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Sulfur Chelates. 38.[1] Preparations and X-ray Structure Determinations of M(S₂CNEt₂)(PR₃)Cl (M = Ni, R = Et; M = Pd, Pt, R = C₆H₅)

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The preparations and single-crystal X-ray structures of the title compounds are described. All compounds are monomeric as solids with essentially planar metal–donor atom sets. Relevant crystallographic parameters are as follows: Ni-(S₂CNEt₂)(PEt₃)Cl triclinic, space group $P\bar{1}$, $a = 7.678$ (2) Å, $b = 9.775$ (5) Å, $c = 12.030$ (5) Å, $\alpha = 97.61$ (4)°, $\beta = 91.26$ (3)°, $\gamma = 95.43$ (3)°, $V = 890.30$ (64) Å³, $Z = 2$, $R = 0.055$, Ni–Cl = 2.190 (2) Å, Ni–S (trans P) = 1.723 (7) Å, Ni–S (trans Cl) = 1.728 (7) Å; Pd(S₂CNEt₂)(PPh₃)Cl triclinic, space group $P\bar{1}$, $a = 9.894$ (3) Å, $b = 11.731$ (4) Å, $c = 14.115$ (2) Å, $\alpha = 98.19$ (2)°, $\beta = 118.89$ (2)°, $\gamma = 108.04$ (2)°, $V = 1277.09$ (58) Å³, $Z = 2$, $R = 0.045$, Pd–P = 2.284 (1) Å, Pd–Cl = 2.338 (2) Å, Pd–S (trans P) = 2.352 (2) Å, Pd–S (trans Cl) = 2.283 (2) Å; Pt(S₂CNEt₂)(PPh₃)Cl orthorhombic, space group $P2_12_12_1$, $a = 15.350$ (4) Å, $b = 9.431$ (2) Å, $c = 16.930$ (6) Å, $V = 2451.0$ (1.1) Å³, $Z = 4$, $R = 0.035$, Pt–P = 2.253 (7) Å, Pt–Cl = 2.331 (6) Å, Pt–S (trans P) = 2.349 (7) Å, Pt–S (trans Cl) = 2.294 (7) Å. Comparisons are made between the structural properties of the title compounds and with the structures of the parent M(S₂CNEt₂)₂ species. These structural relationships are correlated with spectroscopic measurements, suggesting that several different, nearly equally energetic, processes lead to the observed dynamic NMR spectra of these complexes in solution. A structural trans effect P > S > Cl is observed in the metal–sulfur bonding.

Introduction

The interactions of Lewis bases with group 8 dithiolates is a topic of considerable interest,[1–4] a variety of species being isolated, several of which have been structurally characterized. We have established relationships between the solid-state and solution structures[1,5] of several 1,1-dithiolates, M(S–S)₂, and their phosphine adducts, M(S–S)₂Lₙ (L = phosphine; n = 1, 2). In addition, ⁷⁷Se NMR studies[6,7] have been used to probe the dynamics of the Se analogues of these S compounds.

Asymmetric chelates of type I, first reported by Maxfield,[8]

I
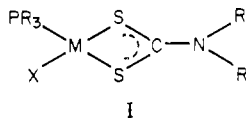
can be obtained by the reaction of metal dithiocarbamates with bases.[5,9,10] We have measured[11] the large barrier to C⇌N bond rotation in these compounds by ¹H NMR. In contrast to the palladium and platinum analogues, the nickel(II) compounds of type I have NMR-equivalent alkyl groups at room temperature, behavior variously ascribed to phosphine dissociation[10] or chloride exchange.[11]

We report here the solid-state structures of the type I compounds M(S₂CNEt₂)(PR₃)Cl (M = Ni, R = Et; M = Pd, Pt, R = Ph). These compounds permit a quantitative determination of the effects of phosphine plus halide substitution on the symmetric bischelates M(S–S)₂, since the structures of the M(S₂CNEt₂)₂ (M = Ni, Pd, Pt) compounds are known.[12–14] These results also provide structural information

that augments our determination of the barriers to C⇌N bond rotation in type I species. We have, in addition, determined the structures of the complexes Pt(Se₂CN(i-Bu)₂)₂ and M-(Se₂CNEt₂)(PR₃)Cl (M = Ni, R = Et; M = Pd, Pt, R = Ph) as part of our investigations into the coordination chemistry and NMR properties of selenium.[15,16] These last structural results, to be presented separately, when compared with the present work, permit a careful analysis of the relative donor atom effects of sulfur and selenium to be made.

Experimental Section

Physical Measurements. Microanalyses were by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were determined with a Laboratory Devices Mel-Temp melting point block and are uncorrected. Infrared spectra were recorded on Beckman IR-8 and IR-10 spectrophotometers using KBr pellets. ¹H NMR spectra were recorded on Varian XL-100-15, HA-100, and A-60A spectrometers. Fourier-transform mode ³¹P and ¹³C NMR spectra were recorded on the Varian XL-100-15 operated at 40.5 and 25.16 MHz, respectively, with broad-band proton decoupling. Deuterium solvents were used as internal ²H locks.

Syntheses. The compounds were prepared by essentially quantitative metathesis of the appropriate bis(diethyldithiocarbamate) and bis-(phosphine dichloride)[17–19] in refluxing benzene under nitrogen. Typically, stoichiometric amounts of each were refluxed for 1 h, the solutions were filtered in air, the solvent was stripped, and the solids were recrystallized. Satisfactory elemental analyses were obtained in all cases.

X-ray Structural Studies. Crystals were mounted on glass fibers. During data collection standard reflections were monitored every 50 reflections. Programs used in the solution and refinement of the structures have been given previously.[20]

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Table I. Summary of Crystal Data[a]

	NiL(PEt$_3$)Cl	PdL(PPh$_3$)Cl	PtL(PPh$_3$)Cl
molecular formula	NiC$_{10}$H$_{25}$ClNPS$_2$	PdC$_{23}$H$_{25}$ClNPS$_2$	PtC$_{23}$H$_{25}$ClNPS$_2$
fw	360.60	552.42	641.11
ρ_{calcd}, g/cm^3	1.345	1.436	1.737
ρ_{obsd}, g/cm^3	1.367	1.448	1.714
Z, formula units/cell	2	2	4
linear abs coeff, μ, cm^{-1}	15.37	10.47	63.39
λ(Mo Kα), Å	0.71069	0.71069	0.71073
crystal dimens, mm^3	0.4 × 0.4 × 0.2	0.3 × 0.3 × 0.3	0.15 × 0.15 × 0.1
systematic absences	none	none	$h00$ ($h = 2n + 1$); $0k0$ ($k = 2n + 1$); $00l$ ($l = 2n + 1$)
space group[21]	triclinic C_i^1-$P\bar{1}$ (No. 2)	triclinic C_i^1-$P\bar{1}$ (No. 2)	orthorhombic D_2^4-$P2_12_12_1$ (No. 19)
cell constants			
a, Å	7.678 (2)	8.894 (3)	15.350 (4)
b, Å	9.775 (5)	11.731 (4)	9.431 (2)
c, Å	12.030 (5)	14.115 (2)	16.930 (6)
α, deg	97.61 (4)	98.19 (2)	90.00
β, deg	91.26 (3)	118.89 (2)	90.00
γ, deg	95.43 (3)	108.04 (2)	90.00
V, Å^3	890.30 (64)	1277.09 (58)	2451.0 (11)
$F(000)$	368	560	1248
total data collected	3132	6017	1156
data used, $I/\sigma(I) \geqslant 3.0$	2261	4580	1010
no. of varied non-H parameters	154	262	122
reflctns/parameters	14.7	17.5	8.3
final R	0.055	0.045	0.035
final R_w	0.079	0.081	0.043

[a] L = S$_2$CNEt$_2$, data obtained on a Syntex P2$_1$ automatic diffractometer using θ–2θ scans at variable rates of 2.0–29.5°/min with standard Syntex programs.

(Diethyldithiocarbamato)chloro(triethylphosphine)nickel(II). The crystal for data collection (see Table I) was obtained by slow evaporation of acetone/pentane and cut to a suitable size. The lattice parameters were deduced from the angular settings of 15 centered reflections, average $2\theta = 15.98°$. The maximum variation of the standard reflections was 6.5% throughout data collection. The numbers of reduced data with $I/\sigma(I) \geq 0.0$, 3.0, and 15.0 are 3132, 2261, and 1374, respectively.

Determination of the Structure. The nickel atom position was obtained from the Patterson synthesis by standard heavy-atom methods. A structure factor calculation using this position yielded $R = 0.476$ and $R_w = 0.537$ for 1374 reflections. Several cycles of least-squares calculations and Fourier syntheses led to the location of all non-hydrogen atoms. Two cycles of isotropic refinement with full data (2261 reflections) yielded $R = 0.111$ and $R_w = 0.135$. A block-matrix least-squares refinement using anisotropic thermal parameters for all non-hydrogen atoms gave the final residuals.

(Diethyldithiocarbamato)chloro(triphenylphosphine)palladium(II). A suitable crystal (see Table I) was obtained for data collection by recrystallization from chloroform/pentane. The lattice parameters were deduced from the angular settings of 15 centered reflections, average $2\theta = 20.53°$. The maximum variation of the standard reflections was 4.8% throughout data collection. The numbers of reduced data with $I/\sigma(I) \geq 0.0$, 3.0, and 40.0 are 6017, 4580, and 1346, respectively.

Determination of the Structure. The palladium position was deduced from the Patterson map by standard heavy-atom techniques. A structure factor calculation using this position yielded $R = 0.388$ and $R_w = 0.452$ for 1346 reflections. Subsequent cycles of least-squares calculations and Fourier syntheses led to the location of all non-hydrogen atoms, with $R = 0.088$ and $R_w = 0.107$. A further cycle of isotropic refinement followed by two cycles of anisotropic refinement gave $R = 0.046$ and $R_w = 0.060$ with unit weights and 4580 reflections. At this stage, the error function was 9.74, and so a Cruickshank type weighting scheme was introduced.[20] Two more cycles of anisotropic refinement varying the positions of all non-carbon atoms and the carbon atoms bonded to the sulfur atoms yielded an error function of 2.26 and the final residuals.

(Diethyldithiocarbamato)chloro(triphenylphosphine)platinum(II). A suitable crystal (see Table I) was obtained for data collection by

Table II. Positional Parameters and Estimated Standard Deviations of Ni(Cl)(PEt$_3$)(S$_2$CNEt$_2$)

atom	x	y	z
Ni	0.05947 (1)	0.3142 (1)	0.2373 (1)
S(1)	0.7112 (3)	0.5291 (2)	0.2644 (2)
S(2)	0.3913 (2)	0.4177 (2)	0.3392 (2)
P	0.7965 (2)	0.2352 (2)	0.1275 (1)
Cl	0.4547 (3)	0.1066 (2)	0.2247 (2)
C(1)	0.7059 (12)	0.1746 (10)	−0.0149 (7)
C(2)	0.6263 (15)	0.2932 (14)	−0.0657 (8)
C(3)	0.9865 (10)	0.3585 (8)	0.1125 (7)
C(4)	1.1281 (12)	0.3025 (10)	0.0303 (9)
C(5)	0.8850 (12)	0.0796 (8)	0.1669 (8)
C(6)	0.9667 (13)	0.1081 (13)	0.2865 (10)
C(S)	0.5248 (9)	0.5687 (7)	0.3349 (5)
C(N1)	0.6130 (11)	0.8169 (7)	0.3691 (6)
C(N2)	0.7253 (13)	0.8598 (9)	0.4763 (7)
C(N3)	0.3289 (11)	0.7132 (9)	0.4406 (7)
C(N4)	0.1854 (12)	0.7496 (12)	0.3570 (10)
N	0.4917 (7)	0.6927 (5)	0.3778 (5)

recrystallization from acetone/heptane. The lattice parameters were deduced from the angular settings of 15 centered reflections, average $2\theta = 17.97°$. The maximum variation of the standard reflections was 5.8% throughout data collection. The numbers of reduced data with $I/r(I) \geq 0.0$, 3.0, and 10.0 are 1053, 1010, and 809, respectively.

Determination of the Structure. The distribution plot of the X-ray intensities and the distribution of the $|E|$'s were in good agreement with the theoretical values for a noncentric space group. The platinum position was obtained from the $[U\ V\ ^1/_2]$, $[U\ ^1/_2\ W]$, and $[^1/_2\ V\ W]$ planes of the Patterson synthesis. A structure factor calculation using this position yielded $R = 0.213$ and $R_w = 0.262$ for 809 reflections. Subsequent cycles of structure factor and difference Fourier calculations led to the location of all non-hydrogen atoms. Two cycles of full-matrix isotropic refinement gave $R = 0.054$ and $R_w = 0.062$ with unit weights and 1010 reflections. Two further cycles of refinement with anisotropic thermal parameters used for the platinum atom and a statistical weighting scheme yielded $R = 0.057$ and $R_w = 0.067$. Two cycles of refinement using negative coordinates gave the final residuals.

Final refinements, atomic positions, thermal parameters, and bond distances are summarized in Tables II–VI and S1–S3 (supplementary material). Figures 1–3 are ORTEP diagrams of the molecules.

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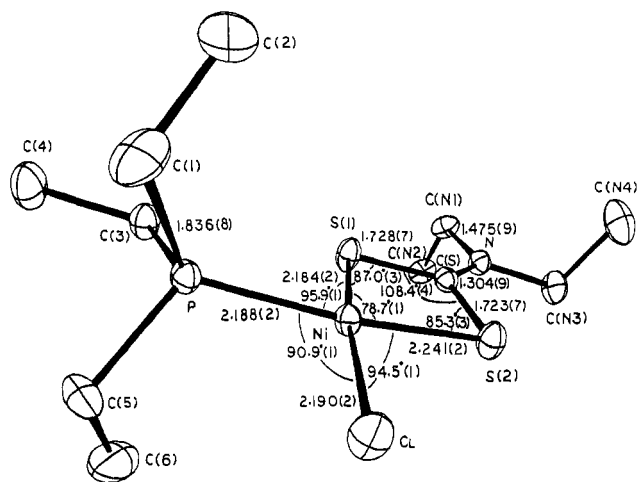
Figure 1. ORTEP diagram of Ni(S₂CNEt₂)(PEt₃)Cl.
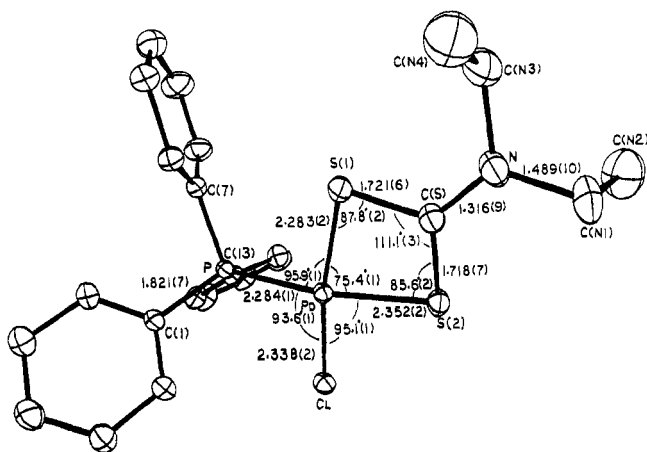
Figure 2. ORTEP diagram of Pd(S₂CNEt₂)(PPh₃)Cl.
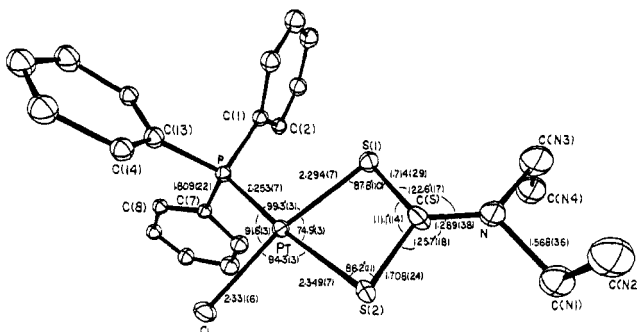
Figure 3. ORTEP diagram of Pt(S₂CNEt₂)(PPh₃)Cl.

Structural Results

The nickel and palladium derivatives of M(S₂CNEt₂)-(PR₃)Cl crystallize in the space group $P\bar{1}$ and the platinum complex crystallizes in $P2_12_12_1$. In this respect they contrast with their bischelated precursors, which crystallize in $P2_1/c$, $P4_2/n$, and $P4_2/n$, respectively.[12-14] All of these compounds are monomeric and square planar. In each case, the dithiocarbamate ligand is also appropriately planar, excluding the C atoms not bonded to N. The MS(1)S(2)PCl and S(1)S-(2)CNCC planes subtend a "stepping" angle across S(1)···S(2). A "hinging" angle of the dithiocarbamato ligands along M···C(S)–N also is observed. These angles are close to 180°, however.

No large distortions of the triphenylphosphine ligands are apparent. However, in Ni(S₂CNEt₂)(PEt₃)Cl two of the triethylphosphine ethyl groups become coplanar and approx-

Table III. Positional Parameters and Estimated Standard Deviations of Pd(Cl)(PPh₃)(S₂CNEt₂)

atom	x	y	z
Pd	0.0363 (0)	0.3910 (0)	0.2178 (0)
S(1)	0.0361 (2)	0.5650 (1)	0.1530 (1)
S(2)	0.2859 (2)	0.4691 (1)	0.2272 (1)
P	0.0809 (1)	0.2349 (1)	0.2911 (1)
Cl	−0.2293 (1)	0.3359 (1)	0.1941 (1)
C(1)	0.0608 (6)	0.2463 (5)	0.4134 (4)
C(2)	−0.0248 (8)	0.1387 (6)	0.4281 (5)
C(3)	−0.0340 (11)	0.1540 (8)	0.5250 (6)
C(4)	0.0411 (10)	0.2767 (8)	0.6046 (5)
C(5)	0.1247 (9)	0.3839 (7)	0.5894 (5)
C(6)	0.1340 (8)	0.3689 (6)	0.4922 (5)
C(7)	0.2940 (6)	0.2443 (4)	0.3447 (4)
C(8)	0.3333 (6)	0.2233 (5)	0.2635 (5)
C(9)	0.4969 (7)	0.2359 (5)	0.2968 (6)
C(10)	0.6191 (8)	0.2704 (6)	0.4111 (7)
C(11)	0.5823 (8)	0.2915 (7)	0.4934 (5)
C(12)	0.4192 (7)	0.2803 (6)	0.4612 (5)
C(13)	−0.0623 (6)	0.0697 (4)	0.1897 (4)
C(14)	−0.0079 (7)	−0.0255 (5)	0.2006 (5)
C(15)	−0.1222 (8)	−0.1524 (5)	0.1166 (6)
C(16)	−0.2849 (8)	−0.1778 (5)	0.0284 (5)
C(17)	−0.3392 (7)	−0.0829 (5)	0.0196 (5)
C(18)	−0.2266 (7)	0.0417 (5)	0.1002 (4)
C(S)	0.2275 (7)	0.5824 (5)	0.1746 (5)
N	0.3258 (6)	0.6701 (4)	0.1570 (4)
C(N1)	0.2689 (10)	0.7632 (6)	0.1080 (6)
C(N2)	0.3501 (12)	0.8910 (6)	0.2010 (8)
C(N3)	0.5021 (9)	0.6805 (7)	0.1889 (7)
C(N4)	0.4760 (11)	0.5858 (8)	0.0896 (8)

Table IV. Positional Parameters and Estimated Standard Deviations of Pt(Cl)(PPh₃)(S₂CNEt₂)

atom	x	y	z
Pt	−0.35398 (6)	0.01850 (8)	−0.56560 (6)
S(1)	−0.4666 (4)	0.1354 (7)	−0.6263 (5)
S(2)	−0.3037 (4)	0.0673 (7)	−0.6938 (4)
P	−0.4131 (3)	−0.0105 (6)	−0.4449 (4)
Cl	−0.2284 (4)	−0.1037 (7)	−0.5284 (4)
C(S)	−0.4029 (15)	0.1442 (25)	−0.7094 (18)
N	−0.4323 (13)	0.1878 (21)	−0.7765 (15)
C(N1)	−0.3725 (17)	0.1913 (27)	−0.8516 (17)
C(N2)	−0.3292 (17)	0.3449 (27)	−0.8534 (17)
C(N3)	−0.5251 (19)	0.2285 (31)	−0.7973 (20)
C(N4)	−0.5730 (20)	0.1002 (32)	−0.8189 (19)
C(1)	−0.5273 (12)	0.0393 (20)	−0.4411 (14)
C(2)	−0.5969 (13)	−0.0600 (19)	−0.4435 (15)
C(3)	−0.6826 (14)	−0.0100 (25)	−0.4337 (16)
C(4)	−0.7051 (16)	0.1311 (25)	−0.4325 (19)
C(5)	−0.6328 (16)	0.2301 (23)	−0.4349 (18)
C(6)	−0.5489 (15)	0.1873 (23)	−0.4403 (17)
C(7)	−0.4128 (14)	−0.1915 (22)	−0.4095 (15)
C(8)	−0.3942 (15)	−0.2294 (22)	−0.3327 (16)
C(9)	−0.3943 (15)	−0.5154 (25)	−0.3087 (16)
C(10)	−0.4130 (16)	−0.4748 (28)	−0.3609 (16)
C(11)	−0.4318 (19)	−0.4432 (30)	−0.4463 (20)
C(12)	−0.4286 (18)	−0.2994 (29)	−0.4664 (17)
C(13)	−0.3627 (16)	0.0966 (22)	−0.3698 (15)
C(14)	−0.2846 (15)	0.1700 (25)	−0.3870 (15)
C(15)	−0.2453 (17)	0.2552 (26)	−0.3237 (18)
C(16)	−0.2902 (17)	0.2660 (†&)	−0.2508 (17)
C(17)	−0.3688 (17)	0.2031 (28)	−0.2376 (17)
C(18)	−0.4048 (15)	0.1154 (24)	−0.2980 (16)

imately normal to the planes containing the other phosphine ethyl group and nickel–donor atom set.

The effect of replacing one of the M(S₂CNEt₂)₂ ligands by PR₃ and Cl⁻ is best seen by comparing the nickel structures. Substitution of triethylphosphine and chloride for one of the ligands of Ni(S₂CNEt₂)₂ induces asymmetry in the metal-ligand bonding but no significant changes in the remaining dithiocarbamato ligand (Figure 1). This is apparent for the NEt₂ unit, but the shortening and lengthening of the C—S

Table V. Bond Lengths (A), Nonbonding Distances (A), and Bond Angles (Deg) for MLPR$_3$Cl^a

M	bite, S(1)···S(2)	M-S trans P	M-S trans Cl	C-S trans P	C-S trans Cl	C-N	S(1)MS(2)	S(1)CS(2)	MSC(S) trans P	MSC(S) trans Cl
				Significant Bond Lengths and Bond Angles for MLPR$_3$Cl						
Ni (R = Et)	2.807 (3)	2.241 (2)	2.184 (2)	1.723 (7)	1.728 (7)	1.304 (9)	78.7 (1)	108.8 (4)	85.3 (3)	87.0 (3)
Pd (R = Ph)	2.837 (2)	2.352 (2)	2.283 (2)	1.718 (7)	1.721 (6)	1.316 (9)	75.4 (1)	111.1 (3)	85.6 (2)	87.8 (12)
Pt (R = Ph)	2.823 (9)	2.349 (7)	2.294 (7)	1.708 (24)	1.714 (29)	1.289 (38)	74.9 (3)	111.1 (4)	86.2 (1)	87.8 (10)
			Changes in Distances and Angles for MLPR$_3$Cl Compared with ML$_2$ Species							
Ni (R = Et)	0.00 (0)	0.040 (2)	−0.017 (13)	0.017 (18)	0.022 (18)	−0.026 (10)	−0.5 (1)	−1.8 (4)	0.3 (3)	2.0 (3)
Pd (R = Ph)		0.036 (3)	−0.033 (3)			−0.04 (10)	−0.1 (1)			
Pt (R = Ph)	0.011 (9)	0.060 (7)	−0.005 (7)	−0.027 (24)	−0.021 (29)	−0.019 (38)	−0.7 (3)	1.9 (14)	−1.7 (11)	−0.1 (10)

Significant Nonbonding Distances and Bond Angles for MLPR$_3$Cl

M	S(1)···S(2)	P···Cl	P···S	Cl···S	SMP	SMCl	PMCl
Ni (R = Et)	2.807 (3)	3.120 (3)	3.247 (3)	3.392 (3)	95.9 (1)	94.5 (1)	90.9 (1)
Pd (R = Ph)	2.837 (2)	3.370 (2)	3.390 (2)	3.461 (2)	95.9 (1)	95.1 (1)	93.6 (1)
Pt (R = Ph)	2.823 (9)	3.287 (9)	3.465 (10)	3.430 (10)	94.3 (3)	94.3 (3)	91.6 (3)

^{a} L = S$_2$CNEt$_2$.

Table VI. Spectroscopic Observations: ^{1}H NMR Shifts and Coupling Constants^{a,b}

	δ(CH$_2$)	δ(CH$_3$)	ν(C≈N), cm^{-1}
NiL$_2$	3.65	1.23	1527
PdL$_2$	3.74	1.28	1523
PtL$_2$	3.59	1.29	1535
NiL(PPh$_3$)Cl	3.59, 3.44	1.24, 1.17	1542
PdL(PPh$_3$)Cl	3.71, 3.51	1.24, 1.16	1545
PtL(PPh$_3$)Cl	3.62, 3.44	1.24, 1.15	1544
NiL(PEt$_3$)Cl^c	3.58	1.23	1545
NiL(PMePh)Cl^c	3.62	1.20	
NiL(PMePh$_2$)Cl^c	3.54	1.20	

^{a} The spectra, on CDCl$_3$, were recorded on the Varian XL-100; L = S$_2$CNEt$_2$ for all compounds. ^{b} The average J(CH$_2$–CH$_3$) = 7.1 Hz. ^{c} Unresolved quartet and triplet.

and C≈N bonds does indicate that the contribution of the thiouride structure, II, is greater in M(S$_2$CNEt$_2$)(PR$_3$)Cl than

II
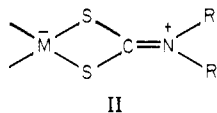
in M(S$_2$CNEt$_2$)$_2$. Unfortunately, the accuracies of the other M(S$_2$CNEt$_2$)$_2$ structures are insufficient to establish whether this variation is a general trend; thus we have sought to test for it spectroscopically (vide infra).

The major structural changes from the bis(dithiocarbamates) are in the vicinity of the metal. Both a shortening (trans to Cl) and a lengthening (trans to PEt$_3$) of the Ni–S bonds are observed on substitution, although we can resolve no asymmetry in the C–S bonds of Ni(S$_2$CNEt$_2$)(PEt$_3$)Cl. The shortening due to the trans Cl is less pronounced than the lengthening due to the trans PEt$_3$. Both compounds have the same chelate "bite" distances and chelate angles (S(1)NiS(2)). To accommodate the asymmetric Ni–S bonding, there is a slight opening of one NiSC angle and of the SCS angle (i.e., a slight swing of the ligand off what had been the C(S)MC(S) axis). Once the restraints of chelation on one side of the nickel are removed, there is a considerable (11°) opening of what was the chelate angle and an accompanying contraction of the interligand (SNiX) angle.

The effects of substitution of a phosphine and a chloride for one ligand of Pd(S$_2$CNEt$_2$)$_2$ are qualitatively the same as those of the nickel analog—there are similar parameters for the dithiocarbamate ligands, their bite distances and chelate angles, an increase in P···Cl relative to the bite, appropriate changes in the angles about the palladium, and asymmetry in the Pd–S bonding of Pd(S$_2$CNEt$_2$)(PPh$_3$)Cl. Again, M–S

(trans P) > M–S (ML$_2$) > M–S (trans Cl). However, in contrast to the nickel case, the magnitudes of these variations are the same. A comparison with the structure of Pd$_2$-(1:3,4-η-C$_4$(tol)$_4$Ph(S$_2$CN(i-Pr)$_2$), which has one dithiocarbamate sulfur trans to a Pd–C σ bond and the other trans to a Pd–olefin π bond, reveals a similar asymmetry in the Pd–S bonding.^{22} In this latter complex, the Pd–S bond trans to the σ-bonded carbon is considerably (0.115 Å) longer than Pd–S in Pd(S$_2$CNEt$_2$)$_2$, that trans to the olefinic portion of the ligand being approximately the same length as Pd–S (trans Cl) in Pd(S$_2$CNEt$_2$)(PPh$_3$)Cl. We have observed a similar large trans influence of a σ-bonded carbon in the related structure Pt(Se$_2$CNEt$_2$)(PPh$_3$)CH$_3$.^{23} Asymmetry in the C–X bonds and a lengthening relative to those of Pd(S$_2$CNEt$_2$)$_2$ are also suggested by the Pd(1:3,4-η-C$_4$(tol)$_4$Ph)(S$_2$CN(i-Pr$_2$)) data, but the low level of significance and variation in substituents on N renders definitive conclusions difficult.^{22}

In the triphenylphosphine complexes, a small "distortion", similar to that noted by Green et al.,^{24} is apparent such that the phenyl rings are at approximately 50° with respect to each other. Apart from inter-ring distances, there are no intramolecular approaches of the phenyl rings of less than 3.13 Å in Pd(S$_2$CNEt$_2$)(PPh$_3$)Cl or 3.39 Å in Pt(S$_2$CNEt$_2$)(PPh$_3$)Cl.

Trends similar to those above are observed when comparisons are made between the structures of Pt(S$_2$CNEt$_2$)$_2$ and Pt(S$_2$CNEt$_2$)(PPh$_3$)Cl, although the statistical significance is not as good as in the nickel or palladium structures. We can, however, be confident that the effects are real, as they are consistent with those in the nickel and palladium structures and those in the selenium analogues (M(Se$_2$CNEt$_2$)(PR$_3$)Cl (M = Ni, Pd, Pt).^{15} Thus, the general trend in these compounds is a lengthening (trans phosphine) and a shortening (trans chloride) of the M–S bonds when compared with those of the symmetric M(S$_2$CNEt$_2$)$_2$ compound. A comparison of sums of covalent and metallic radii reveals no large metal dependence of the metal–ligand bonding. There may be a slight tendency to favor resonance structure II more in M-(S$_2$CNEt$_2$(PR$_3$)Cl than in M(S$_2$CNEt$_2$)$_2$, an observation also suggested spectroscopically.

While there is very little structural change in the dithiocarbamate ligands of M(S$_2$CNEt$_2$)(PR$_3$)Cl (M = Ni, Pd, Pt), there is, however, a significant increase in nonbonded param-

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eters about the metal (P···Cl, P···S, Cl···S, angle PMCl) on going from nickel to palladium (where the increase is greatest) to platinum (where the increase is small, suggesting that an optimum ligand disposition has been achieved). The increase in the nonbonded distances on formally replacing nickel by palladium vary as P···Cl (0.250 (3) Å) > P···S (0.143 (3) Å) > Cl···S (0.069 (3) Å). Of the angles around the metal, angle PMCl is the only one found to vary. These changes indicate that the P···Cl nonbonding interaction in the nickel compound is the most important, the chloride being relatively favorably oriented with respect to the dithiocarbamate and nickel. In the nickel complex, the phosphorus atom is crowded somewhat by the chloride and to a lesser degree by the sulfur atom. With metals the size of palladium or larger, the phosphorus atom is far enough away from the other ligands to satisfy steric demands.

The crowding of the phosphine in $Ni(S_2CNEt_2)(PEt_3)Cl$ appears to be reflected in the disposition of the phosphine ethyl groups. A similar packing to alleviate crowding in analogous triphenylphosphine complexes is neither possible nor observed. Thus, crowding of the phosphine in $Ni(S_2CNEt_2)(PPh_3)Cl$ cannot be alleviated as readily as in $Ni(S_2CNEt_2)(PEt_3)Cl$. This causes a lower dissociative stability in the PPh_3 complex as is observed by ourselves and others[9,10] in the NMR spectra of $Ni(PR_3)(S-S)Cl$ complexes.

Solution NMR Observations

The average dithiocarbamate ^1H NMR parameters (Table VI) of the compounds $M(S_2CNEt_2)(PR_3)Cl$ (M = Ni, Pd, Pt) are similar, as expected from the small structural variations observed in the ligand on changing the metal. Halide and phosphine dependences of the dithiocarbamate chemical shifts are very small. Comparisons between the ^1H NMR spectra of the $Ni(S_2CNEt_2)_2$ compound with those of the mixed-ligand products reveal only small shifts of the dithiocarbamate resonances upon substitution. With Pd and Pt, the shifts observed in the average positions are consistent with an increased positive charge on nitrogen in $ML(PR_3)Cl$ compared with that in ML_2.

In the Pd and Pt complexes of $M(S_2CNEt_2)(PPh_3)Cl$, the methyl and methylene resonances are split into a doublet of triplets and a doublet of quartets, respectively, at room temperature, indicating a substantial barrier to C⇌N bond rotation as reported previously.[11] However, two types of ^1H NMR behavior are observed for the dithiocarbamate ligand in $Ni(S_2CNEt_2)(PR_3)Cl$ complexes. When R = phenyl, a broad triplet and a broad quartet are observed at temperatures between −60 and +30 °C. McCleverty[10] has reported ^{31}P spectra consistent with a phosphine-exchange process for this compound. Indeed, the PPh_3 derivative appears to be sterically highly strained (vide supra) and unable to alleviate this strain as readily as with a less bulky (PMe_2Ph) or less rigid (PEt_3) phosphine. Thus, the structural ^1H and ^{31}P NMR results support the contention that a dissociative phosphine-exchange process leads to NMR equivalence[10] of the alkyl groups of $Ni(S_2CNEt_2)(PR_3)Cl$ (R = Ph). The dithiocarbamate alkyl groups also are equivalent with R = Et or with PMe_2Ph, but the quartet and triplet are sharp at 30 °C in contrast to the behavior when R = Ph3. The crystal structures of NiL-$(PEt_3)Cl$ (L = S_2CNEt_2, Se_2CNEt_2,[15] $C_5H_7S_2$[25]) all show that

this phosphine can relax the steric strain by internal deformation, thereby obviating the need for phosphine dissociation. Thus phosphine exchange appears insufficient to explain the NMR data.

The ^1H and ^{31}P NMR results along with the crystal structures suggest that at least three processes lead to the observed magnetic equivalence of the dithiocarbamate alkyl groups in solution: (i) C⇌N rotation, (ii) phosphine exchange, and (iii) a third process, possibly halide exchange.[11] The first of these is the only process observed with the palladium and platinum compounds in the absence of excess phosphine, where the metals are large enough to accommodate the phosphine comfortably. With nickel(II) process ii seems important for bulky, nondeformable phosphines such as PPh_3 and appears rapid even at low temperature.[10] In $NiL(PR_3)Cl$ complexes a third process appears necessary to explain some of the NMR observations. Structural results for R = Et are inconsistent with steric effects causing a faster phosphine exchange than in $NiL(PPh_3)Cl$. Also the barrier to C⇌N rotation is not likely to have decreased the ~10 kcal/mol required to prevent observation[11,25] of NMR asymmetry above −60 °C. Halide exchange, which has been suggested previously, is consistent with observations made here and is known to occur rapidly when $NiL(PR_3)Cl$ and $NiL(PR_3)I$ are mixed.[11]

Vibrational Spectra

The frequency of the C⇌N stretching vibration, $\nu(C⇌N)$ has long been used as a measure of the degree of C–N double-bond character in the dithiocarbamates.[26] High-resolution infrared spectral data for the $M(S_2CNEt_2)(PR_3)Cl$ complexes (as solids, to allow for comparisons with the structural results) have been collected. Our results, Table VI, demonstrate a clear shift of $\nu(C⇌N)$ to higher frequencies when a S_2CNEt_2 ligand is replaced by chloride and triphenylphosphine. Such shifts have previously been interpreted as indicating an increase in C⇌N double-bond character and, in the present series, would add support to the contention that the apparent lengthening of the C–S bond and shortening of the C–N bond relative to observations in the symmetric dithio bischelates are real effects. McCleverty[10] has interpreted this increase in $\nu(C⇌N)$ in terms of a "mesomeric drift of electrons from the...dithiocarbamate group to the metal" caused by the acceptor properties of chloride and phosphine. The photoelectron spectra (UV) do, in fact, indicate a greater electron density on the nickel in the asymmetric complexes.

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