process is intramolecular. These spectra are temperature invariant between 183 and 363 K. This is similar to what is observed in the ^{13}C NMR spectra of $Fe(CO)_5$, where a single resonance is observed even at very low temperatures,[33] but contrasts with what is observed for $Pt[P(OCH_3)_3]_5^{2+}$, where site exchange is completely stopped[3d] at 133 K. The observation of a large ^{119}Sn–^{195}Pt coupling constant is consistent with a considerable degree of s character in the platinum–tin bond. The near equivalence of the axial and equatorial platinum–tin bonds is consistent with the very low activation energy barrier for Berry pseudorotation in this complex.

The relative intensities of the resonances in both the ^{119}Sn and ^{195}Pt NMR spectra (Figure 3) establish the identity[31] of

the $[Pt(SnCl_3)_5]^{3-}$ species in solution. No other species such as $[Pt(SnCl_3)_4]^{2-}$ or $[Pt(SnCl_3)_2Cl_2]^{2-}$ could be detected in these solutions even after they stood for nearly a year. Hence, in the absence of protic solvents, the $[Pt(SnCl_3)_5]^{3-}$ species has long-term stability. In protic solvents, the species has only short-term stability and metallic platinum is slowly precipitated from either methanol or water/HCl solutions.

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Binding Mode of Thiocyanate in Palladium(II) Complexes: X-ray Crystal Structure of cis-(Isothiocyanato)(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II)

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The crystal structure of cis-(isothiocyanato)(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II) has been determined from three-dimensional X-ray diffraction techniques. The molecule crystallizes in the triclinic space group $P\bar{1}$ in a unit cell of dimensions $a = 9.902$ (2) Å, $b = 17.526$ (4) Å, $c = 8.909$ (4) Å, $\alpha = 109.10$ (2)°, $\beta = 113.02$ (2)°, $\gamma = 87.49$ (2)°, $\rho_{calcd} = 1.869$ g cm^{-3}, and $\rho_{obsd} = 1.859$ g cm^{-3}. Refinement converged to $R = 0.042$, with 3345 independent reflections. Both phosphole rings are planar, and the intracyclic phosphole bond lengths differ for the two distinct phospholes. The phosphole trans to the N-bound thiocyanate possesses more aromatic character than the phosphole trans to the S-bound thiocyanate. The two Pd-P bonds are significantly different, with that trans to the S-bound thiocyanate being longer (2.290 (2) Å) than that trans to the N-bound thiocyanate (2.248 (2) Å), reflecting the greater trans influence of thiocyanate than isothiocyanate. The thiocyanate bond distances and angles are compared to those found for analogous complexes. The data suggest that electronic effects are important in determining both the coordination geometry and thiocyanate bonding mode in $(R_3P)_2Pd(CNS)_2$ complexes. Electronic effects favor both the cis geometry about palladium and the S-bonding mode unless steric effects are large. Steric effects, however, are the discriminator for both the geometry and thiocyanate bonding mode. When steric effects become large, the favored geometry becomes trans rather than the electronically favored cis and the thiocyanate bonding mode becomes N rather than the electronically favored S-bonding mode. The thiocyanate bonding mode seems to be more responsive to small changes in steric effects than is the coordination geometry. Consequently, steric effects smaller than those necessary to stabilize the trans geometry promote N-bound thiocyanate.

Introduction

Thiocyanate[2] complexes of class "B" metal often behave in an antisymbiotic[3] manner, and this behavior has been rationalized over the years in terms of electronic and steric effects.[4–10] There has been considerable discussion concerning

the relative importance of these two effects. We have shown[11] that 1-substituted-3,4-dimethylphospholes form strong bonds with palladium(II), consistent with their sterically undemanding nature and with their greater potential for metal–ligand π interaction when compared with ordinary phosphines.[12,13] Thus a study of the structures of palladium–phosphole–thiocyanate complexes of the type $L_2Pd(CNS)_2$ can provide new information about the factors affecting symbiosis in thiocyanate complexes, as well as allow us greater understanding of the nature of the palladium–phosphole bond. We

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(2) Throughout this paper we represent metal–isothiocyanate bonding as M–NCS and metal–thiocyanate bonding as M–SCN. M–CNS is used when no specific bonding mode is implied.

(3) The term symbiosis was coined by Jorgensen (Jorgensen, C. K. *Inorg. Chem.* **1964,** *3,* 1201) and the term antisymbiosis by Burmeister and Melpolder (Burmeister, J. L.; Melpolder, J. B. *J. Chem. Soc., Chem. Commun.* **1973,** 613). The latter is more fully discussed in ref 18.

(4) Detailed discussions of the various factors that influence the thiocyanate bonding mode can be found in Burmeister and Norbury (Burmeister, J. L. In "The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives"; Newman, A. A., Ed.; Academic Press: Condon, 1975; pp 68–130. Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1975,** *17,* 231).

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Table I. Atomic Coordinates ($\times 10^4$) for (Isothiocyanato)(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II)[a]

| atom	x	y	z	$U,$[b] $Å^2$	atom	x	y	z	$U,$[b] $Å^2$
Pd	304.7 (5)	2575.6 (3)	766.7 (6)	33	C(224)	−565 (8)	5138 (4)	2137 (9)	47
P(1)	−1493.2 (16)	1783.6 (9)	−1683.2 (19)	28	C(225)	67 (10)	6009 (4)	3030 (11)	65
P(2)	−1150.0 (18)	3594.8 (9)	1296.8 (21)	32	C(226)	−113 (7)	4544 (3)	2811 (8)	39
S(1)	1790 (2)	1502 (1)	183 (2)	47	H(112)	−2539 (90)	409 (50)	−4761 (107)	62 (26)
S(2)	3788 (2)	3860 (1)	6589 (3)	55	H(113)	−2082 (91)	−90 (50)	−7240 (108)	65 (26)
N(1)	3331 (12)	1305 (6)	3381 (12)	106	H(114)	−178 (91)	595 (50)	−7573 (108)	48 (26)
N(2)	1886 (6)	3154 (3)	3152 (7)	41	H(115)	1115 (91)	1752 (50)	−5388 (107)	71 (26)
C(1)	2669 (9)	1397 (5)	2095 (10)	59	H(116)	744 (90)	2279 (50)	−2560 (107)	77 (26)
C(2)	2667 (7)	3444 (4)	4585 (8)	41	H(121)	−1435 (92)	620 (50)	−763 (107)	53 (26)
C(111)	−1011 (6)	1396 (3)	−3540 (7)	34	H(1231)	−4903 (95)	81 (50)	−1792 (111)	83 (26)
C(112)	−1805 (7)	690 (4)	−4879 (8)	41	H(1232)	−3619 (96)	258 (51)	−304 (111)	90 (26)
C(113)	−1482 (9)	403 (5)	−6316 (9)	50	H(1233)	−4533 (92)	892 (51)	37 (108)	93 (26)
C(114)	−400 (9)	804 (5)	−6459 (9)	60	H(1251)	−6493 (92)	1369 (52)	−2902 (111)	83 (26)
C(115)	393 (8)	1497 (5)	−5144 (9)	56	H(1252)	−5743 (92)	1899 (51)	−1104 (109)	117 (26)
C(116)	88 (7)	1794 (4)	−3681 (9)	44	H(1253)	−6101 (92)	2059 (52)	−3157 (108)	117 (26)
C(121)	−2052 (7)	981 (4)	−1167 (8)	40	H(126)	−3659 (91)	2506 (50)	−2958 (108)	65 (26)
C(122)	−3452 (7)	1019 (4)	−1351 (8)	43	H(212)	−1254 (91)	2381 (50)	2537 (108)	43 (26)
C(123)	−4258 (10)	495 (5)	−878 (12)	66	H(213)	−3216 (91)	1884 (50)	3407 (108)	80 (26)
C(124)	−4177 (7)	1662 (4)	−2051 (8)	40	H(214)	−5347 (91)	2737 (50)	3509 (108)	140 (26)
C(125)	−5743 (8)	1795 (6)	−2332 (12)	69	H(215)	−4878 (92)	4049 (50)	3737 (108)	101 (26)
C(126)	−3315 (6)	2083 (5)	−2391 (8)	35	H(216)	−3483 (91)	4288 (50)	2139 (107)	103 (26)
C(211)	−2370 (7)	3319 (4)	2150 (8)	41	H(221)	−3164 (91)	3760 (50)	−1389 (107)	55 (26)
C(212)	−2280 (7)	2604 (4)	2511 (8)	42	H(2231)	−3200 (94)	5232 (51)	−1514 (109)	77 (26)
C(213)	−3199 (8)	2401 (4)	3184 (9)	53	H(2232)	−1855 (93)	5711 (51)	−748 (108)	97 (26)
C(214)	−4217 (8)	2922 (5)	3521 (11)	72	H(2233)	−2915 (91)	5871 (50)	451 (108)	110 (26)
C(215)	−4288 (9)	3649 (6)	3202 (14)	105	H(2251)	253 (128)	6234 (71)	2127 (150)	156 (40)
C(216)	−3379 (9)	3852 (5)	2517 (12)	68	H(2252)	675 (91)	6033 (51)	4117 (109)	100 (26)
C(221)	−2217 (7)	4070 (4)	−253 (8)	43	H(2253)	506 (129)	6330 (71)	2746 (151)	184 (40)
C(222)	−1786 (7)	4871 (4)	384 (9)	49	H(226)	692 (90)	4576 (50)	4002 (107)	53 (26)
C(223)	−2469 (10)	5452 (4)	−533 (11)	70					

[a] Standard deviations in parentheses. [b] Average isotropic U ($\times 10^3$) given for anisotropic atoms.

previously reported[14] the structure of *cis*-$L_2Pd(SCN)_2$ (I) (L = 1,3,4-trimethylphosphole) and the preparation and solution behavior of *cis*-$L_2Pd(SCN)$ (II) (L = 1-phenyl-3,4-dimethylphosphole) but were unable to unambiguously assign the solid-state and solution structures of II. We have now determined the X-ray crystal structure of II with the above objectives in mind.

Experimental Section

cis-(Isothiocyanato)(thiocyanato)bis(1-phenyl-3,4-dimethyl-phosphole)palladium(II) was prepared by a metathesis reaction[14] of the chloride complex[11] with NaSCN, and single crystals were grown by slow evaporation from chloroform. Crystal data: $C_{38}H_{36}N_2P_2PdS_2$, M_r = 753.2, triclinic, $P\bar{1}$, a = 9.902 (2) Å, b = 17.526 (4) Å, c = 8.909 (4) Å, α = 109.10 (2)°, β = 113.02 (2)°, γ = 87.49 (2)°, V = 1338.2 (7) $Å^3$, ρ_{calcd} = 1.869 g cm^{-3}, ρ_{obsd} = 1.859 g cm^{-3}, Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 9.92 cm^{-1}. Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with a scan range ±0.8° (2θ) around the $K\alpha_1$–$K\alpha_2$ angles and a scan speed of 1–29° min^{-1}, depending on the intensity of a 2-s prescan; backgrounds were measured at each end of the scan for 0.25 of the scan time.

Three standard reflections were monitored every 100 reflections and showed no significant changes during data collection. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. There were 3345 observed reflections ($I/\sigma(I)$ < 3.0) used in refinement, which were corrected for Lorentz, polarization, and absorption effects, the last with ABSCOR;[15] maximum and minimum transmission factors were 0.95 and 0.64, respectively. Space group $P\bar{1}$ was assumed and shown to be correct by the refinement. Space group $P\bar{1}$ was assumed and shown to be correct by the refinement. The palladium atom was located from a Patterson synthesis, and the remaining atoms were readily found from successive Fourier and difference Fourier syntheses. After anisotropic refinements, the hydrogen atoms could be seen on a difference Fourier synthesis and were refined with isotropic temperature factors. Final
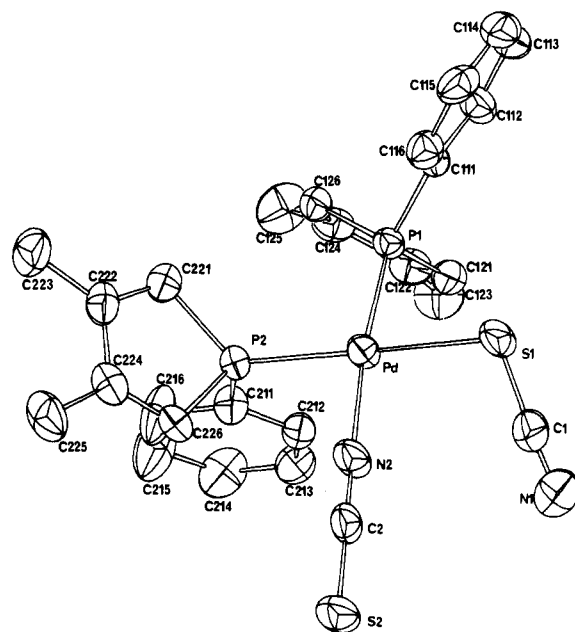
Figure 1. View of the complex, with atom numbering scheme. Thermal ellipsoids are scaled at the 50% probability level.

refinement by least-squares analysis (in large blocks) gave R = 0.042. There were no significant residual peaks on a difference Fourier synthesis. Weights were used of the form $W = XY$ with X = 1.0 or $((\sin \theta)/\lambda)/0.43$ for $(\sin \theta)/\lambda$ < 0.43 and Y = 1.0 or $40.0/F$ for F > 40° or $F/13.0$ for F < 13.0. Final atomic coordinates are listed in Table I, and bond lengths and angles are listed in Table II. A view of the molecule with the atom numbering scheme is shown in Figure 1. The molecular packing shows no features of particular note, and a packing diagram is not included. All computing was done with the XRA76 system[16] on a Burroughs B6700 computer.

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Table II. Selected Bond Lengths (Å) and Angles (Deg) for (Isothiocyanato)(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II), with Standard Deviations in Parentheses[a]

Bond Lengths

Pd-P(1)	2.248 (2)	Pd-N(2)	2.030 (5)	N(2)-C(2)	1.151 (7)
Pd-P(2)	2.290 (2)	S(1)-C(1)	1.651 (9)	C(2)-S(2)	1.619 (6)
Pd-S(1)	2.385 (2)	C(1)-N(1)	1.137 (13)		

	phosphole 1	phosphole 2
P-C(11)	1.811 (7)	1.811 (9)
P-C(21)	1.785 (8)	1.802 (7)
P-C(26)	1.781 (6)	1.800 (5)
C(11)-C(12)	1.399 (7)	1.383 (10)
C(12)-C(13)	1.371 (12)	1.381 (13)
C(13)-C(14)	1.374 (14)	1.384 (12)
C(14)-C(15)	1.378 (9)	1.387 (16)
C(15)-C(16)	1.383 (12)	1.381 (18)
C(16)-C(11)	1.385 (11)	1.398 (11)
C(21)-C(22)	1.332 (10)	1.348 (9)
C(22)-C(23)	1.496 (15)	1.488 (12)
C(22)-C(24)	1.488 (10)	1.488 (8)
C(24)-C(25)	1.492 (10)	1.500 (9)
C(24)-C(26)	1.329 (11)	1.343 (10)

Bond Angles

P(1)-Pd-P(2)	94.55 (6)	Pd-S(1)-C(1)	102.8 (3)
P(1)-Pd-S(1)	84.66 (6)	S(1)-C(1)-N(1)	176.3 (10)
S(1)-Pd-N(2)	92.32 (17)	Pd-N(2)-C(2)	171.0 (7)
N(2)-Pd-P(2)	88.44 (17)	N(2)-C(2)-S(2)	178.8 (8)

	phosphole 1	phosphole 2
Pd-P-C(11)	115.4 (2)	110.5 (2)
Pd-P-C(21)	106.4 (2)	124.2 (3)
Pd-P-C(26)	120.6 (2)	113.3 (2)
C(11)-P-C(21)	111.5 (3)	107.1 (3)
C(11)-P-C(26)	108.4 (3)	107.8 (3)
C(21)-P-C(26)	92.0 (3)	91.9 (3)
P-C(11)-C(12)	118.7 (6)	121.2 (5)
P-C(11)-C(16)	121.6 (4)	119.5 (7)
C(16)-C(11)-C(12)	119.7 (7)	119.3 (8)
C(11)-C(12)-C(13)	119.3 (8)	120.9 (7)
C(12)-C(13)-C(14)	120.8 (6)	119.9 (8)
C(13)-C(14)-C(15)	120.4 (8)	119.5 (10)
C(14)-C(15)-C(16)	119.7 (8)	120.8 (9)
C(15)-C(16)-C(11)	120.1 (6)	119.5 (9)
P-C(21)-C(22)	110.0 (5)	110.0 (5)
C(21)-C(22)-C(23)	125.3 (7)	124.3 (6)
C(21)-C(22)-C(24)	113.5 (7)	113.8 (6)
C(23)-C(22)-C(24)	121.2 (7)	121.9 (5)
C(22)-C(24)-C(25)	120.9 (8)	121.0 (7)
C(22)-C(24)-C(26)	114.3 (6)	114.5 (5)
C(25)-C(24)-C(26)	124.8 (8)	124.6 (6)
C(24)-C(26)-P	109.7 (5)	109.9 (4)

[a] Every atomic number has a prefixed 1 for phosphole 1, and a 2 for phosphole 2. Phosphole 1 is trans to N(2), and phosphole 2 is trans to S(1).

Results and Discussion

cis-Dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium-(II) reacts[14] cleanly with sodium thiocyanate in chloroform-methanol solution to produce analytically pure bis(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II). The infrared data[14] for this complex indicated that it was either a mixture of $L_2Pd(NCS)_2$ and $L_2Pd(SCN)_2$ or $L_2Pd(NC-S)(SCN)$ in the solid state. NMR data[14] in chloroform solution indicated rapid exchange among several isomers. As a consequence we were unable to assign the structure of this complex unequivocally. As can be seen in Figure 1, the complex is approximately square planar, is cis, and contains one thiocyanate and one isothiocyanate coordinated to palladium. The distances within the coordination plane (Table II) are of note. There is a considerable difference in the two Pd-P distances, which could result from interligand steric effects,

electronic effects, or both. The difference in these two distances (0.042 Å) is greater than the difference (0.031 Å) found[17] in the complex *cis*-Pt(NCS)(SCN)(Ph$_2$C≡C-*t*-Bu)$_2$. Hence, the trans influence exerted in the palladium complex is greater than that exerted in the platinum complex even though it is commonly believed that the trans influence increases in importance from the first to the third transition series.[18] The Pd-P distance trans to S is the largest yet observed for the *cis*-(R$_3$P)$_2$Pd(SCN)(NCS) complexes (see Table III). Compared to other *cis*-palladium thiocyanate complexes, d(Pd-N) is normal, d(Pd-S) is somewhat long, and the Pd-N-C and Pd-S-C angles are larger and smaller than usual, respectively. The P-Pd-P angle is the largest yet observed in cis palladium thiocyanate complexes and is slightly larger than the 93.93 (9)° angle observed[11] for *cis*-dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II). This may result from the smaller combined size of the (NCS)(SCN) pair relative to the chloride pair. Also, the average Pd-P distance in the chloride complex is 2.241 Å, shorter than either of the two Pd-P distances reported herein. This is probably a manifestation of the trans influence order[19] SCN > NCS > Cl.

The data point to significant electronic effects operating within this complex. The extent of these effects is revealed in part by the bond distances within the coordinated phosphole. There are two bond-distance criteria for the phospholes that are currently used to ascertain the degree of aromaticity of the phosphole ring. These are (1) the difference between the endo- and exocyclic P-C bond lengths (a greater difference indicates greater aromaticity) and (2) the difference between the C(2)-C(3)-C(4) bond lengths (a smaller difference indicates greater aromaticity). This latter criterion was concluded[20] to be a most accurate and useful one, and from it we conclude that the phosphole trans to S is more aromatic than the phosphole trans to N. Both are slightly more aromatic than the phospholes in *cis*-bis(thiocyanato)bis(1,3,4-trimethylphosphole)palladium(II) and slightly less aromatic than the phospholes in *cis*-dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II). The phosphole rings are essentially planar in all three complexes (see Table IV for planes of the $L_2Pd(NCS)(SCN)$ complex), even though the ring methyl groups are well within van der Waals contact in each case. The degree of aromaticity of the coordinated phosphole in these complexes is also indicated by the Pd-P bond length; the longer the Pd-P bond, the greater the degree of aromaticity. Thus, when the σ interaction between palladium into the phosphole ring is small. The data also suggest that coordination of phospholes to palladium(II) involves some retrodative π bonding. The amount of metal-to-ligand π bonding increases as the electron density at the palladium center increases. Therefore, when the other ligands coordinated to palladium become better σ donors, the electron density at palladium increases, the π back-bonding to the phosphole increases, and the degree of aromaticity within the phosphole ring decreases. consequently, both σ donation and π back-bonding serve to decrease phosphole aromaticity.

One of the reasons we undertook this study was to further understand the factors controlling the thiocyanate bonding mode. It has been repeatedly shown that *cis*-(R$_3$P)PdX$_2$ complexes are thermodynamically more stable than *trans*-(R$_3$P)PdX$_2$ complexes unless the phosphines become very bulky. Furthermore, platinum and palladium thiocyanate complexes generally[4] contain S-bound thiocyanates unless the

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Table III. Compilation of Distances and Angles in Phosphine–Palladium–CNS Complexes

complex	d(Pd-P), Å	d(Pd-N), Å	d(Pd-S), Å	∠PdNC, deg	∠PPdP, deg	∠PPdP, deg	ref
Pd[Ph₂P(CH₂)₃PPh₂](NCS)₂	2.241 (1)	2.055 (3)		165.0 (2)		89.23 (3)	a
Pd[Ph₂P(CH₂)₂PPh₂](SCN)(NCS)	2.243 (3), 2.258 (3)	2.062 (10)	2.364 (4)	163.5 (1)	115.5 (5)	85.1 (1)	a
Pd[Ph₂P(CH₂)₃NMe₂](SCN)(NCS)	2.243 (2)	2.063 (7)	2.295 (2)	177.7 (6)	107.3 (3)	92.4	b
Pd[Ph₂PCH₂PPh₂](SCN)₂	2.264 (2), 2.282 (2)		2.366 (2), 2.362 (2)		108.5, 108.3	73.33 (5)	a
Pd[Ph₂PCH₂C(CF₃)=CHPPh₂](SCN)₂	2.270 (6), 2.278 (6)		2.371 (6), 2.369 (6)			90.6 (2)	c
trans-Pd[P(OPh)₃]₂(SCN)₂	2.312 (1)		2.352 (2)		99.2 (0)		d
trans-Pd[C₆F₅PMe₂]₂(SCN)₂	2.318 (1)		2.351 (1)				e
trans-Pd[Ph₂PC≡C-*t*-Bu]₂(SCN)₂	2.326 (3)		2.336 (3)		98.0 (4)		f
cis-Pd(1,3,4-trimethylphosphole)₂(SCN)₂	2.277 (2)		2.382 (2)		105.9 (2)	91.30 (6)	g
cis-Pd(1-phenyl-3,4-dimethylphosphole)₂(SCN)(NCS)	2.248 (2), 2.290 (2)	2.030 (5)	2.385 (2)	171.0 (7)	102.8 (3)	94.55 (6)	this work
K₂Pd(SCN)₄			2.392 (9)		101 (2), 109 (1)		h
trans-Pd(PPh₃)₂(NCS)₂	2.3404 (9)	1.969 (3)		170.9 (2)			i
trans-Pd[Ph₂PC≡C-*t*-Bu]₂(SCN)(NCS)	2.279 (5), 2.270 (4)	1.951 (28)	2.367 (5), 2.428 (10)		105.9 (7), 96.5 (1.5)	94.4	f, j

a Palenik, G. J.; Mathew, M.; Steffen, W. L.; Beran, G. *J. Am. Chem. Soc.* **1975**, *97*, 1059. *b* Clark, G. R.; Palenik, G. J.; Meek, D. W. *Ibid.* **1970**, *92*, 1077. *c* Simpson, R. T.; Jacobson, S.; Carty, A. J.; Mathew, M.; Palenik, G. J. *J. Chem. Soc., Chem. Commun.* **1973**, 388. *d* Jacobson, S.; Wong, Y. S.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc. Chem. Commun.*, **1974**, *520.* *e* Steffan, W. L. M.S. Thesis, University of Florida, 1972. *f* Beran, G.; Carty, A. J.; Chieh, P. C.; Patel, H. A. *J. Chem. Soc., Dalton Trans.* **1973**, 488. *g* Macdougall, J. J.; Holt, E. M.; deMeester, P.; Alcock, N. W.; Mathey, F.; Nelson, J. H. *Inorg. Chem.* **1980**, *19*, 1439. *h* Mawby, A.; Pringle, G. E. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2213. *i* Carty, A. J.; Chieh, P. C.; Taylor, N. C.; Wong, Y. S. *J. Chem. Soc., Dalton Trans.* **1976**, 572. *j* This compound is disordered such that one thiocyanate group is 50% N bonded and 50% S bonded.

Table IV. Equations of Least-Squares Planes and Distances (Å) of Atoms from the Planes[a]

plane 1: P(1), C(121), C(122), C(124), C(126), C(123), C(125)
  [phosphole(1)]
$-0.1128X + 0.6424Y + 0.7580Z = 6.0887$
[P(1), 0.04; C(121), −0.04; C(122), 0.02; C(124), 0.02; C(126), −0.04; C(123), 0.11; C(125), 0.09]
angle from plane normal to P(1)–C(111) line = 33.3°

plane 2: P(2), C(221), C(222), C(226), C(224), C(223), C(225)
  [phosphole(2)]
$0.9118X - 0.1756Y - 0.3713Z = -1.8471$
[P(2), C(221), C(222), C(226) all 0; C(224), 0.01; C(223), −0.05; C(225), 0.02]
angle from plane normal to P(2)–C(211) line = 25.7°

  plane 3: Pd, P(1), P(2), S(1), N(2)
  $0.5830X + 0.4679Y - 0.6641Z = 2.6463$
  [Pd, 0.07; P(1), −0.09; P(2), 0.06; S(1), 0.07; N(2), −0.10]
  dihedral N(2)PdS(1)C(1) = 35.8°
  dihedral C(111)P(1)PdP(2) = 49.8°
  dihedral C(211)P(2)PdP(1) = 76.5°
  dihedral P(2)PdS(1)C(1) = 86.1°
  dihedral C(111)P(1)PdP(1) = 87.5

[a] Planes on orthogonal axes ($X = a$, Y in plane $a - b$, $Z = C^*$).

Figure 3. View of the coordination sphere of *cis*-(isothiocyanato)-(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II).
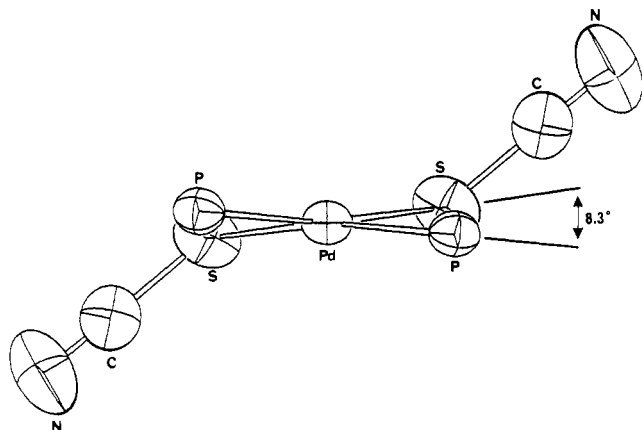

Figure 2. View of the coordination sphere of *cis*-bis(thiocyanato)-bis(1,3,4-trimethylphosphole)palladium(II). See ref 14 for the complete structure.
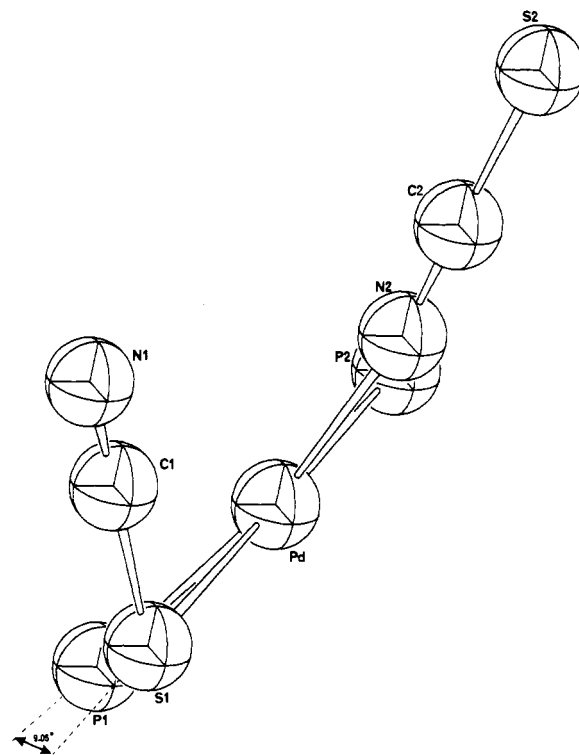
other ligands become very bulky. However, two examples of electronic control are the switch[21] to N bonding in [Pd(5-NO₂-1,10-phen)(NCS)₂] compared to [Pd(1,10-phen)-(SCN)₂], and the partial conversion[4] to S bonding in [Pd-(4,4'-(CH₃)₂-2,2'-bpy)(SCN)(NCS)] compared to [Pd(2,2'-bpy)(NCS)₂]. The thiocyanate bonding mode in (R₃P)₂Pd-(CNS)₂ complexes is illustrated in Figures 2 and 3 where the coordination spheres of *cis*-bis(thiocyanato)bis(1,3,4-trimethylphosphole)palladium(II) are illustrated. In the former

(21) Fultz, W. C.; Burmeister, J. L. *Inorg. Chim. Acta* **1980**, *45*, L271.

complex, the phospholes are not bulky, and a small degree of distortion of the complex toward tetrahedral geometry occurs. In the latter complex, the phosphole is significantly larger, and this gives rise to a larger amount of tetrahedral distortion and forces one of the thiocyanates to become N bound. The second thiocyanate, which remains S bound, is bent away from the phosphole toward the N-bound thiocyanate.

This leads us to the following conclusions. For linear complexes[22] such as LAu(CNS) where steric effects are unimportant, the thiocyanate bonding mode is determined by electronic effects. Burmeister[22] has recently studied a series of $(R_3P)Au(CNS)$ complexes and found them to be S bound in the solid state. In 1,2-dichloroethane, some of the N-bound isomer is present, varying from 13.4% for $[Au(P(OC_6H_{83})-SCN]$ to 4.9% for $[Au(P(C_6H_8)_3SCN]$. Apparently the electronic influence on bonding mode, while operational, is small in magnitude, since a large change in the nature of the trans ligand brings only a small change in bonding mode. For square-planar complexes, electronic effects play a very important part in determining the coordination geometry as well as the thiocyanate bonding mode in $(R_3P)_2Pd(CNS)_2$ complexes. They favor the cis coordination geometry and the S-bonding mode. Steric effects are the discriminator for both of these structural features only when they are large in magnitude. When the steric effects are moderate, the coordination geometry will be cis, and as ligand bulk increases, first one and then the second thiocyanate will become N bound to accommodate this increasing steric demand. Then, as steric effects increase even further the coordination geometry will switch to trans and the thiocyanate will be S bound. With

the largest steric effects the trans N-bound complexes will result. Bond distances and angles within any given complex will result from maximized electronic stability and minimized steric interactions. Further, it seems that the electronic effects are σ bonding in nature, and π bonding is not necessary to rationalize the observed structures. It also seems that the thiocyanate bonding mode is more responsive to small steric changes than is the coordination geometry. Additional structural data that will further test these ideas are currently being obtained.

For the title complex, it could be argued that because the two phospholes have different bond lengths to palladium, their electronic trans influences would determine the different thiocyanate bonding modes. In light of the results with the LAu(CNS)complexes, it is more likely that the different Pd–P bond lengths are a consequence of the different trans influences of thiocyanate and isothiocyanate.

There is one other structural feature of note for this complex. The ortho hydrogen H(212) of the phenyl ring on phosphole 2 essentially occupies the fifth coordination position, being situated 2.70 Å from palladium. This position is along the trajectory for orthometalation and perhaps for this complex orthometalation would be a low-energy process in the solid state.

Registry No. *cis*-Pd(1-phenyl-3,4-dimethylphosphole)$_2$(SCN)-(NCS), 73193-79-0.

Supplementary Material Available: Listings of temperature factors and observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

(22) Melpolder, J. B.; Burmeister, J. L. *Inorg. Chim. Acta,* in press, and references contained therein. We thank J. L. Burmeister for providing this manuscript in advance of publication.

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Molecular Structure Determination of Methyldiborane

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The microwave spectra of ten isotopic species of $B_2H_5CH_3$ were investigated in the region between 18.5 and 40.0 GHz. The complete structure (except the methyl group) was determined from these data by the Kraitchman method: B_1–B_2, 1.82 (2) Å; B_2–H_μ, 1.34 (6) Å; B_1–H_μ, 1.34 (4) Å; B_1–H_6, 1.195 (9) Å; B_1–H_7, 1.187 (5) Å; B_2–H_8, 1.20 (1) Å; H_μ–H_μ, 1.96 (3) Å; B_2–C, 1.49 (10) Å; $\angle B_2B_1H_\mu$, 47 (1)°; $\angle B_1B_2H_\mu$, 47 (1)°; $\angle B_1B_2C$, 120 (1)°. Thus, the B–H_μ–B group appears to be distorted such that the H_μ is displaced toward the methyl group.

Introduction

Bridge hydrogens in boron hydrides and carboranes present interesting structural problems. Strong evidence has been obtained for the existence of a face-centered bridge hydrogen in CB_5H_7.[1] More recently, a microwave study of hexaborane(10), B_6H_{10},[2] has indicated an anomalous behavior of bridge hydrogens. Line splittings in the spectrum are dependent on hydrogen substitution. However, there are not sufficient data to determine uniquely the origin of these line splittings. The separations are too large to be due to electron nuclear quadrupole effects from the boron nuclei. Similar line

splittings have been found in tetraborane(10),[3] B_4H_{10}, and pentaborane(9), B_5H_9.[4] In an attempt to add more data to these problems, we have undertaken a complete structural investigation of some simpler boron hydrides by microwave spectroscopy. The present purpose was to study the effect of terminal hydrogen substitution on the symmetry of the bridge hydrogen bonds by determining the structure of methyldiborane.

The structures of diborane and a few substituted derivatives have been studied by various techniques. Although the proton bridge structure was first confirmed by IR spectroscopy,[5–7]

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