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Steric *vs.* Electronic Effects in Palladium–Thiocyanate Complexes. The Crystal Structures of Dithiocyanato[bis(diphenylphosphino)methane]palladium(II), Isothiocyanatothiocyanato[1,2-bis(diphenylphosphino)ethane]palladium(II), and Diisothiocyanato[1,3-bis(diphenylphosphino)propane]palladium(II)

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Abstract: The crystal structures of the series $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2Pd(CNS)_2$, CNS represents the thiocyanate ion without specifying the mode of attachment (n = 1–3), have been determined by X-ray diffraction techniques. The most important observation is that the thiocyanate coordination changes from S,S when n = 1 to S,N for n = 2 and N,N with n = 3. The conclusion is that the mode of thiocyanate coordination in palladium thiocyanate-phosphine complexes is determined by steric rather than electronic effects. The crystals of $(C_6H_5)_2PCH_2P(C_6H_5)_2Pd(SCN)_2$ are monoclinic, space group $P2_1/n$, with a = 10.426 (8) Å, b = 29.353 (10) Å, c = 9.884 (6) Å, and β = 119.86 (4)°. The final R value for the 2814 reflections used in the analysis was 0.039. The complex $(C_6H_5)P(CH_2)_2P(C_6H_5)Pd(SCN)(NCS)$ crystallizes with the orthorhombic space group $P2_12_12_1$. The cell dimensions are a = 17.773 (6), b = 23.212 (15), and c = 8.502 (4) Å. A total of 2249 reflections was used in the analysis and the final R value was 0.056. The last compound $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2Pd(NCS)_2$ is monoclinic with the space group $I2/a$ and cell dimensions of a = 14.774 (6) Å, b = 9.181 (5) Å, c = 21.182 (10) Å, and β = 95.48 (2)°. The molecule has twofold symmetry, as required for four molecules per unit cell. The final R value for the 1781 reflections used in the analysis was 0.025. The Pd–P bond distances are a function of the nature of the trans atom, a σ-bond rather than a π-bond effect. The Pd–S distances appear to be independent of the tip of the thiocyanate ion from the coordination plane. A comparison of the angular changes in the three compounds is easily interpreted in terms of increasing steric effects with an increase in the chain length between the phosphorus atoms. The changing mode of the thiocyanate ion is explainable in terms of steric effects without invoking any π-bonding arguments.

The thiocyanate ion is an ambidentate ligand that can coordinate either through the sulfur or nitrogen atom.[2] This ambidentate nature can be interpreted in terms of the "soft–hard" concepts developed by Pearson.[3] Therefore, in the case of class b or "soft" metals, such as Pd(II) or Pt(II), coordination of thiocyanate is expected to occur through the "soft" sulfur atom. Indeed, Pd(II) complexes with many amine ligands form S-bonded thiocyanates. In contrast, a limited number of phosphine complexes of Pd(II) were found to have N-bonded thiocyanates, a fact which has been rationalized on the basis of π-bonding,[4] polyelectronic perturbation theory,[5] and the so-called antisymbiosis effects.[6]

A study of palladium- and platinum-thiocyanate complexes involving PPh_3, $AsPh_3$, and $SbPh_3$ was complicated by the fact that the steric and electronic factors operated in the same direction.[7] Nevertheless, steric control was used to prepare the N-bonded complex $Pd[(C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2](NCS)^+$ rather than the usual S-bonded thiocyanates.[8] However, despite this early evidence that steric effects could explain the changes in thiocyanate coordination, π-bonding arguments continued to be invoked.[9,10] In fact contrary evidence such as nmr coupling constants which suggested that π-bonding in Pt(π)-phosphine complexes was minimal at best[11] was ignored. The presence of both N-bonded and S-bonded thiocyanates in Pd(dppn)(NCS)(SCN), dppn is $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$,[12] appeared to support these π-bonding arguments and has also been used as an example of "antisymbiosis."[6] However, the existence of both N- and S-bonded thiocyanates in Pd(dpe)(NCS)(SCN),[13] dpe is $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, suggested that steric effects were extremely important and tended to refute the "antisymbiosis" arguments, at least for palladium complexes.

The problem in all of the previous studies has been the difficulty in separating steric from electronic effects. Therefore, after the completion of our study of Pd(dpe)(NCS)(SCN), we undertook an investigation of two other closely related complexes $Pd(dpm)(SCN)_2$, dpm is $(C_6H_5)_2PCH_2P(C_6H_5)_2$, and $Pd(dpp)(NCS)_2$, dpp is $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$. The series of complexes $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2Pd(CNS)_2$, CNS does not specify the mode of attachment, will have approximately equivalent electronic effects but vastly different steric require-

Table I. Crystal Data

	Pd(dpm)(SCN)$_2$	Pd(dpe)(NCS)(SCN)	Pd(dpp)(NCS)$_2$
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$I2/a$
a, Å	10.426 (8)	17.773 (6)	14.774 (6)
b, Å	29.353 (10)	23.212 (15)	9.181 (5)
c, Å	9.884 (6)	8.502 (4)	21.182 (10)
β, deg	119.86 (4)		95.48 (2)
Volume, Å^3	2623.5	2718.1	2860.0
Molecular weight	606.97	620.99	635.02
Z	4	4	4
ρ(calcd), g/cm^3	1.536	1.517	1.475
ρ(measd), g/cm^3	1.54	1.51	1.48
Crystal size, mm^3	0.28 × 0.19 × 0.19	0.078 × 0.085 × 0.090	0.41 × 0.38 × 0.38
Method of data collection	Moving crystal moving counter	Stationary crystal stationary counter	Moving crystal moving counter
Radiation used	Mo Kα	Cu Kα	Mo Kα
μ, cm^{-1}	9.9	83.1	9.1
2θ range, deg	0–45	0–135	0–45
No. of unique reflections	3432	2808	1874
No. of observed reflections	2814	2249	1781

ments for the phosphine ligand. Therefore, these effects can be delineated. Our results show a change in thiocyanate coordination from S,S when $n = 1$ to S,N for $n = 2$ and to N,N for $n = 3$ which parallels the increasing steric requirements of the phosphine ligands.[14] Therefore, the structural studies presented in this paper suggest that the primary mode of coordination of thiocyanate to Pd(II) is *via* the sulfur atom (an electronic effect) but that steric effects can be used to alter the mode of thiocyanate coordination.

Experimental Section

All three compounds Pd(dpm)(SCN)$_2$, Pd(dpe)(NCS)(SCN), and Pd(dpp)(NCS)$_2$ were kindly supplied by Professor D. W. Meek. The relevant crystal data are summarized in Table I.

Pd(dpm)(SCN)$_2$. Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic. The systematic absences of $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group to be $P2_1/n$. The unit cell dimensions were determined from a least-squares fit of 2θ, ω, ϕ and χ values for 15 reflections.

The intensity data were collected on a Syntex $P\bar{1}$ automatic difractometer using graphite monochromatized Mo Kα radiation (λ = 0.71069 Å) and a variable scan rate. The background was measured for a time equal to one-half of the total scan time at a point 1° to each side of the α_1 and α_2 peak. Four standard reflections were measured after every 100 reflections and were used to correct for a small variation (maximum 2%) of intensities with time. Reflections with an intensity $I > 1.4\sigma(I)$ were used in the structure analysis. The remaining reflections were flagged with a minus sign and not used in the determination. The data were reduced to a set of structure amplitudes in the usual manner.

Table II. Scheme of Refinement

	Pd(dpm)-(SCN)$_2$	Pd(dpe)-(NCS)(SCN)	Pd(dpp)-(NCS)$_2$
R index with all atoms from Fourier syntheses	0.20	0.19	0.12
Refinement with isotropic thermal parameters	3 cycles	3 cycles	3 cycles
R index	0.089	0.086	0.072
Refinement with anisotropic thermal parameters	6 cycles	6 cycles	3 cycles
R index	0.052	0.062	0.037
Refinement with hydrogen atoms included, but not refined	3 cycles	3 cycles	3 cycles
R index (final)	0.039	0.056	0.025
F(low) for weighting scheme	36.0	52.0	16.8
F(high) for weighting scheme	72.0	104.0	25.2

Pd(dpe)(NCS)(SCN). The systematic absences of $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$ indicated the space group to be $P2_12_12_1$. The unit cell dimensions were determined from a least-squares fit of 2θ values measured using the Cu Kβ peak (λ 1.39217 Å). The intensity measurements were made with a General Electric XRD-6 diffractometer, using a wide beam of Cu Kα_1 radiation (λ = 1.54051 Å) with 0.35 mil Ni foil in front of the scintillation counter. All reflections with $2\theta \leq 135°$ in the unique quadrant were measured first and then those in the half-hemisphere, thus giving three measurements for each reflection. Measurements of four standard reflections after ever 100 reflections indicated that the change in intensity with time was not significant. An experimental background curve was derived by measurement of the background in areas of reciprocal space which were known to be free from reflections and streaking. Those reflections which had intensities greater than 1.3 times the appropriate background were used in the structure analysis. An empirical correction for the α_1-α_2 splitting was made for reflections with $2\theta > 80°$. No absorption corrections were applied. The data were reduced to a set of structure amplitudes in the usual manner.

Pd(dpp)(NCS)$_2$. The crystals belong to the monoclinic system. The systematic absences of hkl for $h + k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$ indicated the possible space group to be Ia or $I2/a$. Intensity statistics indicated that the most probable space group was $I2/a$ and was confirmed by the successful structure analysis.

A spherical shape was obtained by dissolving a large crystal slowly in CH$_2$Cl$_2$ with a rotary motion. This crystal was used in the measurement of cell constants and intensity data. The procedure was similar to those given in the case of Pd(dpm)(SCN)$_2$. The relevant data are summarized in Table I.

Structure Determination and Refinement. All three structures were solved by the heavy atom method and refined by least-squares techniques. The scheme of refinement and R index at various stages are summarized in Table II. Three cycles of full-matrix least-squares calculations using individual isotropic thermal parameters were carried out on each compound. In the case of Pd(dpe)(NCS)(SCN), the imaginary part of the anomalous dispersion correction[15] was applied and the present enantiomorph was selected on the basis of Hamilton R-test.[16] Refinements using anisotropic thermal parameters were carried out by block-diagonal approximation for Pd(dpm)(SCN)$_2$ and Pd(dpe)(NCS)(SCN) and full-matrix calculation for Pd(dpp)(NCS)$_2$. At this stage a difference Fourier synthesis was computed, and the positions of hydrogen atoms were located in all three compounds. Their positions were included in subsequent least-squares calculations but were not refined. Refinement was terminated when the indicated shifts in parameters were less than one-third of the corresponding estimated standard deviation.

The quantity minimized by the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$ where $\sqrt{w} = F_o/F(\text{low})$ if $F_o < F(\text{low})$, $\sqrt{w} = 1$ if $F(\text{low}) \leq F_o \leq F(\text{high})$ and $\sqrt{w} = F(\text{high})/F_o$ if $F(\text{high}) < F_o$. The values of F(low) and F(high) in each case are listed in Table II. The atomic scattering factor for Pd was from Cromer, Larson,

Table III. The Final Parameters of Nonhydrogen Atoms in Pd(dpm)(SCN)$_2$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	1952 (4)	12,774 (1)	24,269 (4)	643 (4)	88 (1)	780 (5)	−40 (3)	530 (7)	7 (4)
S(1)	−2259 (2)	1,218 (1)	338 (2)	71 (2)	16 (1)	122 (2)	−13 (1)	9 (3)	14 (1)
S(2)	−530 (2)	1,196 (1)	4,333 (2)	102 (2)	23 (1)	125 (2)	−5 (1)	135 (4)	2 (2)
P(1)	2609 (1)	1,294 (1)	4,301 (1)	57 (1)	8 (1)	60 (2)	−1 (1)	38 (3)	−1 (1)
P(2)	1523 (1)	1,372 (1)	1,181 (1)	78 (2)	9 (1)	63 (2)	−7 (1)	56 (3)	−2 (1)
N(1)	−2516 (9)	1,633 (5)	−2,298 (10)	186 (13)	74 (3)	233 (15)	−75 (10)	40 (23)	141 (12)
N(2)	−3630 (6)	1,208 (2)	2,844 (8)	120 (8)	23 (1)	317 (14)	−19 (5)	235 (18)	−18 (7)
C(1)	−2347 (8)	1,456 (3)	−1,202 (8)	105 (10)	31 (2)	148 (12)	−38 (6)	15 (18)	34 (7)
C(2)	−2379 (6)	1,200 (2)	3,420 (7)	109 (8)	13 (1)	186 (11)	−13 (5)	168 (16)	−7 (5)
C(3)	3317 (6)	1,454 (2)	3,000 (6)	80 (7)	13 (1)	66 (7)	−10 (4)	57 (12)	3 (4)
C(1a)	3223 (6)	1,714 (2)	5,832 (6)	71 (7)	9 (1)	83 (8)	−3 (4)	73 (12)	−8 (4)
C(2a)	3809 (7)	1,591 (2)	7,366 (7)	133 (9)	14 (1)	90 (9)	14 (5)	80 (15)	−11 (5)
C(3a)	4286 (8)	1,921 (3)	8,526 (7)	173 (12)	25 (1)	101 (11)	17 (7)	97 (19)	−25 (6)
C(4a)	4143 (8)	2,371 (3)	8,121 (9)	158 (11)	19 (1)	190 (13)	−20 (6)	164 (20)	−56 (7)
C(5a)	3516 (9)	2,503 (2)	6,593 (9)	256 (15)	10 (1)	219 (14)	−17 (6)	288 (24)	−23 (6)
C(6a)	3043 (8)	2,167 (2)	5,435 (8)	206 (12)	10 (1)	137 (11)	−3 (5)	173 (19)	−14 (5)
C(1b)	3376 (6)	750 (2)	5,183 (6)	100 (8)	9 (1)	78 (8)	14 (4)	79 (13)	1 (4)
C(2b)	4901 (7)	705 (2)	6,100 (7)	124 (10)	16 (1)	125 (10)	26 (5)	91 (17)	0 (5)
C(3b)	5469 (8)	281 (3)	6,840 (7)	158 (11)	22 (1)	107 (10)	57 (6)	69 (18)	12 (6)
C(4b)	4511 (9)	−70 (2)	6,612 (8)	259 (14)	13 (1)	158 (12)	38 (6)	218 (22)	12 (6)
C(5b)	3018 (9)	−28 (2)	5,668 (9)	241 (14)	13 (1)	183 (13)	17 (6)	260 (23)	13 (6)
C(6b)	2451 (7)	391 (2)	4,990 (7)	151 (10)	10 (1)	138 (10)	4 (5)	152 (17)	6 (5)
C(1c)	1241 (5)	1,858 (2)	−52 (6)	71 (7)	10 (1)	81 (8)	5 (4)	77 (12)	5 (4)
C(2c)	673 (7)	1,795 (2)	−1,655 (7)	133 (9)	12 (1)	90 (9)	−4 (5)	97 (15)	6 (5)
C(3c)	453 (8)	2,171 (2)	−2,587 (8)	180 (12)	17 (1)	109 (10)	14 (6)	148 (18)	14 (6)
C(4c)	794 (8)	2,608 (2)	−1,976 (8)	150 (10)	16 (1)	145 (11)	13 (5)	168 (17)	24 (6)
C(5c)	1331 (7)	2,665 (2)	−408 (8)	130 (9)	11 (1)	174 (12)	8 (5)	138 (17)	6 (5)
C(6c)	1531 (7)	2,299 (2)	550 (7)	133 (9)	9 (1)	122 (10)	12 (4)	127 (16)	8 (5)
C(1d)	1693 (6)	881 (2)	170 (6)	132 (9)	9 (1)	76 (8)	−8 (4)	103 (14)	0 (4)
C(2d)	526 (9)	580 (3)	−519 (9)	224 (13)	15 (1)	190 (13)	−41 (6)	255 (23)	−48 (6)
C(3d)	643 (12)	204 (3)	−1,320 (11)	398 (22)	17 (1)	271 (18)	−75 (9)	451 (35)	−60 (8)
C(4d)	1904 (11)	146 (3)	−1,431 (10)	377 (20)	14 (1)	214 (15)	−14 (8)	397 (31)	−23 (7)
C(5d)	3043 (10)	445 (3)	−769 (9)	276 (15)	16 (1)	173 (13)	38 (7)	301 (24)	10 (6)
C(6d)	2933 (8)	824 (2)	44 (7)	165 (11)	13 (1)	134 (10)	13 (5)	159 (18)	0 (5)

[a] All values are $\times 10^4$ except for Pd which is $\times 10^5$. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

and Waber's compilation,[17] the scattering factors for P, S, N, and C were from Hanson, Herman, Lea, and Skillman[18] and the hydrogen curve was from Stewart, Davidson, and Simpson.[19] The scattering factors were corrected for the real part of the anomalous dispersion. The final atomic parameters for the nonhydrogen atoms are given in Tables III, IV, and V. The hydrogen atom parameters are given in Tables VI, VII, and VIII. A table of observed and calculated structure factor amplitudes is available.[20]

Results and Discussion

In all three compounds the crystal consists of discrete complexes, with no unusual intermolecular interactions between the molecules. A view approximately normal to the coordination plane, giving the atomic numbering, bond distances, and angles, is given in Figures 1–3. The distances and angles in the ten phenyl rings are normal.[20] Similarly, the P–C (of CH$_2$) distances in the three compounds range from 1.820 (12) to 1.855 (6) Å, are not significantly different, and are consistent with the available data. The average P–CH$_2$ distance of 1.832 Å is slightly longer than the P–C (of phenyl ring) distance of 1.801 Å although the difference is not significant. The difference in P–C (of CH$_2$) *vs.* P–C (of phenyl ring) is not unexpected since the hybridization of the carbon atoms is different in the two cases. The dimensions of the thiocyanate groups in the three compounds are similar to those found in other thiocyanates.[12] Distances and angles not included in Figures 1–3 are given in Table IX. The estimated standard deviations for distances and angles are given in Table X.

There is an approximately square-planar arrangement of donor atoms around the palladium atom in each case. The deviations from the least-squares plane for Pd(dpm)(SCN)$_2$ are Pd 0.023, S(1) −0.041, S(2) 0.032, P(1) −0.053, and P(2) 0.038 Å. In the case of Pd(dpe)(SCN)(NCS) the deviations from planarity are Pd 0.004, S(1) −0,033, N(2) 0.036, P(1) −0.037, and P(2) 0.030 Å. The thiocyanate groups are required to be cis because of the constraints imposed by the chelating phosphine ligands $Ph_2P(CH_2)_nPPh_2$. The number of CH$_2$ groups between the phosphorus atoms is the only difference between the ligands in the three complexes. Therefore, these three ligands should have approximately the same σ-donor and π-acceptor properties. However, the steric requirements of the three ligands will not be identical. An increase in steric requirements with an increase in the alkyl chain length is nicely illustrated by the change in P–Pd–P angle from 73.2° for $n = 1$, to 85.1° for $n = 2$ and to 89.1° for $n = 3$. Concomitant with the increasing P–Pd–P angle is a decrease in the P–Pd–S or N (other atom in coordination sphere) angle. For example, P(1)–Pd–S(2) is 90.94 (6)° when $n = 1$ and P(1)–Pd–N$_2$) is 90.2 (3)° when $n = 2$ and 89.82 (8)° for $n = 3$. The P(2)–Pd–S(1) angle goes from 102.79 (6)° for $n = 1$ to 100.3 (1)° for $n = 2$ to the P(2)–Pd–N of 89.82 (3)° when $n = 3$. The increasing steric effects are also illustrated in the increase of the Pd–S(1)–N(1) angle from 108.5 (3)° when $n = 1$ to 115.5° for $n = 2$. There is also an increase in the Pd–P–C (chelate ring) angles from 95.9 and 94.7° in the dpm case to 110.8 and 107.0° in the dpe complex to 114.4° in dpp ring. However, in spite of large angular changes involving the phosphorus atom and the chelate ring system, the angle between the phenyl rings is almost constant. The angles C(1a)–P(1)–C(1b) and C(1c)–P(2)–C(1d) show a maximum difference of 2.6°. Presumably, there is less flexibility for the angles involving the phenyl rings than in the chelating system. The net result of the various angular changes is to move the phenyl rings toward the other two coordination sites in the square-planar arrangement. Therefore, although

Table IV. The Final Parameters of Nonhydrogen Atoms in Pd(dpe)(SCN)(NCS)[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	−10,431 (6)	−15,313 (3)	−8114 (10)	356 (3)	93 (1)	655 (8)	−29 (6)	19 (17)	45 (9)
S(1)	−520 (3)	−1,029 (2)	1453 (4)	92 (3)	16 (1)	76 (5)	−19 (3)	−16 (7)	−5 (3)
S(2)	−3,217 (3)	−2,311 (3)	2934 (6)	66 (3)	53 (2)	139 (7)	−59 (4)	67 (8)	−4 (6)
P(1)	−1,674 (2)	−2,039 (1)	−2833 (4)	30 (2)	8 (1)	79 (4)	−3 (2)	−3 (5)	−2 (3)
P(2)	−171 (2)	−1,080 (1)	−2667 (4)	30 (2)	8 (1)	72 (4)	−2 (2)	3 (5)	4 (3)
N(1)	303 (9)	49 (5)	753 (19)	103 (11)	21 (3)	216 (24)	−36 (9)	5 (36)	−12 (19)
N(2)	−1,864 (7)	−2,003 (4)	756 (14)	50 (6)	19 (2)	101 (15)	−19 (6)	48 (22)	42 (13)
C(1)	−23 (9)	−403 (5)	992 (16)	52 (8)	20 (3)	91 (20)	−5 (8)	4 (25)	−17 (14)
C(2)	−2,397 (9)	−2,132 (5)	1614 (15)	38 (7)	11 (2)	108 (19)	−10 (7)	−22 (21)	8 (12)
C(3)	−1,220 (8)	−1,772 (4)	−4706 (12)	46 (8)	9 (2)	88 (18)	−9 (7)	15 (19)	7 (9)
C(4)	−134 (7)	−1,556 (5)	−4379 (12)	36 (6)	14 (2)	59 (15)	−4 (8)	4 (17)	−17 (13)
C(1a)	−2,959 (9)	−1,995 (5)	−2865 (14)	51 (8)	9 (2)	81 (18)	6 (7)	−8 (22)	−12 (11)
C(2a)	−3,558 (9)	−2,438 (5)	−2271 (16)	37 (7)	15 (3)	135 (22)	−3 (7)	−20 (23)	4 (14)
C(3a)	−4,524 (9)	−2,399 (7)	−2307 (19)	36 (8)	30 (4)	182 (28)	−11 (10)	1 (27)	2 (19)
C(4a)	−4,947 (10)	−1,895 (6)	−2847 (19)	39 (8)	30 (4)	171 (27)	−9 (10)	−32 (27)	−29 (18)
C(5a)	−4,424 (9)	−1,447 (6)	−3391 (17)	52 (8)	18 (3)	179 (24)	22 (9)	−24 (25)	−24 (16)
C(6a)	−3,438 (9)	−1,499 (6)	−3387 (15)	58 (8)	12 (2)	150 (21)	2 (9)	0 (23)	−31 (15)
C(1b)	−1,359 (8)	−2,793 (5)	−2761 (15)	39 (8)	11 (2)	109 (20)	10 (7)	33 (20)	3 (12)
C(2b)	−640 (10)	−2,971 (6)	−1691 (18)	60 (10)	20 (3)	194 (29)	4 (9)	60 (28)	22 (17)
C(3b)	−318 (11)	−3,541 (6)	−1658 (19)	84 (11)	18 (3)	224 (30)	29 (11)	40 (32)	19 (19)
C(4b)	−732 (13)	−3,892 (7)	−2806 (22)	120 (16)	23 (4)	272 (38)	36 (13)	202 (42)	31 (21)
C(5b)	−1,423 (12)	−3,738 (5)	−3876 (20)	107 (13)	12 (3)	207 (34)	−12 (9)	38 (34)	−33 (16)
C(6b)	−1,753 (10)	−3,173 (5)	−3888 (20)	66 (10)	15 (3)	215 (33)	−11 (9)	34 (32)	−29 (16)
C(1c)	1,040 (10)	−923 (5)	−2211 (13)	42 (7)	14 (2)	96 (17)	2 (9)	33 (26)	−6 (11)
C(2c)	1,550 (10)	−1,252 (6)	−1175 (17)	54 (9)	27 (4)	152 (29)	−2 (9)	−58 (26)	49 (16)
C(3c)	2,552 (11)	−1,175 (7)	−876 (25)	60 (10)	34 (4)	249 (33)	3 (11)	−65 (40)	46 (26)
C(4c)	3,017 (11)	−717 (7)	−1532 (19)	48 (10)	28 (4)	214 (31)	−7 (10)	−30 (29)	−11 (19)
C(5c)	2,534 (11)	−342 (6)	−2519 (22)	49 (10)	21 (3)	295 (39)	−31 (10)	−3 (34)	−27 (20)
C(6c)	1,556 (10)	−447 (7)	−2847 (20)	39 (8)	26 (4)	223 (31)	13 (10)	−23 (29)	−9 (19)
C(1d)	−771 (8)	−420 (4)	−3361 (13)	45 (8)	7 (2)	83 (17)	−13 (7)	−14 (19)	−10 (10)
C(2d)	−1,409 (9)	−151 (6)	−2378 (18)	40 (8)	21 (3)	169 (26)	3 (8)	3 (25)	16 (16)
C(3d)	−1,878 (10)	343 (6)	−2928 (20)	49 (9)	16 (3)	247 (33)	20 (9)	22 (31)	13 (17)
C(4d)	−1,697 (10)	555 (5)	−4432 (20)	64 (9)	11 (2)	228 (31)	1 (8)	−115 (31)	24 (16)
C(5d)	−1,058 (12)	278 (5)	−5345 (15)	61 (8)	15 (2)	154 (25)	2 (10)	−29 (30)	30 (12)
C(6d)	−592 (10)	−214 (5)	−4882 (15)	60 (9)	16 (3)	106 (20)	10 (9)	−37 (23)	34 (13)

[a] All values are $\times 10^4$ except for Pd which is $\times 10^5$. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table V. The Final Parameters of Nonhydrogen Atoms in Pd(dpp)(NCS)$_2$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	25,000 (0)[b]	15,164 (4)	0 (0)[b]	367 (2)	861 (5)	136 (1)	0 (0)[b]	22 (2)	0 (0)[b]
S	42,325 (8)	−18,429 (10)	13,507 (5)	698 (6)	1209 (13)	293 (3)	232 (13)	−306 (7)	210 (9)
P	31,922 (5)	32,522 (8)	6,134 (3)	350 (4)	889 (11)	121 (2)	−148 (10)	65 (4)	−41 (7)
N	3,057 (2)	−47 (3)	614 (1)	44 (1)	102 (4)	18 (1)	1 (4)	−4 (2)	10 (3)
C(1)	3,544 (2)	−791 (3)	923 (1)	41 (2)	80 (4)	15 (1)	−25 (4)	4 (2)	−4 (3)
C(3)	3,362 (2)	4,961 (4)	204 (2)	55 (2)	99 (4)	18 (1)	−27 (5)	7 (2)	4 (3)
C(4)	2,500 (0)[b]	5,837 (6)	0 (0)[b]	69 (3)	93 (6)	24 (1)	0 (0)[b]	0 (3)	0 (0)[b]
C(1a)	2,590 (2)	3,670 (3)	1,295 (1)	36 (2)	109 (4)	14 (1)	8 (4)	6 (2)	−3 (3)
C(2a)	1,906 (2)	2,727 (4)	1,454 (2)	41 (2)	149 (5)	16 (1)	−22 (5)	7 (2)	−7 (3)
C(3a)	1,436 (2)	3,043 (5)	1,977 (2)	43 (2)	226 (7)	18 (1)	−25 (6)	15 (2)	−4 (4)
C(4a)	1,649 (3)	4,266 (5)	2,333 (2)	56 (2)	209 (7)	19 (1)	43 (7)	18 (2)	−24 (4)
C(5a)	2,323 (3)	5,197 (5)	2,180 (2)	75 (3)	137 (6)	24 (1)	15 (6)	18 (3)	−28 (4)
C(6a)	2,789 (3)	4,897 (4)	1,657 (2)	60 (2)	113 (5)	20 (1)	−14 (5)	17 (2)	−16 (3)
C(1b)	4,337 (2)	2,678 (4)	888 (1)	29 (1)	106 (4)	16 (1)	−25 (4)	5 (2)	−5 (3)
C(2b)	4,658 (2)	2,739 (5)	1,520 (2)	39 (2)	194 (6)	16 (1)	−3 (5)	9 (2)	−18 (4)
C(3b)	5,541 (3)	2,271 (6)	1,714 (2)	43 (2)	272 (8)	20 (1)	4 (7)	−2 (2)	−16 (5)
C(4b)	6,079 (2)	1,734 (5)	1,275 (2)	35 (2)	210 (7)	29 (1)	2 (6)	2 (2)	−13 (4)
C(5b)	5,763 (2)	1,677 (5)	648 (2)	42 (2)	187 (6)	27 (1)	−2 (6)	25 (2)	−39 (4)
C(6b)	4,891 (2)	2,129 (4)	451 (2)	40 (2)	173 (5)	17 (1)	−9 (5)	12 (2)	−26 (4)

[a] All values are $\times 10^4$ except for Pd, S, and P which are $\times 10^5$. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Parameters defined by space group symmetry.

the three ligands will have similar electronic properties, the steric requirements are different, and a clear separation of steric and electronic effects is possible.

A truly remarkable trend was found in the structures of these three compounds, namely, that the mode of thiocyanate coordination changes from S,S for n = 1, to S,N for n = 2, and to N,N for n = 3—a dramatic demonstration that the mode of bonding of the thiocyanate ion to palladium is controlled by steric considerations. Since Pd(II) is considered a "soft" metal ion[3-6] and sulfur is a "soft" base, the primary mode of bonding of thiocyanate to Pd(II) will be *via* the sulfur end. However, since the M–S–C angle is usually about 110° compared to 180° for M–N–C (the N-bonded variety), there are larger steric requirements for the S-bonded ion. Therefore, when n = 1 and either N- or S-bonded groups can be accommodated, the fact that both ions are S-bonded is not surprising. In fact, one thiocyanate is tipped 23.7° out of the coordination sphere (*vide infra*) yet the group still remains S bonded. Now as the alkyl chain length increases the steric factors become dominant

Table VI. Final Parameters of Hydrogen Atoms in Pd(dpm)(SCN)$_2$[a]

Atom	x	y	z	B (Å^2)	Distance (Å)
H1(3)	429	125	318	5.7	1.11
H2(3)	379	177	316	5.7	1.02
H(2a)	412	130	770	6.2	0.91
H(3a)	500	186	976	7.4	1.08
H(4a)	439	265	886	7.5	1.04
H(5a)	336	285	621	7.5	1.06
H(6a)	243	229	426	6.7	1.07
H(2b)	548	95	597	6.7	0.99
H(3b)	656	18	765	7.0	1.06
H(4b)	502	−40	718	7.5	1.12
H(5b)	229	−27	590	7.6	1.14
H(6b)	123	40	407	6.3	1.14
H(2c)	54	146	−190	5.9	1.01
H(3c)	22	206	−353	6.7	0.90
H(4c)	27	287	−295	6.8	1.13
H(5c)	177	297	−2	6.3	1.01
H(6c)	191	233	170	6.5	1.01
H(2d)	−24	67	−22	6.6	1.01
H(3d)	−25	−5	−221	8.8	1.18
H(4d)	200	−22	−201	8.0	1.25
H(5d)	374	44	−116	7.1	0.98
H(6d)	374	100	47	5.7	0.89

[a] The positional parameters are × 10^3. The number in parentheses is the number of the carbon atom to which the hydrogen atom is bonded at a distance given in the last column.

Table VII. Final Parameters of Hydrogen Atoms in Pd(dpe)(NCS)(SCN)[a]

Atom	x	y	z	B (Å^2)	Distance (Å)
H1(3)	−101	−209	−553	6.2	1.06
H2(3)	−154	−151	−524	6.2	0.88
H1(4)	15	−141	−540	5.4	1.00
H2(4)	38	−197	−407	5.4	1.21
H(2a)	−305	−284	−171	5.6	1.25
H(3a)	−501	−260	−177	4.0	0.94
H(4a)	−579	−185	−279	5.4	1.16
H(5a)	−477	−107	−411	6.0	1.17
H(6a)	−305	−116	−357	5.5	0.95
H(2b)	15	−271	−170	6.8	1.23
H(3b)	41	−352	−74	5.7	1.29
H(4b)	−36	−430	−277	6.5	1.08
H(5b)	−188	−402	−456	5.0	1.07
H(6b)	−255	−314	−422	7.2	1.15
H(2c)	121	−160	−59	6.0	1.06
H(3c)	304	−152	−30	8.2	1.15
H(4c)	380	−52	−125	6.8	1.18
H(5c)	290	−2	−294	7.2	0.96
H(6c)	104	−20	−337	5.6	1.01
H(2d)	−186	−30	−112	5.6	1.28
H(3d)	−259	44	−282	5.8	1.00
H(4d)	−232	76	−485	7.0	1.06
H(5d)	−86	44	−641	6.5	1.01
H(6d)	9	−33	−574	6.1	1.21

[a] The positional parameters are ×10^3. The number in parentheses is the number of the carbon atom to which the hydrogen atom is bonded at a distance given in the last column.

Table VIII. Final Parameters of Hydrogen Atoms in Pd(dpp)(NCS)$_2$[a]

Atom	x	y	z	B (Å^2)	Distance (Å)
H1(3)	378	552	49	4.7	0.96
H2(3)	370	469	−16	4.7	0.99
H1(4)	235	651	38	5.5	1.05
H(2a)	176	179	122	4.6	1.01
H(3a)	87	237	205	5.4	1.06
H(4a)	129	464	264	5.9	0.94
H(5a)	250	621	243	5.9	1.09
H(6a)	325	559	153	5.1	0.99
H(2b)	426	316	183	5.2	0.99
H(3b)	577	240	218	6.3	1.03
H(4b)	669	141	140	5.9	0.96
H(5b)	616	131	33	5.6	1.00
H(6b)	466	202	−1	5.0	1.00

[a] The positional parameters are ×10^3. The number in parentheses is the number of the carbon atom to which the hydrogen atom is bonded at a distance given in the last column.

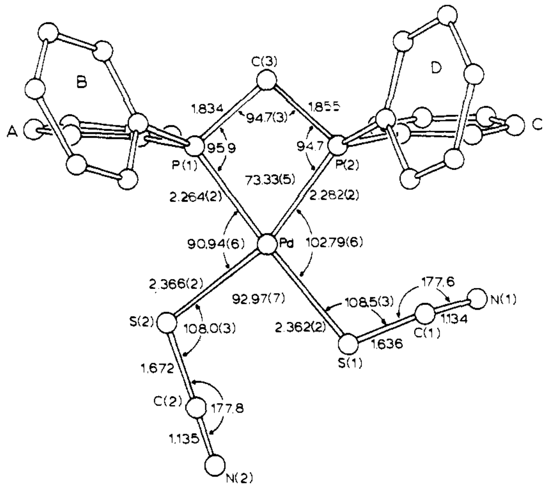

Figure 1. A view of dpmPd(SCN)$_2$ approximately normal to the coordination plane showing the atomic numbering and pertinent bond distances and angles. The phenyl rings are labeled A, B, C, and D, and individual numbering has been omitted for clarity.

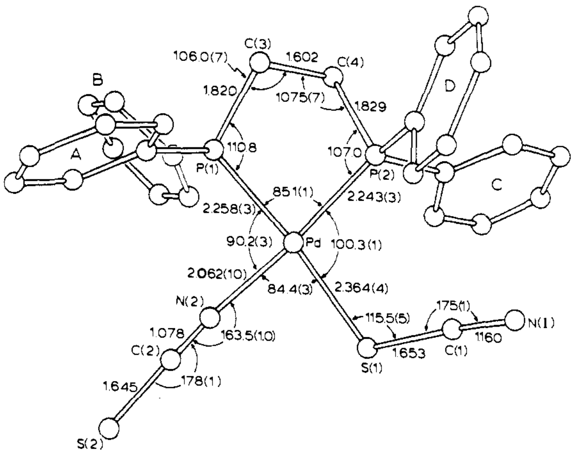

Figure 2. A view of the dpePd(SCN)(NCS) approximately normal the coordination plane showing the atomic numbering and pertinent bond distances and angles. Note the movement of the four phenyl rings A, B, C, and D relative to Figure 1 which illustrates the changing steric requirements of the ligand.

and the mode of bonding changes from S,S to S,N and finally to N,N. This trend parallels the steric changes in the phenyl groups (*vide supra*) and is strictly a steric effect.

Before any further discussion of the factors influencing the coordination mode of thiocyanate ion, we should consider the Pd–P, Pd–S, and Pd–N distances and the evidence for π-bonding between the palladium and phosphorus atoms. A compilation of Pd–P bond distances as a function of the trans atom is given in Table XI. We see that the longest Pd–P distances occur when P is trans to P. However, the usual problem of separating steric from electronic effects is present. For example, in the complex with the constrained ligand $Ph_2PN(C_2H_5)PPh_2$ the Pd–P distances of 2.219 (4) and 2.228 (4) Å[23] are significantly shorter than the distance of 2.260 (2) Å[24] found in the complex with the bulkier $PhP(CH_3)_2$ ligand. Similarly, in *trans*-$I_2Pd[PhP(CH_3)_2]_2$ complexes the P···I contacts range

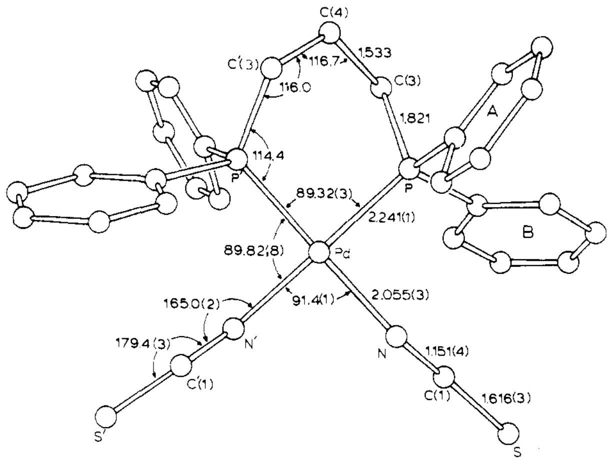

Figure 3. A view of dppPd(NCS)$_2$ approximately normal to the coordination plane. The molecule has a twofold axis of symmetry through Pd and C4 and hence the atoms P, P′, Pd, N, and N′ are required to be coplanar. The phenyl rings A and B are in approximately the same orientation as the C, D rings in the dpePd(SCN)(NCS) complex but the A′, B′ rings have moved relative to the A, B rings in the dpe case. The movement of the phenyl rings is related to the steric factors in the three ligands.

from 3.414 to 3.523 Å[30] which is significantly shorter than a van der Waals contact of 4.05Å, and any decrease in the Pd–P distance would produce intolerably short P ··· I distances. Unfortunately, the trends in steric factors parallel those of π-acceptor properties, and a separation of these effects is virtually impossible. However, before further discussion of π-effects, we might consider the Pd–S distances in various molecules.

Arguments have been given[3-5] that the π-acceptor properties of phosphines changed the character of the palladium atom so that "soft-soft" interactions were no longer preferred. Presumably in the case of the thiocyanate ion the sulfur atom will not compete effectively with the phosphorus atom for the d orbitals of the palladium atom and, therefore, the nitrogen end bonds to the metal atom. Although the present study has demonstrated that steric effects will control the mode of thiocyanate coordination, a survey of Pd–S distances is informative. A number of Pd–S distances have been summarized in Table XII. While the Pd–S trans to a P atom is longer than Pd–S trans to a N atom, the Pd–S trans to a S atom is very similar to Pd–S trans to a P atom. There appears to be a strong steric influence in the Pd–S bond lengths. Nevertheless, a reasonable conclusion from the data in Table XII is that either there is no d–d π-bonding in the Pd–S case or that the same amount of π-bonding exists regardless of the nature of the trans atom. A third possibility, that d–d π-bonding does not appeciably alter the bond length, would require rationalizing the Pd–P bond distances on the basis of steric arguments. The tip of the SCN group has been included in Table XII and we find very little correlation between the Pd–S distance and the tip of the thiocyanate ion. Unfortunately, the absence of a correlation between the tip of the thiocyanate ion and the Pd–S distance cannot be used to exclude π-bonding in the Pd–S bond. The possibility exists that a tip of the thiocyanate decreases π-bonding in one direction and increases π-bonding in another direction. The net result is that the total overlap is independent of the tip. The experimental evidence gives no definitive proof for or against π-bonding in the Pd–S bond. However, the variations in the Pd–S bond lengths can be explained on the basis of a σ-effect related to the trans atom as well as steric constraints.

Table IX. Bond Lengths and Angles not Given in Figures 1–3

	Pd(dpm)-(SCN)$_2$	Pd(dpe)-(NCS)(SCN)	Pd(dpp)-(NCS)$_2$
	(a) Bond Lengths (A)		
P(1)–C(1a)	1.804 (6)	1.772 (13)	1.808 (3)
P(1)–C(1b)	1.803 (6)	1.804 (11)	1.813 (3)
P(2)–C(1c)	1.803 (6)	1.750 (14)	
P(2)–C(1d)	1.812 (6)	1.837 (11)	
	(b) Bond Angles (deg)		
Pd–P(1)–C(1a)	119.1	111.4	112.5
Pd–P(1)–C(1b)	114.9	112.9	109.8
C(ring)–P(1)–C(1a)	108.3	108.0	107.3
C(ring)–P(1)–C(1b)	109.3	106.1	103.7
C(1a)–P(1)–C(1b)	108.2	107.3	108.7
Pd–P(2)–C(1c)	121.5	116.9	
Pd–P(2)–C(1d)	116.9	112.0	
C(ring)–P(2)–C(1c)	107.4	106.0	
C(ring)–P(2)–C(1d)	108.0	105.1	
C(1c)–P(2)–C(1d)	106.5	109.1	

A compilation of Pd–N distances in Table XIII shows a variation in the Pd–N bond which is dependent on both steric factors and the nature of the trans atom. In this case the difference between a nitrogen trans to a phosphorus *vs.* nitrogen trans to a nitrogen is only about 0.03 Å compared to the Pd–P case, where the difference was about 0.08 Å. The difference between the variation of Pd–P and Pd–N bonds *vs.* the trans atom probably lies in the more polarizable nature of the P atom. The importance of the ligand geometry is nicely illustrated by the differences in Pd–N distances in the Pd[Me$_2$dpma]Cl$^+$Cl$^-$ complex[34] where the Pd–N trans to N is one of the longest observed to date, while the Pd–N trans to Cl is one of the shortest. These Pd–N distances are particularly noteworthy since Cl and pyridine are almost identical in their trans effect.[39,40] Furthermore, the N(sp^3) radius is expected to be larger than that of N(sp^2) which predicts a shorter Pd–N(py) distance compared to Pd–N(amine). The effect of ligand geometry is also important in the Pd[(CH$_3$)$_2$N(CH$_2$)$_3$PPh$_2$](SCN)(NCS) complex. The Pd–N (of the N(CH$_3$)$_2$ group) is extremely long compared to the other Pd–N distances and to that in Pd(H$_2$NCH$_2$CH$_2$NH$_2$)$_2{}^{2+}$ cation. The question is whether the lengthening is a trans effect or a steric effect.[41] In the case of the Cu[(CH$_3$)$_2$NCH$_2$CH$_2$NH$_2$]$^{2+}$ cation the Cu–N (to CH$_3$ end) is 2.083 (3) Å while Cu–N (of the NH$_2$ end) is 1.995 (3) Å,[1c] predominantly a steric effect. Therefore, the long Pd–N distance in Pd[(CH$_3$)N(CH$_2$)$_3$PPh$_2$](SCN)(NCS) must result in part from a steric effect of the –N(CH$_3$)$_2$ group. This conclusion is important in explaining the N- and S-bonded thiocyanate ions reported in this complex.

Conclusions

The structural studies reported in this paper together with other studies suggest that steric factors are the prime reason for the change from S-bonded to N-bonded thiocy-

Table X. Summary of Average Estimated Standard Deviations for Bond Lengths and Angles not Given in Figures 1–3

	Pd(dpm)-(SCN)$_2$	Pd(dpe)-(NCS)(SCN)	Pd(dpp)-(NCS)$_2$
	(a) Esd for Bond Lengths, σ (Å)		
S–C	0.008	0.013	0.003
P–C	0.006	0.012	0.003
N–C	0.012	0.017	0.004
C–C	0.011	0.020	0.005
	(b) Esd for Angles (deg)		
Pd–P–C	0.2	0.4	0.1
S–C–N	0.8	1.3	0.3
P–C–C	0.5	0.9	0.2
C–P–C	0.3	0.5	0.15
C–C–C	0.7	1.3	0.35

Table XI. A Compilation of Pd–P Bond Distances as a Function of the Trans Atom

Pd–P distance (Å)	Atom/group trans to P	Coordination sphere	Compound	Ref
2.241 (1)	N/NCS	P,P,N,N	$Pd[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](NCS)_2$	This work
2.243 (3)	N/NCS	P,P,S,N	$Pd[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2](SCN)(NCS)$	This work
2.243 (2)	N/NCS	P,S,N,N	$Pd[(C_6H_5)_2P(CH_2)_3N(CH_3)_2](SCN)(NCS)$	12
2.247 (2)	N/NCS (bridge)	P,P,S,N	$Pd_2(SCN)_2\{[(C_6H_5)_2PO]_2H\}_2$	21
2.259 (3)	N/tetrazole	P,P,N,N	$Pd[(CH_3)_2PC_6H_5]_2[5\text{-}CH_3CN_4]$	22
2.265 (3)	N/tetrazole	P,P,N,N	$Pd[(CH_3)_2PC_6H_5]_2[5\text{-}CH_3CN_4]$	22
2.219 (4)	Cl	P,P,Cl,Cl	$Pd[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]Cl_2$	23
2.228 (4)	Cl	P,P,Cl,Cl	$Pd[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]Cl_2$	23
2.260 (2)	Cl	P,P,Cl,Cl	*cis*-$Pd[(CH_3)_2PC_6H_5]_2Cl_2$	24
2.258 (3)	S/SCN	P,P,S,N	$Pd[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2](SCN)(NCS)$	This work
2.264 (2)	S/SCN	P,P,S,S	$Pd[(C_6H_5)_2PCH_2P(C_6H_5)_2](SCN)_2$	This work
2.282 (2)	S/SCN	P,P,S,S	$Pd[(C_6H_5)_2PCH_2P(C_6H_5)_2](SCN)_2$	This work
2.270 (6)	S/SCN	P,P,S,S	$Pd[(C_6H_5)_2PCH_2C(CF_3){=}CHP(C_2H_5)_2](SCN)_2$	25
2.278 (6)	S/SCN	P,P,S,S	$Pd[(C_6H_5)_2PCH_2C(CF_3){=}CHP(C_2H_5)_2](SCN)_2$	25
2.270 (2)	S/SCN (bridge)	P,P,N,S	$Pd_2(SCN)_2\{[(C_6H_5)_2PO]_2H\}_2$	21
2.312 (1)	P/ligand	P,P,S,S	*trans*-$Pd[P(OC_6H_5)_3]_2(SCN)_2$	26
2.317 (3)	C/π-bond	P,Sn,C,C	$(\pi\text{-}C_3H_5)Pd[P(C_6H_5)_3]SnCl_3$	27
2.318 (1)	P/ligand	P,P,S,S	*trans*-$Pd[C_6F_5P(CH_3)_2]_2(SCN)_2$	28
2.326 (3)	P/ligand	P,P,S,S	*trans*-$Pd[(C_6H_5)_2PC{\equiv}CC(CH_3)_3]_2(SCN)_2$	29
2.333 (7)	P/ligand	P,P,I,I	*trans*-$Pd[C_6H_5P(CH_3)_2]_2I_2$	30

Table XII. A Compilation of Some Pd–S Bond Distances as a Function of the Trans Atom[a]

Pd–S distance (Å)	Atom/group trans to S	Tip of SCN (deg)	Coordination sphere	Compound	Ref
2.392 (9)	S/SCN	74.8	S,S,S,S	$K_2Pd(SCN)_4$	31
2.371 (6)	P/ligand	24.5	P,P,S,S	$Pd[Ph_2PCH_2C(CF_3)CHPPh_2](SCN)_2$	25
2.369 (6)	P/ligand	52.6	P,P,S,S	$Pd[Ph_2PCH_2C(CF_3)CHPPh_2](SCN)_2$	25
2.366 (2)	P/ligand	5.8	P,P,S,S	$Pd[Ph_2PCH_2PPh_2](SCN)_2$	This work
2.362 (2)	P/ligand	23.7	P,P,S,S	$Pd[Ph_2PCH_2PPh_2](SCN)_2$	This work
2.364 (4)	P/ligand	19.6	P,P,S,N	$Pd[Ph_2PCH_2CH_2PPh_2](SCN)(NCS)$	This work
2.359 (1)	S[SCN		S,S,S,S	$Pd[SP(Ph_2)CH_2(Ph_2)PS](SCN)_2$	28
2.340 (1)	S/SCN		S,S,S,S	$Pd[SP(Ph_2)CH_2(Ph_2)PS](SCN)_2$	28
2.351 (1)	S/SCN	74.3	P,P,S,S	*trans*-$Pd[C_6F_5P(CH_3)_2]_2(SCN)_2$	28
2.352 (2)	S/SCN		P,P,S,S	$Pd[P(OC_6H_5)_3]_2(SCN)_2$	26
2.347 (1)	S/ligand	48.9	S,S,S,S	$Pd[SP(Ph)_2CH_2(Ph)_2PS](SCN)_2$	28
2.342 (1)	S/ligand	45.3	S,S,S,S	$Pd[SP(Ph)_2CH_2(Ph)_2PS](SCN)_2$	28
2.336 (3)	S/SCN	74.0	P,P,S,S	*trans*-$Pd[Ph_2PCCC(CH_3)_3]_2(SCN)_2$	29
2.312 (9)	S/SCN	17.5	S,S,S,S	$K_2Pd(SCN)_4$	31
2.299 (2)	S/ligand		S,S,Cl,Cl	*trans*-$Pd[(CH_3)_2SO]_2Cl_2$	32
2.295 (2)	N/ligand	9.8	P,S,N,N	$Pd[Ph_2P(CH_2)_3N(CH_3)_2](SCN)(NCS)$	9
2.28 (1)	Cl		S,Cl,Cl,N	$Pd(methionine)Cl_2$	33

[a] If the distance involves a thiocyanate group, the tip of the thiocyanate group from the coordination sphere is also listed.

Table XIII. A Compilation of Some Pd–N Distances as a Function of the Trans Atom

Pd–N Distance (Å)	Atom/group trans to N	Coordination sphere	Compound	Ref
2.148 (7)	N/SCN	P,N,S,N	$Pd[Ph_2P(CH_2)_3N(CH_3)_2](SCN)(NCS)$	12
2.068 (6)	N/ligand	N,N,N,Cl	$ClPd[Me_2dpma]^+Cl^-$	34
2.063 (7)	P/ligand	P,S,N,N	$Pd[Ph_2P(CH_2)_3N(CH_3)_2](SCN)(NCS)$	12
2.062 (10)	P/ligand	P,P,S,N	$Pd[Ph_2PCH_2CH_2Ph_2](SCN)(NCS)$	This work
2.055 (3)	P/ligand	P,P,N,N	$Pd[Ph_2P(CH_2)_3PPh_2](NCS)_2$	This work
2.036 (7)	N/ligand	N,N,N,N	$Pd[H_2NCH_2CH_2NH_2]_2{}^{2+}2Cl^-$	35
2.032 (3)	N/ligand	N,N,O,O	Pd[*N*-isopropyl-3-methylsalicylaldiminato]$_2$	36
2.031 (2)	N/ligand	N,N,O,O	Pd[*N*-isopropyl-3-ethylsalicylaldiminato]$_2$	37
2.022 (7)	N/ligand	N,N,N,N	Pd[2,2′-dipyridyliminato]$_2$	38
2.018 (8)	Cl	N,N,N,Cl	$ClPd[Me_2dpma]^+Cl^-$ [a]	34

[a] Me_2dpma is methyldi[(6-methyl-2-pyridyl)methyl]amine.

anate in palladium complexes. The importance of steric factors had been recognized earlier,[8] but these results were not generalized to the phosphine case and, unfortunately, have also tended to be ignored. The changing mode of coordination of the thiocyanate ion in the series of complexes $Pd[Ph_2P(CH_2)_nPPh_2](CNS)_2$, $n = 1\text{-}3$, is most easily explained in terms of an increasing steric effect. A similar series of complexes Pd[*cis*-$Ph_2PCH{=}CHPPh_2$]$(SCN)_2$,[42] Pd[*cis*-$Ph_2PCH{=}CHAsPh_2$](NCS)(SCN),[43] and Pd[*cis*-$Ph_2AsCH{=}CHAsPh_2$]$(SCN)_2$[43] can also be easily rationalized on the basis of steric arguments.[44] Finally, the preparation and characterization of *trans*-$Pd[P(OPh)_3]_2(SCN)_2$,[26] *trans*-$Pd[P(CH_3)_2C_6F_5]_2(SCN)_2$,[28] and $Pd[SP(Ph_2)CH_2CH_2(Ph_2)PS](SCN)_2$[28] have shown that S-bonded thiocyanates in the coordination sphere are possible even if other "soft" ligands are bonded to the Pd atom. These results suggest that antisymbiosis in palladium complexes may actually represent steric effects and should be reconsidered, at least in the palladium case.

A second important conclusion from this study involves the role of π-bonding in the trans effect. Our results suggest that the variation in bond lengths as a function of the trans atom is not a π-effect transmitted across the metal atom. This conclusion is similar to that reached by others[40,45] in the case of Pt(II) complexes. In fact our results can be most consistently interpreted in terms of no π-interactions between phosphine and sulfur ligands and metal, in agreement with the nmr results.[11]

Acknowledgments. We are grateful for a Department of Chemistry Postdoctoral Fellowship (M.M.), a Graduate School Fellowship (W.L.S.), and a grant of computer time from the Northeast Regional Data Center at the University of Florida (G.J.P.). The preliminary stages of this research were supported in part by a grant from the National Research Council of Canada (G.J.P.).

Supplementary Material Available. A table of the distances and angles in the phenyl rings of the diphosphine ligands together with a comparison of the observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $6.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-1059.

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