and angles (°) for $[Pd(NCS)_2(PPh_3)_2]$ (I)

Pd–P	2.340 4(9)	N–Pd–P	92.4(1)
Pd–N	1.969(3)	Pd–N–C(1)	170.9(2)
N–C(1)	1.138(6)	N–C(1)–S	178.8(2)
C(1)–S	1.621(5)	Pd–P–C(11)	117.3(1)
P–C(11)	1.813(4)	Pd–P–C(21)	110.8(1)
P–C(21)	1.817(4)	Pd–P–C(31)	111.1(1)
P–C(31)	1.826(4)	C(11)–P–C(21)	104.3(1)
		C(11)–P–C(31)	105.0(1)
		C(21)–P–C(31)	107.7(1)
Phenyl ring (1)			
C(11)–C(12)	1.401(6)	P–C(11)–C(12)	119.1(1)
C(12)–C(13)	1.381(7)	P–C(11)–C(16)	121.4(1)
C(13)–C(14)	1.380(8)	C(16)–C(11)–C(12)	119.5(2)
C(14)–C(15)	1.380(7)	C(11)–C(12)–C(13)	119.7(2)
C(15)–C(16)	1.381(6)	C(12)–C(13)–C(14)	120.3(2)
C(16)–C(11)	1.390(6)	C(13)–C(14)–C(15)	120.3(3)
C(12)–H(12)	0.96(5)	C(14)–C(15)–C(16)	120.1(2)
C(13)–H(13)	0.93(6)	C(15)–C(16)–C(11)	120.1(2)
C(14)–H(14)	0.96(5)		
C(15)–H(15)	1.00(5)		
C(16)–H(16)	0.99(4)		
Phenyl ring (2)			
C(21)–C(22)	1.383(7)	P–C(21)–C(22)	122.9(2)
C(22)–C(23)	1.410(8)	P–C(21)–C(26)	117.5(1)
C(23)–C(24)	1.373(9)	C(26)–C(21)–C(22)	119.6(2)
C(24)–C(25)	1.376(9)	C(21)–C(22)–C(23)	118.9(3)
C(25)–C(26)	1.392(7)	C(22)–C(23)–C(24)	121.0(3)
C(26)–C(21)	1.398(6)	C(23)–C(24)–C(25)	120.3(3)
C(22)–H(22)	0.96(4)	C(24)–C(25)–C(26)	119.4(3)
C(23)–H(23)	1.04(6)	C(25)–C(26)–C(21)	120.8(2)
C(24)–H(24)	0.96(5)		
C(25)–H(25)	0.99(5)		
C(26)–H(26)	1.01(5)		
Phenyl ring (3)			
C(31)–C(32)	1.373(7)	P–C(31)–C(32)	122.0(2)
C(32)–C(33)	1.384(9)	P–C(31)–C(36)	120.1(2)
C(33)–C(34)	1.341(8)	C(36)–C(31)–C(32)	117.9(3)
C(34)–C(35)	1.355(7)	C(31)–C(32)–C(33)	120.1(3)
C(35)–C(36)	1.387(7)	C(32)–C(33)–C(34)	121.5(3)
C(36)–C(31)	1.368(6)	C(33)–C(34)–C(35)	119.2(3)
C(32)–H(32)	0.99(6)	C(34)–C(35)–C(36)	120.1(2)
C(33)–H(33)	0.85(7)	C(35)–C(36)–C(31)	121.1(2)
C(34)–H(34)	1.04(6)		
C(35)–H(35)	0.96(6)		
C(36)–H(36)	0.86(5)		

TABLE 5

Intramolecular bond lengths (Å) and angles (°) for $[Pd(SCN)_2\{P(OPh)_3\}_2]$ (II)

Pd–S	2.352(2)	S–Pd–P	91.6(0)
Pd–P	2.312(2)	Pd–S–C(1)	99.2(0)
S–C(1)	1.672(8)	Pd–S–O(1)	116.0(1)
P–O(1)	1.590(5)	Pd–P–O(2)	115.6(1)
P–O(2)	1.583(5)	Pd–P–O(3)	116.1(1)
P–O(3)	1.594(5)	P–O(1)–C(11)	120.7(2)
O(1)–C(11)	1.407(7)	P–O(2)–C(21)	123.0(2)
O(2)–C(21)	1.432(7)	P–O(3)–C(31)	122.1(2)
O(3)–C(31)	1.422(8)	S–C(1)–N	177.3(4)
N–C(1)	1.16(1)	O(1)–P–O(2)	105.6(2)
		O(1)–P–O(3)	100.6(2)
		O(2)–P–O(3)	100.8(2)
Phenyl ring (1)			
C(11)–C(12)	1.38(1)	O(1)–C(11)–C(12)	122.6(3)
C(12)–C(13)	1.37(1)	O(1)–C(11)–C(16)	116.9(3)
C(13)–C(14)	1.38(1)	C(12)–C(11)–C(16)	120.5(4)
C(14)–C(15)	1.38(1)	C(11)–C(12)–C(13)	119.2(4)
C(15)–C(16)	1.37(1)	C(12)–C(13)–C(14)	121.3(4)
C(16)–C(11)	1.39(1)	C(13)–C(14)–C(15)	118.4(4)
C(12)–H(12)	1.09(12)	C(14)–C(15)–C(16)	121.7(4)
C(13)–H(13)	0.83(12)	C(15)–C(16)–C(11)	118.9(4)
C(14)–H(14)	1.10(11)		
C(15)–H(15)	0.95(12)		
C(16)–H(16)	1.03(10)		
Phenyl ring (2)			
C(21)–C(22)	1.38(1)	O(2)–C(21)–C(22)	120.0(3)
C(22)–C(23)	1.39(1)	O(2)–C(21)–C(26)	117.0(3)
C(23)–C(24)	1.36(1)	C(22)–C(21)–C(26)	123.0(4)
C(24)–C(25)	1.39(1)	C(21)–C(22)–C(23)	117.8(4)
C(25)–C(26)	1.40(1)	C(22)–C(23)–C(24)	121.6(4)
C(22)–H(22)	0.90(7)	C(23)–C(24)–C(25)	119.5(6)
C(23)–H(23)	1.01(11)	C(24)–C(25)–C(26)	121.3(4)
C(24)–H(24)	1.10(10)	C(25)–C(26)–C(21)	116.8(4)
C(25)–H(25)	0.77(11)		
C(26)–H(26)	0.95(8)		
Phenyl ring (3)			
C(31)–C(32)	1.35(1)	O(3)–C(31)–C(32)	117.2(3)
C(32)–C(33)	1.42(1)	O(3)–C(31)–C(36)	118.7(3)
C(33)–C(34)	1.41(1)	C(32)–C(31)–C(36)	123.9(4)
C(34)–C(35)	1.36(1)	C(31)–C(32)–C(33)	119.2(4)
C(35)–C(36)	1.39(1)	C(32)–C(33)–C(34)	117.0(4)
C(36)–C(31)	1.38(1)	C(33)–C(34)–C(35)	121.8(4)
C(32)–H(32)	0.97(10)	C(34)–C(35)–C(36)	120.6(5)
C(33)–H(33)	0.91(9)	C(35)–C(36)–C(31)	117.4(3)
C(34)–H(34)	0.88(14)		
C(35)–H(35)	1.01(12)		
C(36)–H(36)	0.74(10)		

tive drawings of the molecular structures. For each complex the crystal consists of discrete molecules. The shortest inter- and intra-molecular contacts are tabulated in Tables 6 and 7. All intermolecular distances are larger than the corresponding sums of van der Waals radii and are not therefore considered structurally significant.

TABLE 6

Some inter- and intra-molecular contacts (Å) for (I)

(*a*) Intermolecular			
S ··· H(24)	3.12(5)	H(14) ··· H(24)	2.95(7)
S ··· H(25)	3.47(6)	H(14) ··· H(25)	2.66(7)
S ··· H(34)	3.20(6)	H(16) ··· H(26)	2.75(7)
N ··· H(25)	3.24(6)	H(16) ··· H(35)	2.75(7)
C(1) ··· H(24)	3.49(6)	H(16) ··· H(36)	2.91(7)
C(1) ··· H(25)	3.06(6)	H(23) ··· H(35)	2.91(8)
C(1) ··· H(36)	3.07(5)	H(26) ··· H(26)	2.96(7)
		C(22) ··· H(35)	2.91(8)
		C(23) ··· H(35)	2.74(7)
(*b*) Intramolecular			
Pd ··· H(26)	2.23(5)	N ··· H(26)	3.35(5)
Pd ··· H(36)	3.11(5)	N ··· H(36)	2.75(5)
P ··· N	3.121(4)	C(1) ··· H(12)	3.14(4)
P ··· N	2.994(4)	C(1) ··· H(36)	3.07(5)
P ··· H(12)	2.90(4)	C(21) ··· H(16)	2.54(5)
P ··· H(16)	2.91(4)	C(26) ··· H(16)	2.70(5)
P ··· H(22)	2.93(5)	C(31) ··· H(22)	2.74(5)
P ··· H(26)	2.85(5)	C(32) ··· H(22)	2.96(5)
P ··· H(32)	2.90(6)	C(16) ··· H(26)	2.93(5)
P ··· H(36)	2.83(5)	C(11) ··· H(32)	2.64(5)
N ··· H(12)	2.99(4)	C(12) ··· H(32)	2.79(5)

TABLE 7

Some inter- and intra-molecular contacts (Å) in (II)

(*a*) Intermolecular			
N ··· H(13)	3.13(12)	H(14) ··· H(26)	2.30(14)
N ··· H(14)	2.92(11)	H(14) ··· H(32)	2.64(14)
N ··· H(33)	3.02(9)	H(15) ··· H(22)	2.74(15)
N ··· H(34)	2.81(14)	H(23) ··· H(33)	2.43(14)
H(12) ··· H(24)	2.71(16)	H(23) ··· H(34)	2.74(17)
H(12) ··· H(25)	2.95(16)	H(23) ··· H(34)	2.84(17)
H(13) ··· H(26)	2,87(15)	H(25) ··· H(35)	2.88(16)
(*b*) Intramolecular			
S ··· H(16)	3.33(9)	O(1) ··· H(12)	2.78(12)
C(1) ··· H(16)	3.47(9)	O(1) ··· H(16)	2.47(10)
C(1) ··· H(26)	3.15(9)	O(1) ··· H(22)	2.82(9)
C(1) ··· H(32)	3.47(10)	O(2) ··· H(12)	2.70(11)
N ··· H(26)	2.68(9)	O(2) ··· H(22)	2.61(8)
N ··· H(32)	3.21(10)	O(2) ··· H(26)	2.47(9)
P ··· S	3.251(2)	O(3) ··· H(32)	2.63(9)
P ··· S	3.344(2)	O(3) ··· H(36)	2.51(11)
(*c*) Interligand (intramolecular)			
H(13) ··· H(32)	3.03(15)	H(12) ··· H(22)	3.04(13)
H(13) ··· H(33)	2.58(15)		

In both complexes the palladium atom is located on a crystallographic inversion centre. Hence the co-ordination polyhedra are strictly planar. The thiocyanate ion is co-ordinated to palladium *via* nitrogen in (I) but *via* sulphur in (II). The N–Pd–P and S–Pd–P angles [92.4(1)° in (I) and 91.6(2)° in (II)] differ only slightly from the ideal value of 90° for square-planar geometry.

Metal–Ligand Distances and π-Bonding.—The Pd–P distance [2.3404(9) Å] in (I) is very significantly longer ($\underset{\sigma}{\triangleq}$ 28) than that in (II) [2.312(1) Å]. Indeed the Pd–P bond length in (I) is the longest yet reported for a *trans*-palladium complex.[7,13] For comparison, Pd–P distances of 2.331(2) Å in *trans*-[PdI$_2$(PPh$_3$)$_2$],[14] 2.308(4) (mean) in *trans*-[Pd(H)Cl(PEt$_3$)$_2$],[15] 2.333(7) and 2.330(8) (mean) in the yellow and red isomers[16] of *trans*-[PdI$_2$(PMe$_2$Ph)$_2$], and 2.326(3) Å for *trans*-[Pd(SCN)$_2$(Ph$_2$PC$_2$Bu^t)$_2$],[8] have been reported. The shorter Pd–P bonds in (II) could be ascribed to one, or a combination, of the following effects: (*a*) increased π-acceptor ability of triphenyl phosphite compared to triphenylphosphine (*b*) reduced non-bonded repulsions (steric effects) in the phosphite complex compared to the triphenylphosphine derivative, and (*c*) a lower *trans* bond-lengthening influence for triphenyl phosphite compared to triphenylphosphine. The separation of π-bonding and steric effects is difficult owing to the different bonding modes of the thiocyanate ion in the two complexes. However, several other observations lend qualitative support to the interpretation that a combination of effects (*b*) and (*c*) is dominant in the present case. Precise comparison of Pd–P bond lengths in the three complexes [Pd(NCS)$_2$(PPh$_3$)$_2$], [Pd(SCN)$_2$(Ph$_2$PC$_2$Bu^t)$_2$],[8] and [Pd(SCN)$_2${P(OPh)$_3$}$_2$] shows a gradual and significant decrease [2.3404(9), 2.326(3), and 2.312(1) Å] as the cone angle of the phosphorus ligands changes from 145° for PPh$_3$ through 135° for $\mathrm{Ph_2P{\cdot}C{\vdots}C{\cdot}Bu^t}$, to 121° for P(OPh)$_3$. By contrast, the group $\mathrm{{\cdot}C{\vdots}CBu^t}$ is expected to be less electron-withdrawing than Ph, hence Ph$_2$PC$_2$Bu^t is unlikely to be a significantly better π-acceptor than PPh$_3$.

The decrease in Pd–P distance for [Pd(SCN)$_2${P(OPh)$_3$}$_2$] compared to [Pd(NCS)$_2$(PPh$_3$)$_2$] (Δ 0.0284 Å) is considerably smaller than the corresponding change (Δ 0.113 Å) for the compounds [LCr(CO)$_5$] [L = PPh$_3$ or P(OPh)$_3$] where the shorter Cr–P(phosphite) distance has been attributed to greater π-bonding to the phosphite.[17] It is clear that the observed correlation of Pd–P bond length with ligand bulk for the PPh$_3$, $\mathrm{Ph_2P{\cdot}C{\vdots}CBu^t}$, and P(OPh)$_3$ palladium complexes together with the small overall decrease in Pd–P bond lengths compared to the chromium case and the known orders of *trans*-influence for phosphines and phosphites (*vide infra*) leaves little necessity to invoke π-bonding changes. In order to illustrate pictorially the different steric requirements of triphenylphosphine and triphenyl phosphite, ORTEP II plots of the structures, viewed along the P–Pd–P axes, are shown in Figure 3. These plots, together with Figures 1 and 2 demonstrate the relative facility with which two bent $\mathrm{Pd{-}S{-}C{\equiv}N}$ moieties can be arranged within the environment created by two co-ordinated triphenyl phosphite ligands. Conversely, the incompatibility of the Pd(PPh$_3$)$_2$ framework for two bent $\mathrm{Pd{-}S{-}C{\equiv}N}$ moieties can also be appreciated.

There is now a substantial body of ^{31}P n.m.r. coupling-constant data to support the view that M–P d_π–d_π bonding in Pt$^{\mathrm{II}}$ and, by implication, Pd$^{\mathrm{II}}$ phosphine complexes

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[14] T. Debaerdemaker, A. Kutoglu, G. Schmid, and L. Weber, *Acta Cryst.*, 1973, **B29**, 1283.

[15] M. L. Schneider and H. M. N. Shearer, *J.C.S. Dalton*, 1973, 354.

[16] N. A. Bailey and R. Mason, *J. Chem. Soc.* (*A*), 1968, 2594.

[17] H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, 1972, **11**, 160.

is minimal.[2] Variations in the magnitudes of ^1J(P–M) can be adequately explained without resorting to π-bonding. Furthermore metal–phosphorus bond lengths are correlated with the magnitude of ^1J(M–P), the stronger (shorter) bonds corresponding to the larger couplings.[18] It is unfortunately not possible to compare directly ^1J(Pt–P) in *trans*-[PtX$_2$(PPh$_3$)$_2$] and *trans*-[PtX$_2${P(OPh)$_3$}$_2$] since the terms $|S_P(0)|^2$ and $P'(S_PS_{Pt})^2$ in the coupling constant expression are sensitive to changes of substituents on phosphorus. However ^1J(Pt–PBu$_3$) is larger in *trans*-[PtCl$_2$(PBu$_3$){P(OPh)$_3$}] than in *trans*-[PtCl$_2$(PBu$_3$)$_2$],[19] a fact consistent with a strengthening of the Pt–PBu$_3$ bond on substitution of one phosphine by P(OPh)$_3$ but hardly compatible with π-bonding arguments since phosphite and phosphine compete for the same metal d_π orbitals. The coupling-constant data agree with a reduced *trans* bond-lengthening influence operating *via* a σ mechanism or *via* reduced steric pressure in the complex as PBu$_3$ is substituted by P(OPh)$_3$. The lower *trans*-influence of P(OR)$_3$ compared to PR$_3$ (R = alkyl or aryl) is also apparent from metal–halogen stretching frequencies.[20] Conclusive evidence that steric effects can indeed influence metal–bond strengths has recently been obtained from calorimetric enthalpies of platinum–ligand bond formation in *trans*-[MePt(PMe$_2$Ph)$_2$L]$^+$[PF$_6$]$^-$ complexes (L = phosphorus donor).[21] Moreover for phosphines of the same size, increased substituent electronegativity decreased ΔH for Pt–L bond formation, a result contrary to π-bonding arguments. In view of the foregoing results, the shorter Pd–P bond lengths in (II) are best ascribed to a combination of ligand size and σ-*trans* influence effects. These effects will not in general be separable even when *X*-ray data are available.

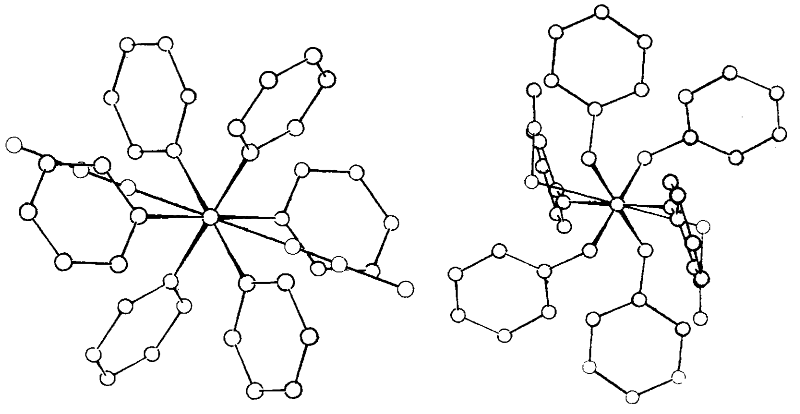
(a) (b)

FIGURE 3 A comparison of ligand stereochemistry in (a) (I) and (b) (II) as viewed along the P–Pd–P axes

The Pd–N distance [1.969(3) Å] in (I) appears to be the first reported value for a di-isothiocyanate complex of palladium. As expected from the relatively low position of NCS$^-$ in the *trans*-influence series, this bond length is *ca.* 0.09 Å shorter than the mean Pd–NCS (*trans* to phosphorus) distance in the compounds [Pd(SCN)(NCS)(Ph$_2$P·[CH$_2$]$_3$·NMe$_2$)],[22] [Pd(SCN)(NCS){Ph$_2$P[CH$_2$]$_2$·PPh$_2$}],[7] and [Pd(NCS)$_2$(Ph$_2$P·[CH$_2$]$_3$·PPh$_2$)].[7] If this bond shortening is compared with the difference (0.08 Å) between the mean Pd–P bond length, *trans* to phosphorus in (II) [2.312(1) Å)], (I) [2.3404(9) Å], *trans*-[Pd(SCN)$_2$(Ph$_2$P·C:CBu^t)$_2$] [2.326(3) Å],[8] and *trans*-[Pd(SCN)$_2${P(C$_6$F$_5$)Me$_2$}$_2$] [2.318(1) Å],[7] and *trans* to nitrogen in [Pd(NCS)$_2$(Ph$_2$P·[CH$_2$]$_3$·PPh$_2$)] [2.241(1) Å],[7] [Pd(SCN)(NCS)(Ph$_2$P·[CH$_2$]$_2$·PPh$_2$)] [2.243(1) Å],[7] [Pd(SCN)(NCS)(Ph$_2$P·[CH$_2$]$_3$·NMe$_2$)] [2.243(2) Å],[22] and [Pd$_2$(SCN)$_2${(Ph$_2$PO)$_2$H}$_2$] [2.247(2) Å],[23] it can be seen that there is evidently a remarkable consistency in the mutual *trans* bond-lengthening influences of phosphine and isothiocyanate ligands. Considering now the Pd–S distances in (II) [2.352(2) Å] and related *trans*-thiocyanates a mean of 2.348 Å is obtained for Pd–S *trans* to thiocyanate. The mean Pd–S bond length *trans* to phosphorus in thiocyanates [7,8,13] is 2.366 Å, showing that a phosphine has a stronger labilising influence than the sulphur atom of a thiocyanate group. It is interesting that for the known thiocyanate complexes, a comparison of mean Pd–P (*trans* to P) (2.324 Å) and Pd–S (*trans* to S) (2.348 Å) distances with the Pd–Cl (*trans* to Cl) bond length [2.291(1) Å)] in *trans*-[PdCl$_2${Ph$_2$P·CH:C(Cl)·CF$_3$}$_2$] [13] suggests that Pd–S distances in the dithiocyanato-complexes are anomalously long if the expected *trans*-influence series is R$_3$P > SCN$^-$ > Cl$^-$ and the covalent radii P (1.10 Å), S (1.04 Å), and Cl (0.99 Å). This result appears incompatible with a significant π-contribution to Pd–S bonding. A further feature of these bond lengths is the significant increase in Pd–S distance from 2.336(3) Å in *trans*-[Pd(SCN)$_2$(Ph$_2$P·C:CBu^t)$_2$] [8] to 2.352(2) Å in (II)

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[18] G. G. Mather, A. Pidcock, and G. J. N. Rapsey, *J.C.S. Dalton*, 1973, 2095.

[19] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

[20] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 3674.

[21] L. E. Manzer and C. A. Tolman, *J. Amer. Chem. Soc.*, 1975, **97**, 1955.

[22] G. R. Clark and G. L. Palenik, *Inorg. Chem.*, 1970, **9**, 2754.

[23] D. V. Naik, G. J. Palenik, S. E. Jacobson, and A. J. Carty, *J. Amer. Chem. Soc.*, 1974, **96**, 2286.

as the Pd–P distance decreases from 2.326(3) to 2.312(1) Å. These observations suggest a ' push–pull ' mechanism for retaining the same electron density on the metal and the same non-bonded repulsions within the co-ordination sphere.

The Ligands.—(*a*) Triphenylphosphine. The mean P–C distance in (I) (1.819 Å) compares favourably with reported P–C(sp^2) distances,[24] as do Pd–P–C and C–P–C angles, and distances and angles in the phenyl rings. The intraligand contacts (Table 6) show that the propeller conformation of the ligands is dictated by C · · · H rather than H · · · H non-bonded interactions. The shortest C–H contact C(21)–H(16) (2.54 Å) is considerably less than the sum of van der Waals radii for hydrogen (1.10—1.30 Å) and carbon (1.70 Å).

(*b*) *Triphenyl phosphite.* The P–O distances (mean 1.589 Å) in (II) are marginally shorter than in *trans*-$[Cr(CO)_4\{P(OPh)_3\}_2]$ (mean 1.604 Å) [25] and $[Cr(CO)_5\{P(OPh)_3\}]$ (1.598 Å) [17] whereas the C–O bonds (mean 1.420 Å) are somewhat longer than in the chromium complexes (means 1.403 and 1.397 Å). As expected from the cone angles [$P(OPh)_3$ 121 ± 10, PPh_3 145 ± 2°] [3] the C–P–O angles in (II) (mean 102.3°) are smaller than the C–P–C angles (mean 105.6°) in (I). The short contacts between the oxygen atoms of the phosphite and *ortho*-hydrogen atoms of the phenyl rings [O(1)–H(16) 2.47(10), O(2)–H(26) 2.47(9), and O(3)–H(36) 2.51(11) Å] are presumably important in determining the ligand conformation.

(*c*) *Thiocyanate groups.* In (I) the co-ordinated ion is almost linear [N–C–S 178.8(2)°] with the Pd–N–C angle [170.9(2)°] lying in the middle of the range of M–N–C angles for isothiocyanates.[7,8] In contrast, co-ordination *via* sulphur in (II) produces a Pd–S–C(4) bond angle of 99.2° a value similar to that in *trans*-$[Pd(SCN)_2(Ph_2PC{:}CBu^t)_2]$.[8] The C–S bond lengths [1.621(5) and 1.672(8) Å] in the phosphine and phosphite complexes emphasise the contributions of resonance forms Pd·N⁚C⁚S and Pd·S·C⁝N respectively to the thiocyanate bonding in these compounds.

A basic assumption of the π-bonding hypothesis originally suggested by Turco and Pecile [5a] to explain the apparent antisymbiotic behaviour exhibited by Pd^{II} in binding the ' hard ' nitrogen end of the thiocyanate ion in the phosphine complex $[Pd(NCS)_2(PEt_3)_2]$, is that phosphines monopolise π-bonding to palladium to such an extent that Pd–S interactions are disfavoured over Pd–NCS bonding. In the absence of strong competing π-bonding ligands, Pd–S bonding is preferred, as for example in $[Pd(SCN)_2(NH_3)_2]$.[4] This theory necessarily presupposes a significant π-component in Pd–P and Pd–S bonds and predicts that the greater the π-acceptor ability of the phosphorus ligands the greater the extent of Pd–NCS bonding. Since triphenyl phosphite is widely accepted as having a greater π-acid character than triphenylphosphine, the presence of *S*-bonded thiocyanate groups in (II) is contrary to the hypothesis. Furthermore, as pointed out earlier, an analysis of Pd–P and Pd–S bond lengths provides no firm evidence for significant metal–ligand π-bonding.

An indication that Pd–SCN bonding in the triphenylphosphine complex may be disfavoured, in the solid state, for steric reasons is apparent from an analysis of intramolecular contacts in the phosphine and phosphite structures. For (I) there are only two interactions between *ortho*-hydrogen atoms and the co-ordinated NCS group of <3.0 Å. These distances [H(36)–N 2.75, and H(12)–N of 2.99 Å] are similar to the van der Waals radii sum for hydrogen (1.10—1.30 Å) and nitrogen (1.55 Å) and are clearly not of major significance. To investigate the effects of a change to Pd–SCN bonding, while retaining exactly the same ligand stereochemistry we calculated non-bonded contacts for a model $[Pd(S)_2(PPh_3)_2]$ having Pd–S distances of 2.352 Å, the same as in (II). With this model, three significant S · · · H interactions are present for each SCN group, namely H(12) · · · S 2.94 Å, H(25) · · · S 3.09, and H(36) · · · S 2.84 Å. Since the van der Waals radius of sulphur is 1.80 Å these contacts would be significantly more repulsive than the corresponding H · · · N interactions in the isothiocyanate. By contrast, in (II) the shortest S · · · H contact is to H(16) (3.33 Å). Additionally the presence of bulky PPh_3 ligand proximate to *S*-bonded thiocyanate groups in the hypothetical compound $[Pd(SCN)_2(PPh_3)_2]$ would necessarily result in a loss of rotational freedom for the thiocyanate owing to the non-linear, sterically demanding, Pd–S–C–N moiety. This can be readily appreciated from Figure 1. These factors, and not π-bonding, are most likely responsible for the observed bonding modes.

We thank the National Research Council of Canada for financial support of this work.

[5/995 *Received*, 28*th May*, 1975]

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[24] J. J. Daly, *Perspectives in Structural Chem.*, 1970, **3**, 165.

[25] H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 1973, **12**, 265.