that similar interionic contacts less than van der Waals contact distances are found in most of the homo- and heteropolyatomic cationic species of the group 6 elements so far studied.

Acknowledgment. We thank the National Research Council for financial support of this work and Mr. G. Cardinal for assistance with some of the absorption spectra measurements.

Registry No. $Se_{10}(AsF_6)_2$, 72827-62-4; $Se_{10}(SbF_6)_2$, 72827-63-5; $Se_{10}(AlCl_4)_2$, 72827-64-6; $Se_8(AsF_6)_2$, 52374-78-4; $Se_8(AlCl_4)_2$, 12522-26-8; Se_2Cl_2, 10025-68-0; selenium, 7782-49-2; AsF_5, 7784-36-3; SbF_5, 7783-70-2; $AlCl_3$, 7446-70-0.

Supplementary Material Available: Listings of structure factor amplitudes and thermal parameters (27 pages). Ordering information is given on any current masthead page.

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Structure and Solution Behavior of Palladium(II)-Thiocyanate Complexes of 1-Substituted 3,4-Dimethylphospholes

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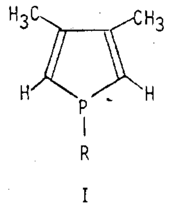
A series of four complexes of the type $L_2Pd(CNS)_2$[2] (L = 1-R-3,4-dimethylphosphole; R = CH_3, $t\text{-}C_4H_9$, C_6H_5, or $CH_2C_6H_5$) have been prepared and characterized by conductance studies, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The complexes appear to be cis in the solid state with the exception of R = $t\text{-}C_4H_9$, which is trans. The phenyl and benzyl complexes exhibit either a single mixed-linkage isomer or a mixture of N-bonded and S-bonded isomers in the solid state. Upon dissolution of the complexes in $CDCl_3$, linkage isomerism occurs in all cases and geometrical isomerism in some cases, giving mixtures of isomers in solution. The methyl and *tert*-butyl complexes are trans in solution, and the benzyl and phenyl complexes exhibit intermediate exchange between cis and trans isomers in solution at room temperature. An NMR shift reagent, $Eu(fod)_3$, was used to facilitate the identification of isomers in solution. The crystal structure of *cis*-bis(thiocyanato)bis(1,3,4-trimethylphosphole)palladium(II) was determined from three-dimensional X-ray diffraction techniques. The molecule crystallizes in the monoclinic space group $C2/c$ in a unit cell of dimensions a = 9.212 (1) Å, b = 15.344 (3) Å, c = 14.572 (4) Å, β = 96.89 (2)°, ρ_{calcd} = 1.542 g/cm³, and ρ_{obsd} = 1.53 (2) g/cm³. Refinement converged to R = 0.035, with 1195 independent reflections. The phosphole ring is planar in this complex, and short intracyclic P–C bond lengths (1.795 Å) indicate the presence of some intracyclic electron delocalization within the coordinated phosphole.

Introduction

The bonding mode of the thiocyanate ion to "soft" metals such as Pd(II) or Pt(II) has been the center of much controversy over the last decade. Both electronic effects[3,4] and steric effects[5] or a combination thereof[6] have been proposed to play the dominant role in determining the thiocyanate bonding mode. The controversy stems from the belief that either steric effects[7-9] or electronic effects[10] exclusively determine this bonding mode. In an attempt to resolve this problem, the question of whether phosphines do or do not function as π acceptors in Pd(II) and Pt(II) complexes in general was reevaluated,[11-13] as π-bonding arguments were being invoked[14] to explain changes in thiocyanate coordination. Whatever the final outcome of this controversy, it is immediately apparent that the steric and electronic effects on the thiocyanate bonding mode are finely balanced for Pd(II) complexes, and subtle changes in either one will tip this balance and determine both linkage and geometrical isomerism.[15]

It has been shown[16] that 1-R-3,4-dimethylphospholes (I)



I

form complexes of the type L_2PdX_2 (X = Cl^-, Br^-, N_3^-) containing Pd–P bonds which are as strong as, if not stronger than, those in structurally similar palladium–phosphine complexes. The enhanced bonding properties of these phospholes could be a consequence of their sterically undemanding nature

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(2) There are six possible square-planar isomers for the complexes $L_2Pd(CNS)_2$, viz., cis and trans N-bound, cis and trans S-bound, and cis and trans mixed-linkage isomers. Throughout the paper "metal–thiocyanate" bonding is represented as N(SCN), metal–isothiocyanate bonding is represented as M(NCS), and when no specific bonding mode is implied, M(CNS) is used; the term "mixed-linkage isomers" is used to imply the presence of two thiocyanate groups coordinated in a monodentate fashion but differing in their point of attachment to the metal.

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0020-1669/80/1319-1439$01.00/0

or of intracyclic phosphorus electron delocalization. In addition, photoelectron spectroscopy studies[17] and Fenske–Hall MO calculations for phosphorus donors possessing electronegative substituents indicate a greater possibility of metal–phosphorus π back-donation in palladium–phosphole complexes than in palladium–phosphine complexes. Without joining into the π-bonding controversy, we can say that the electronic characteristics of the phosphole ligand made it very interesting, and an investigation of the structures and solution behavior of its palladium–thiocyanate complexes could yield valuable information concerning the bonding mode determiners for thiocyanate, as well as the nature of the palladium–phosphole bond.

Experimental Section

The ligands 1-R-3,4-dimethylphosphole (R = CH_3, t-C_4H_9, C_6H_5, or $CH_2C_6H_5$) were synthesized as previously described.[18] All chemicals were reagent grade and were used as received. All solvents were dried when necessary by standard procedures and stored over Linde 4-Å molecular sieves. Melting points were determined on a Meltemp apparatus and are uncorrected.

Conductivity studies were carried out at 25 ± 0.1 °C. Temperature regulation was achieved with a Brinkman Lauda K-2/R temperature controller. Conductance measurements were made by using a Yellow Springs Instruments conductivity cell, Model No. 3403, and measured with an Industrial Instruments conductivity bridge, Model RC16B2, which was adapted in-house for use with a Tektronix Type 310 oscilloscope. Conductance ranges for electrolytes were taken from published values.[19] The complexes are nonelectrolytes in both $CHCl_3$ and CH_3NO_2 solutions in the absence of excess ligand (Table V).

Infrared spectra (Table V) were recorded on a Perkin-Elmer 599 spectrophotometer as Nujol mulls between CsBr plates and as $CHCl_3$ solutions in NaCl cells. Integrated intensities of the CN stretching absorptions were determined by literature methods.[20] When more than one thiocyanate vibration was observed, the total integrated intensity was measured. In all cases, the integrated intensity is per mole of SCN group.

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra (Tables VII–IX) were recorded at 99.54, 25.00, and 40.26 MHz, respectively, on a JEOL FX-100 spectrometer in Fourier transform mode. Proton and carbon-13 chemical shifts were measured relative to internal Me_4Si, while the phosphorus-31 chemical shifts were measured relative to external $P(OCH_3)_3$ (140 ppm downfield from H_3PO_4) and were corrected to 85% H_3PO_4. The preparation of $CDCl_3$ solutions for NMR analysis has been previously described.[21] A lanthanide shift reagent, $Eu(fod)_3$, was used in a 2:1 complex:$Eu(fod)_3$ ratio in $CDCl_3$ solutions.

Preparation of the Compounds. Each of the complexes was prepared by a metathesis reaction of the appropriate chloride complex[16] with NaSCN. An example of a typical preparation is shown as follows.

Bis(thiocyanato)bis(1,3,4-trimethylphosphole)palladium(II). To 1.00 g (2.33×10^{-3} mol) of dichlorobis(1,3,4-trimethylphosphole)palladium(II) in 25 mL of CH_3OH was added 0.38 g (4.66×10^{-3} mol) NaSCN in 10–15 mL of CH_3OH. The resulting solution was heated gently, and a color change from yellow to orange accompanied the addition of NaSCN. The solvent was subsequently removed on a rotary evaporator, and the remaining solid was extracted with hot $CHCl_3$. After it was filtered to remove NaCl, the solution was refrigerated, whence yellow-orange crystals appeared. These were washed with anhydrous diethyl ether and vacuum dried.

Table I. Crystal Data

$C_{16}H_{22}N_2P_2S_2Pd$
cryst system: monoclinic
space group: $C2/c$
$a = 9.212$ (1) Å
$b = 15.344$ (3) Å
$c = 14.572$ (4) Å

$\beta = 96.89$ (2)°
$V = 2044.9$ (8) Å^3
$Z = 4$
mol wt 474.8
$d_m = 1.53$ (2) g/cm^3
$d_c = 1.542$ g/cm^3

radiation: Mo Kα (graphite monochromator)
max 2θ, scan type: 50°, θ–2θ
scan speed: 2.0–29.3° min^{-1} depending on the intensity of a 2-s prescan
scan range: $\Delta(2\theta) = (1.6 + 0.692 \tan \theta)°$, starting the scan from –0.80° below the calculated Kα_1 position
bkgd measurements: stationary-counter, stationary-crystal background counts of a $^1/_4$ scan time at each end of the scan
no. of independent reflctns used with $I > 3\sigma(I)$: 1195
std reflctns: 3 remeasured after every 99 reflections showed no decline during data collection
abs coeff μ(Mo Kα): 12.38 cm^{-1}
trans coeff range on F: 0.939–0.959
cryst faces: (010), $(0\bar{1}0)$, (001), $(11\bar{1})$, $(\bar{1}11)$, $(2\bar{1}1)$, $(\bar{1}\bar{1}\bar{4})$
cryst dimensions: 0.07 × 0.12 × 0.15 mm

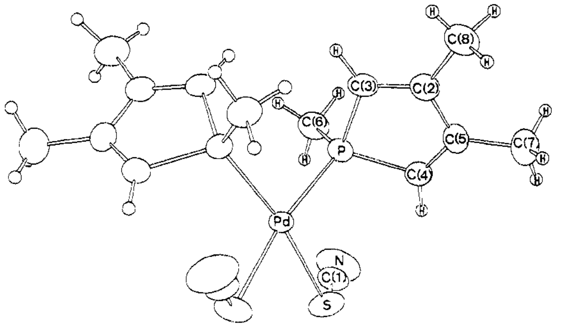

Figure 1. View of the complex molecule, with atom numbering scheme. Thermal ellipsoids are scaled at the 50% probability level. Hydrogen atoms are represented as circles of arbitrary size.

Collection and Reduction of X-ray Data for Bis(thiocyanato)bis(1,3,4-trimethylphosphole)palladium(II). Experimental Section. Brown-yellow prismatic crystals were obtained by recrystallization from methanol. A suitable crystal was mounted on a Syntex P2$_1$ diffractometer. The pertinent crystal data are presented in Table I. After data collection, the data were processed and corrected for Lorentz and polarization effects and for absorption. The XRAY 76 system was used for the calculation.[22]

Solution and Refinement. The structure was solved by standard Patterson and difference Fourier methods. All least-squares refinements were on F, the function minimized being $\sum w(F_o - F_c)^2$. The atomic scattering factors were taken from Cromer and Mann.[23] The effects of the anomalous dispersion for Pd, P, and S were included in the calculation of F_c; the values of $\Delta f'$ and $\Delta f''$ were taken from the "International Tables for X-ray Crystallography".[24] Full-matrix least-squares refinement on the position of the Pd atom alone, deduced from the Patterson function, led to $R = 0.362$. All nonhydrogen atoms were subsequently located and refined. Anisotropic refinement of all nonhydrogen atoms gave $R = 0.044$. In the next difference Fourier map, all 11 hydrogen atoms were located and were included as fixed atoms with U's set at 0.05 Å^2. A weight $W = XY$ was used, where $X = 1.0$ or $(\sin \theta)/0.2$ ($\sin \theta < 0.2$) or $0.31/(\sin \theta)$ ($\sin \theta > 0.31$) and $Y = 1.0$ or $F/45.0$ ($F < 45.0$) or $190.0/F$ ($F > 190.0$).

The final agreement values are $R = 0.035$ and $R_w = 0.034$. The difference Fourier map calculated at the end of the refinement did not show any peak higher than 0.45 e. The final atomic coordinates and isotropic temperature factors for nonhydrogen atoms are presented

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Table II. Positional Parameters (×10^4) and Anisotropic Temperature Factors (×10^3) for Nonhydrogen Atoms with Esd's in Parentheses[a]

atom	*x*	*y*	*z*
Pd	0.0	2024.8 (4)	2500.0
S	1644 (2)	838 (1)	2413 (1)
P	−1780.1 (15)	3062.1 (11)	2352.9 (9)
N	3739 (8)	1371 (5)	1272 (6)
C(1)	2878 (8)	1178 (4)	1734 (5)
C(2)	−3489 (6)	3213 (4)	830 (4)
C(3)	−3362 (6)	2726 (3)	1585 (4)
C(4)	−1442 (7)	3952 (4)	1612 (4)
C(5)	−2381 (7)	3915 (4)	831 (4)
C(6)	−2391 (7)	3472 (4)	3408 (4)
C(7)	−2345 (9)	4514 (5)	22 (5)
C(8)	−4643 (7)	3087 (5)	24 (4)
H(1)	−1610	3810	3750
H(2)	−3150	3980	3320
H(3)	−2690	2980	3860
H(4)	−580	4410	1640
H(5)	−3850	2200	1820
H(6)	−3270	4950	−110
H(7)	−1470	4870	120
H(8)	−2270	4180	−520
H(9)	−4230	2910	−550
H(10)	−5320	2640	160
H(11)	−5180	3620	−110

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
43.9 (4)	26.8 (3)	31.2 (3)	0.0	4.3 (3)	0.0
79.4 (13)	39.4 (10)	65.6 (11)	17.7 (8)	20.3 (10)	4.1 (8)
45.4 (9)	35.3 (9)	35.5 (8)	3.0 (7)	5.0 (7)	2.2 (7)
84 (5)	76 (5)	131 (6)	−19 (4)	51 (5)	−32 (4)
62 (5)	38 (4)	74 (5)	2 (3)	6 (4)	−18 (3)
41 (3)	52 (4)	36 (3)	11 (3)	7 (2)	−6 (3)
48 (4)	38 (3)	46 (3)	0 (3)	7 (3)	−1 (3)
54 (4)	33 (3)	45 (3)	4 (3)	14 (3)	5 (3)
63 (4)	40 (3)	35 (3)	14 (3)	10 (3)	−6 (3)
64 (4)	51 (4)	48 (4)	8 (3)	18 (3)	3 (3)
109 (6)	57 (4)	46 (4)	2 (4)	5 (4)	10 (3)
67 (4)	79 (5)	42 (3)	9 (4)	1 (3)	−6 (4)

[a] Anisotropic temperature factors are in the form $\exp[-2\pi^2 \cdot (U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

Table III. Interatomic Distances (Å) and Angles (Deg) with Esd's in Parentheses

	Distances		
Pd–S	2.382 (2)	Pd–P	2.277 (2)
S–C(1)	1.677 (8)	C(1)–N	1.14 (1)
P–C(3)	1.802 (6)	P–C(6)	1.812 (7)
P–C(4)	1.790 (6)	C(2)–C(3)	1.323 (8)
C(4)–C(5)	1.345 (8)	C(2)–C(8)	1.499 (8)
C(2)–C(5)	1.484 (8)	C(5)–C(7)	1.498 (9)
	Angles		
S–Pd–P	170.03 (6)	P–Pd–P$^{\mathrm{I}}$	91.30 (6)
S–Pd–P$^{\mathrm{I}}$ [a]	94.83 (6)	Pd–S–C(1)	105.9 (2)
S–Pd–S$^{\mathrm{I}}$	80.25 (7)	S–C(1)–N	176.9 (7)
Pd–P–C(3)	112.2 (2)	C(3)–P–C(4)	91.7 (3)
Pd–P–C(4)	114.5 (2)	C(4)–P–C(6)	109.9 (3)
Pd–P–C(6)	117.2 (2)	C(3)–P–C(6)	108.4 (3)
P–C(3)–C(2)	109.9 (4)	P–C(4)–C(5)	109.7 (4)
C(3)–C(2)–C(8)	124.3 (5)	C(4)–C(5)–C(7)	124.6 (6)
C(3)–C(2)–C(5)	114.6 (5)	C(2)–C(5)–C(4)	113.8 (5)
C(8)–C(2)–C(5)	121.1 (5)	C(2)–C(5)–C(7)	121.6 (5)

[a] The roman superscript refers to atoms in the position $-x, y, \frac{1}{2} - z$.

in Table II. A perspective view of the molecule illustrating the atomic numbering scheme is shown in Figure 1. Selected interatomic distances are given in Table III together with bond angles. Figure 2 shows a packing diagram for the molecules in the unit cell as viewed down the crystallographic *b* axis.

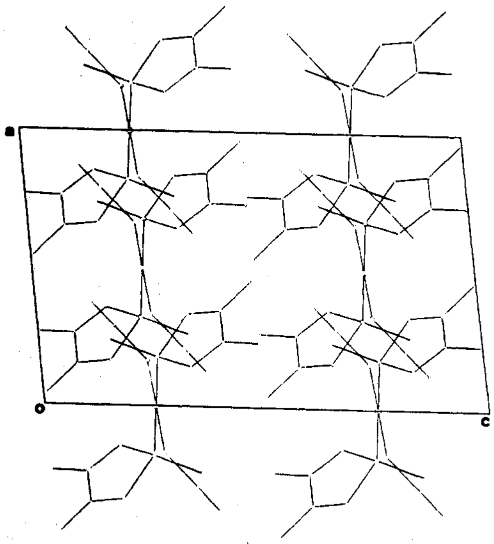


Figure 2. View of the packing of the molecules approximately down the crystallographic *b* axis.

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

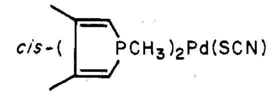
plane 1: S, S,[a] P, P[a]
$0.307x + 0.000y + 14.400z = 3.600$
[S −0.176, S[a] 0.176, P −0.157, P[a] 0.157, Pd 0.000]

plane 2: P, C(2), C(3), C(4), C(5)
$5.598x + 8.663y + 7.019z = 5.329$
[P −0.030, C(2) −0.010, C(3) 0.027, C(4) 0.033, C(5) −0.021, C(6) 1.410, C(7) −0.090, C(8) 0.039]

[a] Atoms in position $-x, y, \frac{1}{2} - z$.

Results

Reaction of L_2PdCl_2 (L = 1-R-3,4-dimethylphosphole) with NaSCN in methanol cleanly produces $L_2Pd(CNS)_2$ complexes. These complexes are nonelectrolytes in both $CHCl_3$ and CH_3NO_2 as evidenced by conductance measurements (Table V). The solid-state geometry and thiocyanate bonding mode were determined from infrared spectroscopy on Nujol mulls. For[15,25] a *cis*-$L_2Pd(SCN)_2$ complex one would expect to see two ν(CN) vibrations in the vicinity of 2100 cm^{-1}, with $\Delta\nu_{1/2}$ values in the 20–30-cm^{-1} range, internal standard ratios less than 1, and two δ(NCS) vibrations in the vicinity of 400 cm^{-1}. For[15,25] a *cis*-$L_2Pd(NCS)_2$ complex one would expect two ν(CN) vibrations in the vicinity of 2085 cm^{-1}, with $\Delta\nu^{1/2}$ values in the 40–60-cm^{-1} range, internal standard ratios greater than 1.5, and two δ(NCS) vibrations in the vicinity of 475–485 cm^{-1}. The mixed-ligand complex *cis*-$L_2Pd(NCS)(SCN)$ would be expected to show a combination of the above, i.e., two ν(CN) vibrations, one near 2100 cm^{-1} with $\Delta\nu_{1/2} \approx 25$ cm^{-1} and one near 2085 cm^{-1} with $\Delta\nu_{1/2} \approx 50$ cm^{-1}, and two δ(NCS) vibrations, one near 440 cm^{-1} and one near 480 cm^{-1}. For a mixed-ligand complex the average ISR would probably be greater than one. The *trans*-$L_2Pd(SCN)_2$, *trans*-$L_2Pd(NCS)_2$, and *trans*-$L_2Pd(SCN)(NCS)$ complexes would display infrared characteristics similar to those of their cis counterparts except that single vibrations should be observed for both ν(CN) and δ(NCS). A solid-state mixture of *cis*-$L_2Pd(NCS)_2$ and *cis*-$L_2Pd(SCN)_2$ would be expected to show four ν(CNS) vibrations. The solid-state geometries cited in Table VI were assigned by using the above criteria, and the assignment for



was confirmed by X-ray crystallography.[26]

The structures in solution were determined from a combination of infrared spectroscopic and nuclear magnetic reso-

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(26) See paragraph at end of paper regarding supplementary material.

Table V. Infrared Spectral and Conductance Data for $(Me_2phosR)_2Pd(CNS)_2$ Complexes[d]

R	mp, °C	state	ν(CN), cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	*A*[a]	ISR[b]	δ(NCS), cm^{-1}	bonding mode	geometry	λ_m[c]	
										$CHCl_3$	
CH_3	129	Nujol	2105	29		0.366	425, 435	SCN	cis	~0	44.5
		$CHCl_3$	2115, 2085	23, 38	5.57			SCN, NCS			
t-C_4H_9	210	Nujol	2095	46		2.15	461	NCS	trans	~0	45.9
		$CHCl_3$	2100	40	14.6			NCS			
C_6H_5	176	Nujol	2116, 2090	22, 69		1.82	450, 465	SCN, NCS	cis	~0	41.7
		$CHCl_3$	2116, 2085	24, 42	5.54			SCN, NCS			
$CH_2C_6H_5$	137	Nujol	2115, 2080	15, 70		2.66	460, 470	SCN, NCS	cis	~0	43.4
		$CHCl_3$	2108, 2080	25, 55	11.43			SCN, NCS			

[a] Integrated intensity × 10^{-4} M^{-1} cm^{-2}. [b] Internal standard ratio. See ref 20 for criteria. [c] Molar conductance, mho's × 10^{-6}. Conductance value ranges can be found in ref 19. [d] Me_2phos = dimethylphosphole.

Table VI. 99.54-MHz ^1H NMR Spectral Data for $(Me_2phosR)_2Pd(CNS)_2$

R	$\delta(^1H)$, line shape,[a] $\lvert {}^nJ_{PH} + {}^{n+2}J_{PH} \rvert$(Hz)				
	ring $C_{3,4}$	ring CH_3	*P*-CH_3	*t*-BuCH_3	Bzl CH_2
CH_3	6.57, t, 33.2	2.11, s	1.73, cm		
t-C_4H_9	6.64, 33.2; 6.48, 33.2; 6.30, t, 33.2	2.10, s		1.33, t, 16.6	
C_6H_5	6.66, cm	2.12, s			
$CH_2C_6H_5$	6.37, cm	1.92, s			3.52, cm

[a] s = singlet, t = triplet, and cm = collapsed multiplet.

nance techniques. The solution infrared criteria are the same as those for the solid state except that in solution the internal standard ratio criteria for the ν(CN) vibrations are replaced by integrated intensity criteria:[25] M–SCN ($A = 1$–3×10^4 M^{-1} cm^{-2}); M–NCS ($A = 7$–11×10^4 M^{-1} cm^{-2}). In $CHCl_3$ solutions δ(NCS) is obscured by solvent vibrations.

The overall geometry of an $(R_3P)_2PdX_2$ complex is readily discerned[3-5,16,21] from a combination of ^1H, ^{13}C, and ^{31}P NMR. For both ^1H and ^{13}C NMR most resonances will be 1:2:1 triplets for *trans*-L_2MX_2 complexes. For *cis*-L_2MX_2 complexes the proton resonances generally appear as doublets, and the $^{13}C\{^1H\}$ resonances may appear as a five-line multiplet, a non-1:2:1 triplet, a doublet of doublets, or a doublet. The $^{31}P\{^1H\}$ resonances will appear as distinct singlets for *cis*-$L_2Pd(SCN)_2$, *cis*-$L_2Pd(NCS)_2$, and each of the *trans*-$L_2Pd(CNS)_2$ and as a doublet of doublets for *cis*-$L_2Pd(SCN)(NCS)$.

Bis(thiocyanato)bis(1,3,4-trimethylphosphole)palladium(II). The appearance of the infrared spectrum indicates that this complex is cis S-bound in the solid state, and this is confirmed by the crystal structure. In solution, the complex is a mixture of trans S-bound and trans N-bound isomers. Conductance measurements indicate that no ionic species are present in solution. The proton NMR indicates one trans isomer from the appearance of the phosphole ring $C_{3,4}$ proton resonance (Table VI), which is a 1:2:1 triplet at δ 6.57. The $^{13}C\{^1H\}$ spectrum (Table VII) also indicates one trans isomer. Two singlets appear in the $^{31}P\{^1H\}$ NMR spectrum (Table VIII). But upon addition of a lanthanide shift reagent, $Eu(fod)_3$, these become three singlets. The lanthanide-induced shifts decrease in the order $ML_2(SCN)_2 > ML_2(SCN)(NCS) > ML_2(NCS)_2$. The appearance of the ^1H and $^{13}C\{^1H\}$ NMR spectra with $Eu(fod)_3$ present, in addition to criteria previously delineated,[15,27-30] allows us to assign the isomers and their relative abundances as follows: 0.07:1:0.26::*trans*-$L_2Pd(NCS)_2$:*trans*-L_2:*trans*-$L_2Pd(NCS)(SCN)$:*trans*-$L_2Pd(SCN)_2$.

It might be anticipated that the lanthanide-shift reagent could influence the thiocyanate bonding mode by interacting with the M–SCN moiety in preference to the M–NCS moiety and thereby stabilize the former. This does not seem to be the case[15] as the integrated areas under the two ^{31}P resonances at δ 15.57 and 13.97 (Table VIII) in the presence of $Eu(fod)_3$

Table VII. 25.00-MHz $^{13}C\{^1H\}$ NMR Spectral Data for $(Me_2phosR)_2Pd(CNS)_2$

R	$\delta(^{13}C)$, line shape,[a] $\lvert {}^nJ_{PC} + {}^{n+2}J_{PC} \rvert$ (Hz)			
	CH_3	t-C_4H_9	C_6H_5[b]	$CH_2C_6H_5$
ring $C_{3,4}$	122.76, t, 50.0	120.65, t, 41.5 119.55, t, 44.0 119.04, t, 44.0	n.o.	132.61, s
ring $C_{2,5}$	154.45, t, 10.9	155.47, t, 9.7 155.27, t, 9.7 154.83, t, 9.7	154.98, s	155.32, s
Ph C_1			n.o.	128.96, s
Ph $C_{2,6}$			132.95, s	129.54, s
Ph $C_{3,5}$			129.10, s	128.13, s
Ph C_4			131.74, s	127.10, s
CH_2/CH_3	7.65, t, 26.0			31.39, s
t-Bu CH_3		29.33, t, 5.8 28.61, t, 5.8 28.12, t, 5.8		
ring CH_3	17.79, s	17.94, t, 11.0	17.87, s	17.79, s
t-Bu, 3 °C		36.36, t, 23.2 35.92, t, 20.8		

[a] s = singlet and t = triplet. [b] n.o. = not observed.

Table VIII. 40.26-MHz $^{31}P\{^1H\}$NMR Spectral Data for $(Me_2phosR)_2Pd(CNS)_2$

R	$\delta\,^{31}P$	
	without $Eu(fod)_3$	with $Eu(fod)_3$[a]
CH_3	13.83,[b] 10.95[c]	15.57 (19.5),[d] 13.97 (75.2),[e] 10.94 (5.3)[c]
t-C_4H_9	47.32,[b] 46.51,[b] 43.63[b]	47.33 (25.3),[e] 46.51 (59.0),[c] 43.67 (15.7)[d]
C_6H_5	24.05[b]	24.08[e]
$CH_2C_6H_5$	26.10[b]	29.60 (27.6),[d] 26.10 (72.4)[c]

[a] Numbers in parentheses indicate relative percent abundances. Positive chemical shifts are downfield of 85% H_3PO_4. [b] For $(CNS)_2$. [c] For $(NCS)_2$. [d] For $(SCN)_2$. [e] For (NCS)(SCN).

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are equal to the integrated area of the δ 13.83 resonance in its absence. Further the area of the δ 10.94 resonance is not affected by Eu(fod)$_3$. The shift reagent also appeared to have no effect on the relative intensities of the ^{31}P NMR resonances for the other complexes.

Bis(thiocyanato)bis(1-*tert*-butyl-3,4-dimethylphosphole)palladium(II). The infrared data indicate that the complex is trans N-bound both in the solid state and in CHCl$_3$ solution. The proton NMR spectrum shows three 1:2:1 triplets for the ring C$_{3,4}$ protons, and the ^{13}C{^{1}H} spectrum also indicates the presence of three trans isomers. In the ^{31}P{^{1}H} spectrum, upon addition of Eu(fod)$_3$, the S-bound isomer ^{31}P chemical shift moves downfield by an amount greater than that for the mixed-linkage isomer. The N-bound isomer chemical shift is unchanged. Thus the isomers are assigned a 1:0.43:0.27::*trans*-L$_2$Pd(NCS)$_2$:*trans*-L$_2$Pd(SCN)(NCS): *trans*-L$_2$Pd(SCN)$_2$ ratio.

Bis(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II). The infrared data indicate that the complex is a mixture of cis N-bound and S-bound isomers in the solid state. The solution IR data also indicate that a mixture of isomers is present. The proton and ^{13}C{^{1}H} NMR spectra indicate intermediate exchange exhibited by broad singlets with no P–C coupling, and the ^{31}P{^{1}H} spectrum shows only one broad singlet that does not shift position in the presence of Eu(fod)$_3$. This indicates that, in solution, this complex is a rapidly exchanging mixture of cis and trans N-bound species and perhaps S-bound species as well. Conductance measurements indicate that no ionic species are present in solution.

Bis(thiocyanato)bis(1-benzyl-3,4-dimethylphosphole)palladium(II). The infrared data indicate that this complex is a mixture of N-bound and S-bound isomers both in the solid state and in CHCl$_3$ solution. As with the 1-phenyl-3,4-dimethylphosphole complex, the ^{1}H and ^{13}C{^{1}H} spectra show broadened singlets with no P–H or P–C coupling, indicative of intermediate exchange. The ^{31}P{^{1}H} NMR spectrum shows one broad resonance and upon addition of Eu(fod)$_3$ shows two resonances. All the data indicate that the species present in solution are N-bound and S-bound isomers rapidly exchanging between cis and trans. The ratio of S-bound to N-bound is 0.38:1.

Description of the Structure of *cis*-Bis(thiocyanato)bis(1,3,4-trimethylphosphole)palladium(II). There is an approximate square-planar geometry around the palladium atom, and a least-squares plane calculated through the four coordinated atoms (Table V) shows that the square-planar geometry at the palladium center is more distorted toward tetrahedral (8.3° dihedral angle) in this complex than in [(dpm)Pd(SCN)$_2$][9] (2.0° dihedral angle). Yet, dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II)[16] (7.2° dihedral angle) is less tetrahedrally distorted than dichlorobis(dimethylphenylphosphine)palladium(II)[31] (8.7° dihedral angle). This suggests that, in (dithiocyanato)bis(1,3,4-trimethylphosphole)palladium(II), the geometry in the solid state is determined mainly by electronic factors and relief from steric interaction results in pseudotetrahedrality (an unstable[32] electronic arrangement for palladium). Thus, unless the steric interactions are substantial, tetrahedral distortion results rather than the trans geometry. The bond angles around palladium are unexceptional although it is worth noting that the P(1)–Pd–P(2) angle of 91.30° is smaller than the corresponding angle in dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II)[16] of 93.93°. This presumably reflects both the larger steric bulk of the thiocyanate ion relative to the chloride ion and the smaller ligand size of the methylphosphole relative to the phenylphosphole.

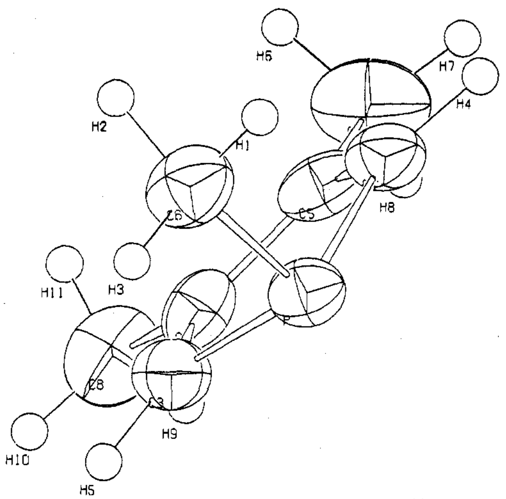
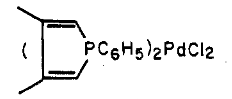


Figure 3. View of the phosphole ring from a direction near the Pd–P bond, demonstrating that the ring is planar and that the exocyclic methyl groups lie in the plane of the ring despite the fact that they are much closer than van der Waals contacts.

The Pd–P bond length in this complex (2.277 (2) Å) is longer than those in other phosphole (2.240 (3) Å in II) and



II

phosphine complexes of palladium(II);[16] it and the Pd–S bond distance (2.382 (2) Å) are slightly longer than those found in [(dpm)Pd(SCN)$_2$][9] (2.273 (4) and 2.364 (2) Å, respectively). This is most likely an effect of antisymbiotic trans bond-lengthening influences for phosphines and the thiocyanate ion and suggests that 1,3,4-trimethylphosphole and probably 1-substituted 3,4-dimethylphospholes in general have a higher trans bond-lengthening influence than ordinary phosphines.

The average intracyclic P–C bond length (1.795 Å) is shorter than the calculated[32] P–C sp^2 single-bond length of 1.84 Å and is very similar to that found for dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) (1.798 Å). This indicates that stabilizing interactions within the phosphole ring still exist in the coordinated ligand. See discussion in ref 16 and 33 for further substantiation of this conclusion.

From Table IV and Figure 3 it can be seen that the phosphole ring is essentially planar and that C(7) and C(8) lie in the plane of the ring, as was previously found[16] for dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II). The bond lengths and angles in the thiocyanate groups are normal and do not differ significantly from their expected values. The angle between the plane Pd, S, N and least-squares plane calculated through P, C(2), C(3), C(4), and C(5) is 75.4°.

The mean C$_{3,4}$–P–C$_6$ bond angle of 109.1° is not too different from that in 1-benzylphosphole[32] (106.1°) and suggests that 1,3,4-trimethylphosphole undergoes minimal electronic reorganization upon coordination. The ramifications of these current data are in agreement with our previous conclusions for phosphole complexes.[16]

Discussion

There are two basic questions which this study addresses: (1) What factors dominate the energy difference between cis and trans isomers in L$_2$PdX$_2$ complexes and (2) what controls linkage isomerism of the thiocyanate ion? We have previously studied the former question in considerable detail.[3-5,34] In

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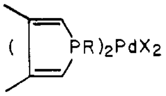
general the cis isomer of L_2PdX_2 complexes is themodynamically more stable than the trans isomer in chloroform solution due to stronger internal bond strengths and a greater solvent–solute interaction with the cis isomer unless steric effects are large, in which case the trans isomer is favored. The isomerization energetics[34] for the series of complexes



where X = Cl, Br, or N_3 demonstrate that the phosphole ligands stabilize the cis geometry to an even greater extent than typical phosphines due to their reduced steric bulk and stronger palladium–phosphorus bonds. The palladium azide complexes of phospholes which are isoelectronic and sterically similar to the palladium–thiocyanate–phosphole complexes are entirely cis is chloroform solution and in the solid state as well. Consequently, one might anticipate that in the solid state the $Pd(phosphole)_2(CNS)_2$ complexes would possess the cis geometry. This is the case except for the *tert*-butyl complex which contains the phosphorus ligand with the greatest steric bulk.

Previous investigators have proposed that the thiocyanate bonding mode is determined predominantly by steric effects,[7–9] electronic effects,[10] or a combination[6] of the two. Though the extent, if any, of retrodative metal–ligand π bonding in square-planar bis(phosphine) complexes is highly controversial,[11–14] several authors have rationalized the bonding mode of thiocyanate with π-bonding arguments. Recently, however, arguments for the dominance[7–9] of steric effects have been put forth. In a preliminary investigation[35] we suggested that palladium(II) is ambivalent toward the thiocyanate ion, and subtle changes in either steric or electronic effects will tip the balance and determine the thiocyanate bonding mode as well as the geometry of any individual $L_2M(CNS)_2$ complex. These ideas were fortified[15] by a more detailed study of $L_2Pd(CNS)_2$ complexes $\{L = R_nP(C_6H_5)_{3-n}$, $n = 0$–3; R = CH_3 and $C_6H_5CH_2\}$ wherein we noted that neither the thiocyanate bonding mode nor the overall geometry was a simple function of the electronic or steric properties of the phosphorus donor ligands (L).

In contrast, the solid-state geometry and thiocyanate bonding mode of the phosphole $L_2Pd(CNS)_2$ complexes seem to be predominantly determined by steric effects. Thus, with the largest ligand (1-*tert*-butyl-3,4-dimethylphosphole) the trans N-bound complex is observed in the solid state. As the ligand bulk decreases, cis complexes with mixed thiocyanate bonding modes are found for the phenyl- and benzylphosphole complexes. Finally with the smallest ligand, the methylphosphole, the *cis*-$L_2Pd(SCN)_2$ complex is found in the solid state. Hence, if crystal packing forces and solubilities are not determining the solid-state structures, the *cis*-$L_2Pd(SCN)_2$ complexes should be the most stable for sterically small ligands, and, as the steric bulk of the phosphorus ligand increases, a change to the sterically more favored N-bound thiocyanate and trans geometry occurs.

In solution, solvation effects become important,[36] and we find that a geometrical isomerization often is accompanied by linkage isomerization upon dissolution in chloroform. In chloroform solution, trans complexes generally predominate as do N-bound thiocyanate. This is probably due to an entropy effect wherein the trans $L_2Pd(NCS)_2$ complexes probably interact less with chloroform than any of the other isomers and so bind fewer solvent molecules in the second coordination sphere than any of the other isomers. One difficulty with this explanation is the observation that $Eu(fod)_3$, which, by virtue of its effect on the chemical shifts of ^1H, ^{13}C, and ^{31}P nuclei, is demonstrated to interact more stongly with the M–SCN moiety than the M–NCS moiety does not stabilize the former in chloroform solution. This can only be explained if this interaction is too weak to influence the thiocyanate bonding mode. Since the observed chemical-shift changes for the $L_2Pd(CNS)_2$ complexes induced by $Eu(fod)_3$ are much smaller in magnitude than those typically found for lanthanide-induced chemical shifts of organic molecules,[37] it seems reasonable to assume a weak interaction between $L_2Pd(SCN)_2$ and $Eu(fod)_3$.

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Registry No. *cis*-(1,3,4-trimethylphosphole)$_2$Pd(SCN)$_2$, 73193-85-8; *trans*-(1-*tert*-butyl-3,4-dimethylphosphole)$_2$Pd(NCS)$_2$, 73193-86-9; *cis*-(1-phenyl-3,4-dimethylphosphole)$_2$Pd(NCS)$_2$, 73245-01-9; *cis*-(1-phenyl-3,4-dimethylphosphole)$_2$Pd(SCN)$_2$, 73245-02-0; *cis*-(1-benzyl-3,4-dimethylphosphole)$_2$Pd(NCS)$_2$, 73245-03-1; *cis*-(1-benzyl-3,4-dimethylphosphole)$_2$Pd(SCN)$_2$, 73245-04-2; *trans*-(1,3,4-trimethylphosphole)$_2$Pd(NCS)$_2$, 73193-87-0; *trans*-(1,3,4-trimethylphosphole)$_2$Pd(NCS)(SCN), 73193-88-1; *trans*-(1,3,4-trimethylphosphole)$_2$Pd(SCN)$_2$, 73245-05-3; *trans*-(1-*tert*-butyl-3,4-dimethylphosphole)$_2$Pd(SCN)$_2$, 73193-89-2; *trans*-(1-*tert*-butyl-3,4-dimethylphosphole)$_2$Pd(SCN)(NCS), 73193-78-9; *cis*-(1-phenyl-3,4-dimethylphosphole)$_2$Pd(SCN)(NCS), 73193-79-0; *trans*-(1-phenyl-3,4-dimethylphosphole)$_2$Pd(SCN)(NCS), 73244-98-1; *trans*-(1-phenyl-3,4-dimethylphosphole)$_2$Pd(SCN)$_2$, 73193-80-3; *trans*-(1-phenyl-3,4-dimethylphosphole)$_2$Pd(NSC)$_2$, 73193-81-4; *cis*-(1-benzyl-3,4-dimethylphosphole)$_2$Pd(NCS)(SCN), 73193-82-5; *trans*-(1-benzyl-3,4-dimethylphosphole)$_2$Pd(NCS)(SCN), 73244-99-2; *trans*-(1-benzyl-3,4-dimethylphosphole)$_2$Pd(NCS)$_2$, 73193-83-6; *trans*-(1-benzyl-3,4-dimethylphosphole)$_2$Pd(SCN)$_2$, 73193-84-7; dichlorobis(1,3,4-trimethylphosphole)palladium(II), 73245-00-8; dichlorobis(1-*tert*-butyl-3,4-dimethylphosphole)palladium(II), 73244-95-8; dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II), 73244-96-9; dichlorobis(1-benzyl-3,4-dimethylphosphole)palladium(II), 73244-97-0.

Supplementary Material Available: Listings of observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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