Synthesis, Crystal Structure, and Infrared Spectra of *trans*-Dithiocyanato-bis-[(3,3-dimethylbutynyl)diphenylphosphine]palladium(II)

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The syntheses, and solid-state and i.r. spectra of three isomers of formula $Pd(CNS)_2(Ph_2P{\cdot}C{\vdots}CBu^t)_2$ are described. The *trans*-isomer (Ic) can be prepared from either of two *cis*-isomers (Ia) and (Ib) by recrystallisation in non-polar solvents. (Ia) contains both Pd–N and Pd–S thiocyanate bonds. *X*-Ray structure analysis of (Ic) revealed monoclinic crystals with $a = 12{\cdot}563(4)$, $b = 10{\cdot}460(3)$, $c = 14{\cdot}781(4)$ Å, $\beta = 97{\cdot}8(5)°$, $Z = 2$, space group $P2_1/c$. The structure was determined by the heavy-atom method and refined by least squares to R 0·069 for 2321 observed diffractometer data. Both thiocyanate groups are *S*-bonded. There is a centre of symmetry with Pd–P 2·326(3) and Pd–S 2·336(3) Å; P–Pd–S is 93·7(3)°. Previous explanations for the predominance of *N*-bonded CNS^- in Pd^{II} phosphine complexes emphasising the role of π bonding are incompatible with the present work. Factors influencing the mode of bonding of CNS^- in these systems are discussed. The use of i.r. and far-i.r. spectroscopy in predicting Pd–NCS, Pd–SCN, and ' mixed ' bonding is assessed.

WE have previously characterised[1] a palladium complex * $[Pd(CNS)_2(Ph_2P{\cdot}C{\vdots}C{\cdot}PPh_2)]_2$ which appeared, from physical measurements to be one of a relatively small group of complexes having both *N*- and *S*-bonded thiocyanate groups.[2] Subsequently a number of *cis*-palladium thiocyanate complexes with chelating bidentate ligands were synthesised.[3] *X*-Ray crystal structure

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* Throughout this paper M(SCN) denotes an *S*-bonded thiocyanate ion and M(NCS) an *N*-bonded ion; M(CNS) is used when no specific interaction is implied.

[1] A. J. Carty and A. Efraty, *Canad. J. Chem.*, 1969, **47**, 2573.

[2] P. Nipcon and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 145.

[3] D. W. Meek, P. E. Nipcon, and V. I. Meek, *J. Amer. Chem. Soc.*, 1970, **92**, 5331.

determinations on *cis*-$\mathrm{Pd(NCS)(SCN)(Ph_2P{\cdot}[CH_2]_3{\cdot}NMe_2)}$ [4] and *cis*-$\mathrm{Pd(NCS)(SCN)(Ph_2P{\cdot}[CH_2]_2{\cdot}PPh_2)}$ [5] have since confirmed the presence of mixed thiocyanate bonding in these complexes. Before this, complexes of the type $\mathrm{Pd(CNS)_2L_2}$ (L = tertiary phosphine) were known to exist in the solid state only in the isothiocyanato-form.[6,7] The various explanations [7,8] for the predominance of *N*-bonded $\mathrm{CNS^-}$ groups in square planar palladium(II) phosphine complexes have a common origin in the π bonding hypothesis of Turco and Pecile [6] although there is an apparent conflict of opinion regarding the 'hardness' [7] or 'softness' [8] (in the Pearson sense) of the $\mathrm{PdL_2^{2+}}$ moiety. Thus the observation of mixed thiocyanate bonding in the diphosphine complexes suggested a re-examination of factors influencing the bonding mode of the $\mathrm{CNS^-}$ ion in $\mathrm{Pd(CNS)_2L_2}$ systems. More recently *X*-ray studies of the complexes *cis*-$\mathrm{Pd(CNS)_2(Ph_2P{\cdot}[CH_2]_{\mathit{n}}{\cdot}PPh_2)}$ (n = 1—3) have conclusively demonstrated the role of steric effects in dictating the mode of bonding of the $\mathrm{CNS^-}$ ion to palladium.[9] With $n = 1$ the P–Pd–P angle is 73·24(7) and both $\mathrm{CNS^-}$ ions are *S*-bonded. For $n = 2$, P–Pd–P is 85·1(1)°, and mixed bonding occurs, and for $n = 3$, P–Pd–P is 89·31(5)° and both $\mathrm{CNS^-}$ ions are *N*-bonded. Our studies with alkynylphosphines of the types $\mathrm{Ph_2PC{\vdots}CPR_2}$ and $\mathrm{Ph_2PC{\vdots}CR}$,[10] particularly the synthesis of a wide range of *cis*-$\mathrm{PdX_2L_2}$ (X = Cl or Br, L = alkynylphosphine) and $\mathrm{Ni(CO)L_3}$ complexes indicated that replacement of R in $\mathrm{Ph_2RP}$ (R = alkyl or aryl) by $\mathrm{-C{\vdots}CR}$ effectively reduced the steric demand of these phosphines since there are no α or β hydrogen atoms on the acetylene substituent. It was therefore of interest to determine whether mixed thiocyanate or even completely *S*-bonded palladium(II) complexes of unidentate phosphines could be synthesised with ligands having low steric requirements. We describe herein a novel isomerism involving the complexes *cis*-$\mathrm{Pd(NCS)(SCN)(Ph_2PC{\vdots}CBu^t)_2}$ and *trans*-$\mathrm{Pd(SCN)_2(Ph_2PC{\vdots}CBu^t)_2}$ as well as an *X*-ray structural determination of the *trans*-isomer, the first purely *S*-bonded palladium(II) complex of a unidentate phosphine to have been synthesised and structurally characterised. Our results indicate that contrary to previous assertions, palladium(II) prefers the sulphur-bonded $\mathrm{CNS^-}$ ion, provided steric constraints are minimal. The complete *X*-ray structure of *cis*-$\mathrm{Pd(NCS)(SCN)(Ph_2PC{\vdots}CBu^t)_2}$ will be described elsewhere.[11]

EXPERIMENTAL

I.r. spectra were measured on Beckmann IR 9 and Perkin-Elmer 180 i.r. spectrophotometers. Solid-state spectra were obtained on Nujol mulls between caesium iodide windows. Solution spectra were measured in matched silver chloride cells of pathlength 0·5 mm. Integrated intensity measurements were made on a Beckman IR 9 as described in the literature.[12] The ligand $\mathrm{Ph_2P{\cdot}C{\vdots}CBu^t}$ was synthesised as previously described.[13]

Preparation of Complexes.—$\mathrm{K_2Pd(SCN)_4}$ (0·42 g) in ethanol (100 ml) was added to $\mathrm{Ph_2PC{\vdots}CBu^t}$ (0·53 g) in ethanol (25 ml) and the mixture stirred for 12 h. The volume of the filtered solution was reduced by evaporation and orange-yellow crystals (Ia) were obtained on cooling to 0° (Found: C, 60·8; H, 5·1. Calc. for $\mathrm{C_{38}H_{38}N_2P_2PdS_2}$: C, 60·5; H, 5·05%).

Recrystallisation of (Ia) from ethanol–dichloromethane–hexane afforded lemon-yellow crystals (Ib), shown by microanalyses to be an isomer of (Ia). The same lemon-yellow complex was obtained from *cis*-$\mathrm{PdCl_2(Ph_2{\cdot}P{\cdot}C{\vdots}CBu^t)_2}$ by metathesis with KSCN in acetone followed by recrystallisation from ethanol–dichloromethane (Found: C, 60·4; H, 5·15%).

The crystals (Ia) and (Ib) dissolved sparingly in hot cyclohexane and somewhat better in warm benzene. Cooled solutions in these solvents deposited large orange-yellow needles (Ic) during 2—3 days. Microanalysis again indicated this complex to have the same molecular formula as (Ia) and (Ib) (Found: C, 60·2; H, 5·1%).

Recrystallisation of (Ic) from ethanol–dichloromethane afforded only the lemon-yellow (Ib).

X-Ray Crystal Structure Analysis of (Ic)

Crystals of the orange-yellow isomer (Ic) are needles elongated along *b* with (101) and (10$\bar{1}$) planes developed. Unit-cell and space group data were obtained from rotation, Weissenberg, and precession photographs, cell constants being refined by least-squares methods from the 2θ (Mo-K_α) values measured on a General Electric XRD 6 diffractometer for 14 reflections.

Crystal Data.—$\mathrm{C_{38}H_{38}N_2P_2PdS_2}$, M = 755·2, Monoclinic a = 12·563(4), b = 10·460(3), c = 14·781(4) Å, β = 97·8(5)°, U = 1924·4 Å^3, D_m = 1·309, (by flotation), Z = 2, D_c = 1·303, $F(000)$ = 776. Space group $P2_1/c$. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 6·89 cm^{-1}.

4424 Reflections with $2\theta \leqslant 60°$ were measured on a General Electric XRD 6 automatic diffractometer by the stationary-crystal–stationary-counter technique. Of these 2321 having intensities greater than the background were considered to be observed, and were used in the structure analysis. The crystal used had dimensions 0·09 × 0·08 × 0·13 mm in [101], [10$\bar{1}$], and [010] directions and was mounted with b^* parallel to the φ axis of the goniostat. No absorption correction was made.

Structure Analysis.—As $Z = 2$ the palladium atom must occupy a special position. A three-dimensional Patterson map revealed the co-ordinates of the phosphorus and sulphur atoms. A Fourier map based on the phase calculated from the palladium, phosphorus, and sulphur atoms gave the location for the nitrogen and all carbon atoms, except for the three methyl carbon atoms which were located in a difference-Fourier synthesis.

The co-ordinates of the atoms, except those of palladium which are fixed by symmetry requirement, and individual isotropic temperature parameters for each atom were then refined by full-matrix least-square methods to R 0·13.

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[5] G. Beran and G. J. Palenik, *Chem. Comm.*, 1970, 1355.

[6] A. Turco and C. Pecile, *Nature*, 1961, **191**, 66.

[7] J. L. Burmeister and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1587.

[8] H. Norbury, *J. Chem. Soc.* (*A*), 1971, 1090.

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[11] G. Beran, A. J. Carty, P. C. Chieh, T. W. Ng, G. J. Palenik, and H. A. Patel, unpublished work.

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[13] A. J. Carty, N. K. Hota, T. W. Ng, T. J. O'Connor, and H. A. Patel, *Canad. J. Chem.*, 1971, **49**, 2706.

Anisotropic thermal parameters were then introduced for all atoms and R was reduced to 0·08; the hydrogen atoms of the two phenyl rings were then assumed to be at the theoretical positions, which all had positive electron density in a difference-Fourier map, with C–H 1·07 Å. Further refinement with the inclusion of an extinction coefficient, reduced R to 0·069. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $\sqrt{w} = (30{\cdot}0 + F_o + 0{\cdot}01\ F_o^2)^{-1}$. The weighted factor, R', was 0·095. The weighting scheme analyses based on ranges of F_o and sin θ/λ indicated that it was satisfactory (mean $w\Delta F^2$ varied from 0·08 to 0·18 and 0·09 to 0·16). Atomic scattering factors for all atoms were taken from ref. 14, with a correction for anomalous scattering for palladium. Final positional and thermal parameters are given in Table 1.*

RESULTS

I.r. Spectra and Characterisation.—The i.r. spectrum of the orange-yellow complex (Ia) in the region 2000—2200 cm^{-1} is shown in Table 2. This type of ν(C⋮N) spectrum, namely a broad band below <2100 and a sharp band at >2100 cm^{-1} is characteristic of complexes with mixed Pd(NCS)(SCN) bonding.[1,3,15] However, the appearance under high resolution of a doublet (at 2120, 2124 cm^{-1}) due

TABLE 1

Positional and thermal parameters (× 10^4, hydrogen atoms × 10^3) with standard deviations in parentheses

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23} †
Pd	0	0	0	48(1)	58(1)	39(1)	1(1)	13(1)	3(1)
P	−1807(2)	0506(3)	−0054(2)	37(2)	61(2)	34(1)	5(2)	12(1)	2(1)
S	0068(10)	0641(3)	−1505(2)	68(2)	117(4)	40(2)	13(2)	19(2)	16(2)
C	0030(10)	2186(13)	−1343(10)	75(9)	106(14)	78(8)	1(9)	25(8)	38(9)
C(10)	−2064(9)	1538(10)	0875(7)	47(7)	74(10)	50(6)	20(7)	4(5)	−9(6)
C(11)	−2930(11)	1325(14)	1347(9)	96(10)	111(15)	47(6)	11(12)	30(8)	4(10)
C(12)	−3102(14)	2212(18)	2033(9)	89(12)	207(23)	49(7)	48(14)	25(9)	−2(11)
C(13)	−2438(16)	3215(21)	2222(12)	20(15)	255(27)	63(9)	96(19)	9(12)	−20(13)
C(14)	−1607(14)	3428(17)	1779(12)	99(13)	173(21)	89(10)	20(17)	−30(12)	−59(15)
C(15)	−1379(12)	2592(13)	1092(9)	79(10)	128(15)	51(7)	24(11)	1(8)	−17(10)
N	0017(12)	3297(13)	−1256(12)	140(13)	109(14)	166(13)	−30(12)	59(13)	35(12)
C(20)	−2542(8)	1219(11)	−1063(7)	47(7)	93(11)	37(3)	15(8)	12(5)	7(7)
C(21)	−3048(12)	0464(14)	−1761(9)	108(13)	77(11)	49(7)	7(11)	−18(9)	−3(9)
C(22)	−3583(13)	1023(17)	−2544(10)	117(14)	166(21)	47(8)	−5(13)	−15(8)	−8(10)
C(23)	−3636(12)	2311(16)	−2636(10)	94(12)	157(20)	54(8)	−8(13)	−9(8)	2(10)
C(24)	−3165(11)	3089(12)	−1946(10)	83(10)	82(12)	76(8)	18(9)	14(6)	28(8)
C(25)	−2610(10)	2537(12)	−1172(8)	78(9)	93(13)	42(6)	−8(9)	−1(6)	−4(7)
C(1)	−2520(9)	−0897(10)	0054(8)	49(7)	67(10)	53(6)	9(7)	17(6)	9(6)
C(2)	−2997(9)	−1855(11)	0043(8)	58(8)	101(13)	44(6)	−3(9)	1(6)	4(8)
C(3)	−3651(11)	−3075(12)	−0004(9)	83(10)	101(13)	68(8)	−44(12)	−1(8)	−2(9)
C(4)	−4097(17)	−3298(20)	−1030(13)	171(20)	252(30)	80(12)	−68(20)	−28(13)	−4(16)
C(5)	−2597(18)	−4154(16)	0345(18)	175(22)	97(16)	212(21)	−17(16)	−74(20)	64(17)
C(6)	−4545(22)	−2900(24)	0540(20)	230(18)	296(28)	233(19)	187(30)	169(25)	−112(27)
		10^3							
H(11)	−338(11)	066(13)	113(8)	4·7 *					
H(12)	−380(12)	199(13)	218(10)	4·5					
H(13)	−266(13)	387(16)	266(11)	6·5					
H(14)	−124(11)	407(13)	192(9)	5·8					
H(15)	−080(10)	260(11)	061(8)	5·4					
H(21)	−290(9)	−048(13)	−171(8)	5·3					
H(22)	−379(12)	058(14)	−295(10)	4·2					
H(23)	−402(10)	248(12)	−306(8)	6·8					
H(24)	−331(9)	394(12)	−202(8)	8·2					
H(25)	−239(88)	311(10)	−068(8)	4·2					

* Isotropic thermal parameters not included in the refinement. † Anisotropic thermal parameters in the form exp $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}kl + 2\beta_{23}kl)$.

TABLE 2

ν(C⋮N) I.r. (cm^{-1}) spectra for solid state and solution

Isomer	Nujol	C_6H_6	CH_2Cl_2	MeCN	$CHCl_3$	Me_2CO	DMF	CCl_4
(Ia)	2124s,sp 2120s,sp 2089s,br	2122m,sp 2088s,br	2122s,sp 2088s,br	2123s,sp 2094s,br	2116s 2098s	2122w,sp 2094s,br 2086sh	2121m,sp 2094s,br	2120m,sp 2090s,br
(Ib) *	2125s,sp 2119s,sp 2090s,br							
(Ic) *	2116s,sp							

* The solution spectra are the same for all three isomers. Values are given only for (Ia). s = Strong, m = medium, w = weak, br = broad, sp = sharp.

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* Tables of observed and calculated structure factors are listed in Supplementary Publication No. SUP 20593 (3 pp., 1 microfiche). For details of Supplementary Publications see *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are sent as full-size copies).

[14] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1968.

[15] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.

to the *S*-bonded CNS$^-$ was unexpected, although readily explicable when the crystal structure was complete (*vide infra*). I.r. spectra in the ν(C–S) and δ(NCS) regions provided no further structural information owing to the presence of strong ligand bands. In dichloromethane solution (Table 2) the two ν(C⋮N) bands were observed at 2122 and 2088 cm^{-1} with integrated intensities of 2·01 and 9·0 ($\times 10^{-4}$ cm^{-2} mol^{-1}), within the ranges for *N*- and *S*-bonded CNS$^-$. Similar two-band spectra were obtained in benzene, carbon tetrachloride, acetonitrile, and dimethylformamide, suggesting that the same species was present in all these solutions.

The lemon-yellow isomer (Ib), obtained by recrystallisation of (Ia) from dichloromethane–ethanol, had an i.r. spectrum in the ν(C⋮N) region (Table 1) virtually identical with that of (Ia). In solution in a variety of solvents its spectra were indistinguishable from those of (Ia). In the far-i.r. spectra of (Ia) and (Ib) however slight differences were apparent (Table 3). Thus two doublets (494·3 and 486·0, and 467·3 and 462·8 cm^{-1}) in (Ib) replaced strong bands (490·6 and 469·7 cm^{-1}) in (Ia); similarly four bands were resolvable between 330 and 260 cm^{-1} for (Ia) but only 3 bands appeared for (Ib). These data implied that both (Ia) and (Ib) were mixed thiocyanate complexes with very similar but not identical molecular structures in the solid state.

TABLE 3

Far-i.r. spectra (500—150 cm^{-1})

Isomer	Frequency/cm^{-1}
(Ia)	490·6vs, 469·7vs, 454·0w, 432·2s, 419·5w, 387·5m, 321·8m, 303·9m, 297·2m, 277·2s,* 228·0w, 209·1w
(Ib)	494·3vs, 486·0vs, 467·3s, 462·8s, 438·4vs, 394·0m, 379·0sh, 321·4m, 308·3m, 278·6s,* 236·0w, 198·1m
(Ic)	490·5vs, 461·5vs, 451·4m, 432·5vs, 416·8m, 389·6s, 323·1m, 309·2m, 256·1w, 232·0w, 197·1w

* Due to ν(Pd–N).

The third isomer, (Ic), obtained by isomerisation of (Ia) and (Ib) in warm benzene or cyclohexane solutions had only a single sharp absorption at 2116 cm^{-1} (Table 2) in the ν(C⋮N) region, characteristic of a *trans*-*S*-bonded complex. Unfortunately on dissolution in benzene, cyclohexane, dichloromethane, or acetonitrile (Ic) gave a spectrum identical with that of (Ia) or (Ib) in the same solvent thus preventing integrated intensity measurements from being made on the pure *S*-bonded species. The isomerisation (Ic)→(Ia) or (Ib) [*viz.*, *trans*-$\mathrm{Pd(SCN)_2L_2}$→*cis*-Pd(NCS)-(SCN)$\mathrm{L_2}$] was too rapid for measurements to be made. However the *X*-ray structural determination has confirmed the indications from i.r. data that compound (Ic) is *S*-bonded and hence possibly the first example of a *trans*-(dithiocyanato)bis(phosphine)palladium(II) complex. A parallel study on complex (Ia) has shown this to be a *cis*-isomer † with one *S*-bonded and one disordered –CNS group.[11]

Description of the Structure of (Ic).—The structure consists of discrete, centrosymmetric square planar molecules of $\mathrm{Pd(SCN)_2(Ph_2P{\cdot}C{\vdots}CBu^t)_2}$. The molecular structure and atomic numbering are shown in Figure 1 together with the bond distances and angles. A stereoscopic pair of the ORTEP drawing is shown in Figure 2 and the molecular packing in Figure 3.

The *S*-bonded thiocyanate ions are bent out of the $\mathrm{PdS_2P_2}$ square plane with Pd–S–C 98·0 (4)°.

The equations of mean planes with maximum displacements from the planes and interplanar angles are listed in Table 4. The geometry of the phosphinoacetylene ligands is as expected; the phenyl rings are planar and the mean P–C(Ph) distances [1·808(11) Å] are in the expected range.[16] The P–C(*sp*) and C–C distances [1·739(11) and 1·167(16) Å] compare favourably with values [1·765(10) and 1·197(14) Å] in $\mathrm{(PhC{\vdots}C)_3P}$.[17] The Pd–P–C angles around the phosphorus atom confirm the low steric requirement of a –C⋮CR group. Thus the mean C(Ph)–P–Pd angle is 116·7(8)° whereas C(*sp*)–P–Pd is 108·6(3)°.

TABLE 4

(*a*) Equations of mean planes in the form $lX + mY + nZ = p$ where *X*, *Y*, *Z* and are co-ordinates in Å, referred to orthogonal axes *a*, *b*, and *c* *

Plane	Atom	*l*	*m*	*n*	*p*	Δ/Å *
(1)	Pd, P, S	0·2055	0·9256	0·3178	0	0
(2)	Pd, S, C, N	0·9841	0·0174	0·1770	0	0·006
(3)	Pd, P, C(1)—(3)	−0·0047	0·0214	0·9998	0	0·07
(4)	C(10), C(11)—(15)	−0·4907	0·5496	−0·6762	1·37	0·005
(5)	C(20), C(21)—(25)	0·9064	−0·0064	−0·4223	−2·06	0·012

(*b*) Interplanar angles (°)

(1)–(2)	74·1	(3)–(4)	48·6
(1)–(3)	70·3	(3)–(5)	64·8
(1)–(4)	78·9		
(1)–(5)	87·4	(4)–(5)	80·7

* Δ is the maximum displacement (Å) from the plane.

DISCUSSION

Structural Aspects.—A comparison of pertinent bond distances and angles in (Ic) and related molecules is given in Table 5.[4,5,11,18-26] The Pd–S–C angles (98·0°) are at the lower end of the range (97—112°) found for *S*-bonded thiocyanate complexes. With the exception of

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† One CNS$^-$ group in this compound is disordered. Hence we refer to the compound as *cis*-Pd(CNS)(SCN)$\mathrm{(Ph_2P{\cdot}C{\vdots}CBu^t)_2}$.

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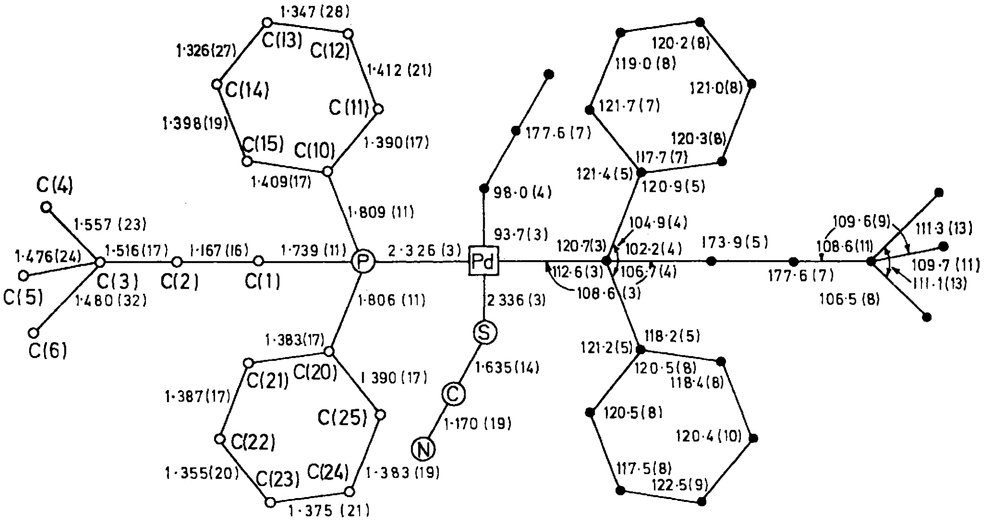

FIGURE 1 Atomic numbering, bond distances, and angles with estimated standard deviation in parentheses for *trans*-$\mathrm{Pd(SCN)_2(Ph_2P{\cdot}C{\vdots}CBu^t)_2}$

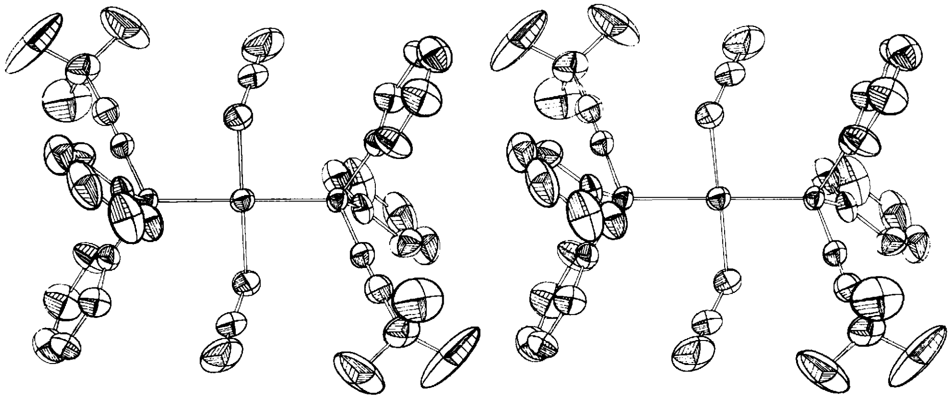

FIGURE 2 Stereoscopic pair of *trans*-$\mathrm{Pd(SCN)_2(Ph_2P{\cdot}C{\vdots}CBu^t)_2}$

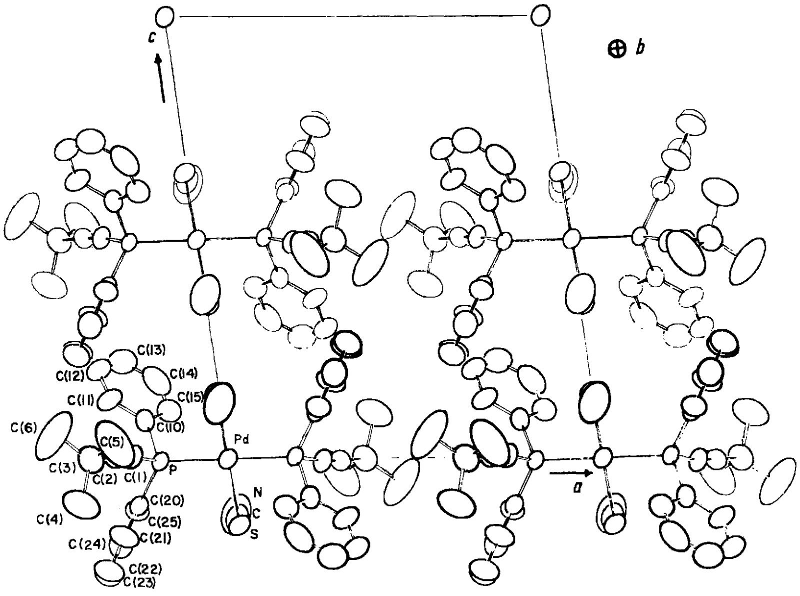

FIGURE 3 Projection of the molecules along *b*

C–N distances for $[Cu(en)_2]Hg(SCN)_4$,[22] $NH_4Ag(SCN)_2$,[26] and α-$[Pt_2(SCN)_2Cl_2(Pr^i{}_3P)_2]$,[25] the S–C and C–N lengths in M–SCN moieties are similar for all the molecules in Table 5.

The orientation of the –SCN groups in (Ic) is of interest since in *cis*-$Pd(CNS)(SCN)(Ph_2P{\cdot}C{:}CBu^t)_2$,[11] *cis*-$Pd(NCS)(SCN)(Ph_2P{\cdot}[CH_2]_2{\cdot}PPh_2)$,[5] and *cis*-$Pd(NCS)(SCN)(Ph_2P{\cdot}[CH_2]_3{\cdot}NMe_2)$ [4] the non linear –S–C–N groups are bent away from the diphenylphosphine group to avoid steric interference. A similar orientation of –SCN groups in (Ic) is precluded by the centrosymmetric *trans*-configuration (Table 4 and Figure 2). Thus a plane containing the Pd atom and the two thiocyanate groups lies almost perpendicular (93·7°) to the P–Pd–P axis. Clearly if phenyl ring–*S*-thiocyanate interactions are present they are not of dominant importance in the solid state since solid complex (Ic) does not appear to isomerise spontaneously to (Ia) or (Ib) over a period of months.

TABLE 5

Comparison of bond distances (Å) and angles (°) in (Ic) and related molecules

Compound	Pd–P	Pd–S	Pd–N	S–C	C–N	M–S–C
(Ic) [a]	2·326(3)	2·336(3)		1·635(14)	1·170(19)	98·0(4)
(Ia) [b]	2·279(5)	2·367(5)		1·621(20)	1·162(27)	105·9(0·7)
	2·270(4)	2·428(10)	1·951(28)	1·630(40)	1·184(57)	96·5(1·5)
cis-$Pd(NCS)SCN)(Ph_2P{\cdot}[CH_2]PPh_2)$ [c]	2·260(4)	2·364(5)				
	2·245(4)		1·998(14)	1·701(17)	1·133(23)	111·8(6)
cis-$Pd(NCS)(SCN)(Ph_2P{\cdot}[CH_2]_3{\cdot}NMe_2)$ [d]	2·243(2)		2·063(7)	1·611(8)	1·136(11)	107·3(3)
		2·295(2)				
$K_2Pd(SCN)_4$ [e]		2·312(10)		1·64(4)	1·24(5)	
		2·392(9)		1·68(5)	1·15(6)	101·2
cis-$PdCl_2(PhMe_2P)_2$ [f]	2·260(2)					
trans-$PdI_2(PhMe_2P)_2$ [g]	2·333(7)					
$Hg(SCN)_2$ [h]				1·62(2)	1·18(3)	97·6(5)
$[Cu(en)_2]Hg(SCN)_4$ [i]				1·57	1·34	102·5
$Se(SCN)_2$ [j]				1·69	1·13	104
$Cd(etu)_2(SCN)_2$ [k]				1·55(5)	1·19(10)	109·1(4)
α$[Pt_2(SCN)_2Cl_2(Pri_3P)_2]$ [l]				1·66	1·31	107·8
$NH_4Ag(SCN)_2$ [m]				1·707	1·095	110

[a] This work. [b] Ref. 11; this compound is disordered such that one thiocyanate group is 50% *N*-bonded and 50% *S*-bonded. [c] Ref. 5. [d] Ref. 4. [e] Ref. 18. [f] Ref. 19. [g] Ref. 20. [h] Ref. 21. [i] Ref. 22. en = ethylenediamine. [j] Ref. 23. [k] Ref. 24; etu = ethylenethiourea. [l] Ref. 25. [m] Ref. 26.

The Pd–P distance [2·326(3) Å] in (Ic) compares favourably with that [2·333(7) Å] in *trans*-$PdI_2(PhMe_2P)_2$ [20] but is significantly longer (9σ) than the Pd–P(*trans* to –SCN) distance in (Ia).[11] Hence the phosphorus donor ligands have a stronger *trans*-influence than the sulphur atom of the thiocyanate ion.

The most important aspect of this structure is the occurrence of *S*-bonded CNS^- groups in a phosphine complex of the B class metal ion, palladium(II). Previously the conversion of *S*-bonded CNS^- in$Pd\ (SCN)_4{}^{2-}$ to the *N*-bonded form in $Pd(NCS)_2(PR_3)_2$ (PR_3 = tertiary phosphine) had been accounted for in terms of a preferential drift of d_π electron density towards the phosphines thus eliminating the possibility of Pd–S multiple bonding or alternatively, conversion of the palladium(II) ion to a ' hard ' acid by co-ordination of phosphine donors hence promoting bonding to the ' hard ' end (–NCS) of the $-CNS^-$ ion.[7,27] More recently[8] it has been suggested that the nitrogen atom of the SCN^- ion may be either the ' softest ' or ' hardest ' centre depending on the acceptor molecule; in this case co-ordination of phosphine to palladium(II) ion enhances the ' softness ' of the acceptor and thus favours Pd–NCS bonding. In their original discussion of the mode of bonding of CNS^- in $Pd(CNS)_2(MR_3)_2$ (M = P, As, or Sb) Basolo *et al.*[7,28] pointed out that steric hindrance to nonlinear M–SCN bonding might account for the observed change in bonding mode within the series $Pd(CNS)_2(Ph_3M)_2$ (M = P, As, or Sb). However this suggestion seems to have been largely ignored in favour of the more fashionable π bonding hypothesis.

A satisfactory (*post facto*) explanation of the CNS^- bonding mode in (Ic) in terms of π bonding requires that the phosphine ligand have a considerably lower inherent π acidity than triphenylphosphine. However the Taft σ* constant for PhC⋮C– is +1·35 compared to +0·60 for Ph and –0·30 for Bu^t.[29] On this basis the Bu^{t}C⋮C-group may be only marginally less electron-withdrawing than Ph. Furthermore the similarity of the Pd–P bond lengths in (Ic) and *trans*-$PdI_2(PhMe_2P)_2$ [20] confirm that if the electronic characteristics of these two phosphines are markedly different, this is not manifested in changes in the Pd–P distance.

We can find no evidence for important intramolecular steric interactions responsible for *S*-bonding. Indeed, a switch to *N*-bonding, followed by a rotation of the

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$Pd(NCS)_2$ moiety about the P–Pd–P axis would give a centrosymmetric *N*-bonded isomer with no increase in intramolecular contacts. If the π-bonding hypothesis does not provide an adequate rationale for the bonding in (Ic) [or in (Ia)] and furthermore the presence of *S*-bonding in *e.g.* $Pd(SCN)_4^{2-}$ and by implication (Ic), is attributed to the affinity of palladium for second-period donors, then it seems pertinent to re-examine the factors effecting *N*-bonding in $Pd(NCS)_2(Ph_3P)_2$ and related *trans*-unidentate phosphine complexes. Without wishing to disregard other parameters of thermodynamic and kinetic[8] importance, we believe that this and other recent work[4,5,9] indicate specifically for palladium(II) thiocyanato-complexes with phenylphosphine ligands a greater involvement of steric repulsions in dictating solid-state structures than has previously been realised. For (Ic), *cis*-$Pd(NCS)(SCN)(Ph_2P{\cdot}[CH_2]_2{\cdot}PPh_2)$, (Ia) and other phenylphosphine complexes,[30] the phenyl groups of the ligands adopt configurations which minimise *ortho*-hydrogen contacts: the CNS^- ligands hence co-ordinate to avoid steric interactions with either group. A non-linear Pd–SCN linkage, being more sterically demanding may be destabilised if such an arrangement requires a less favourable inter- or intra-ligand conformation. For the triphenylphosphine, the preferred propellor configuration of the phenyl groups may impose a particularly severe steric constraint on Pd–SCN bonding. Replacement of a phenyl by a methyl group may not improve the situation since severe steric crowding had been shown to influence ^{31}P chemical shifts of Ph_2MeP complexes.[31] However the presence of a –C⋮C–R grouping, eases the steric problem owing to the lack of α or β hydrogen atoms on the third phosphine substituent to interact with *ortho*-hydrogens of the phenyl groups. Evidence for a reduced steric demand for acetylenic phosphines comes from the *X*-ray study of (Ia) and from the synthesis of a variety of stable *cis*-$PdCl_2(Ph_2P{\cdot}$C⋮CR$)_2$ complexes which do not isomerise in solution.[10] In (Ia) the –C⋮CR groups straddle one another so that the phenyl groups of different Ph_2P units do not interact strongly. The P–Pd–P angle in (Ia) is 94·4° compared with 97·85° in *cis*-$PdCl_2(PhMe_2P)_2$,[19] in which there is steric overcrowding by bulky phosphine groups.

The foregoing arguments are reinforced by the observation of steric control of the CNS^- bonding mode in the *cis*-complexes $Pd(CNS)_2(Ph_2P{\cdot}[CH_2]_n{\cdot}PPh_2)$ ($n = 1$—3).[9] The results of the present work and related studies imply that in favourable circumstances palladium(II) will co-ordinate the sulphur end of the CNS^- ion. Further *X*-ray work on platinum complexes will test the more general significance of steric factors in bis(phosphine) complexes.

The lemon-yellow crystals of isomer (Ib) proved unsuitable for single-crystal *X*-ray work. The marked similarity of the i.r. spectra of (Ia) and (Ib), particularly in the ν(C⋮N)region, appears to eliminate the possibility of a change from *cis* to *trans* stereochemistry. The evidence favours a *cis*-geometry with mixed CNS^- bonding. The structure may differ from that of (Ia) by virtue of a different ligand conformation in the solid state, by crystallising with a different packing, or by having a different type of disorder.

Solution Behaviour and Isomerisation.—Whereas samples (Ia), (Ib), and (Ic) have different solid-state structures, each dissolves in dichloromethane, benzene, acetonitrile, or dimethylformamide to give the same mixed thiocyanato-species. There was no evidence for the formation of bridged thiocyanato-complexes analogous to $[(Ph_3As)Pd(SCN)_2]_2$ thought to be responsible for facile isomeric interconversions in the $Pd(CNS)_2(Ph_3As)_2$ system.[32] The solvent systems investigated include molecules with both high and low dielectric constants yet Pd–SCN bonding appears to be disfavoured in all instances. Warming DMF solutions results in an increase in intensity of the lower, *N*-bonded band in the spectra of all three, although this could possibly be due to liberation of free CNS^-. Only a broad *N*-bonded band, with a shoulder on the high-frequency side appeared for hot acetone solutions. The geometry of the mixed thiocyanato-complex could be *cis* or *trans*, but is most probably the former in view of the overall similarity of band frequencies and intensities with solid sample (Ia).

In chloroform a different solution spectrum was obtained consisting of closely spaced bands of similar half-width and apparent intensity. The nature of the solution species responsible for this spectrum is presently unknown.

It is clear that the thiocyanatopalladium–3,3-dimethylbutynyldiphenylphosphine system is complex and that structures in the solid state and in solution can be very different. Some progress has been made towards an understanding of solution[8,32] and solid-state[5,9,11] data separately. A more sensitive probe than i.r. spectroscopy is necessary for further understanding of the mechanism of interconversion in solution.

I.r. and Far-i.r. Assignments.—Recent attempts have been made to utilise ν(M–N) and ν(M–S) vibrational modes in the far-i.r. and Raman, for structural assignments.[33,34,35]

Lauer[36] *et al.* have however criticised earlier ν(Pd–S) and ν(Pd–N) assignments for a variety of thiocyanato- and isothiocyanato-complexes of Group V ligands. For $[Pd(Et_4dien)(SCN)]^+$ and $[Pd(Et_4dien)NCS]^+$ cations bands at 320 and 365 cm^{-1} respectively were reassigned to ν(Pd–S) and ν(Pd–N). Hence it was concluded that ν(Pd–N) modes were at higher frequency than ν(Pd–S).

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Knowing the full structures of (Ia) and (Ic) and also having high-resolution i.r. and Raman spectra data for *cis*-$PdX_2(Ph_2P{\cdot}C{\vdots}CBu^t)_2$ (X = Cl or Br) and *trans*-$PdI_2(Ph_2P{\cdot}C{\vdots}CBu^t)_2$[10] we attempted to assign ν(Pd–N) and ν(Pd–S). The far-i.r. spectra (Table 3) allowed unequivocal identification of ν(Pd–N) for complexes (Ia) and (Ib). A very strong band, absent from all the compounds *cis*-$PdX_2(Ph_2P{\cdot}C{\vdots}CBu^t)_2$ (X = Cl or Br), *trans*-$PdX_2(Ph_2P{\cdot}C{\vdots}CBu^t)_2$ (X = I or SCN) appeared at 277·2 (Ia) and 278·6 (Ib) cm^{-1}. A band at similar frequency (282·7 cm^{-1}) is present in *cis*-Pd(NCS)(SCN)-$(Ph_2P{\cdot}C{\vdots}CPr^i)_2$ but again absent in the corresponding halogenocompounds. This assignment places ν(Pd–N) somewhat above the range suggested by the work of Keller *et al.*[33] However it seems somewhat surprising that the latter workers found ν(Pd–N) within the narrow region 261—270 cm^{-1} for *cis*- and *trans*-complexes with ligands differing substantially in *trans*-directing influence. By comparison with analogous palladium halide complexes[37] ν(Pd–N) would be expected at lower frequency in *cis*-$Pd(NCS)_2L_2$ (L = tertiary phosphine) than in *cis*-$Pd(NCS)_2L_2$ (L = tertiary amine). In view of our result for (Ia), Burmeister's assignment for $[Pd(Et_4dien)NCS)]^+$ may not be unreasonable. We have found no evidence for bands due to ν(Pd–S) in (Ic), these bands being either too weak to be detected or obscured by two medium-intensity bands at 323·1 and 309·2 cm^{-1}.

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