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Sulfur Chelates. 28.[1] Preparation and Nuclear Magnetic Resonance Studies of Unsymmetrical Planar Halo(*N,N*-disubstituted-dithiocarbamato)phosphinemetal(II) Complexes of Nickel Triad Elements. Barrier to C⋯N Rotations

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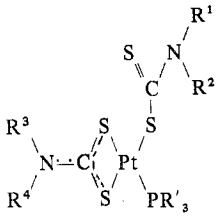
In our continued effort to explore dynamic properties of metal dithiolates, three classes of unsymmetrical dithiocarbamato complexes of nickel triad elements have been prepared: (i) $M(S_2CNR_2)(PR'_3)X$ (M = Pd, Ni; R = isobutyl, ethyl; R′ = alkyl, aryl; X = Cl, Br, I, SCN, SR); (ii) $Pt(S_2CNMePh)(PMe_2Ph)_2X$ (X = Cl, BPh_4, PF_6); (iii) $Pt(S_2CNMePh)_2$. In the first two classes, magnetic nonequivalence can be observed in the proton magnetic resonance (^{1}H NMR) of the ligands. In the third class both cis and trans isomers are observed. Magnetically equivalent R groups on structurally nonsymmetric dtc complexes are observed in the ^{1}H NMR spectra in the presence of free phosphine or upon increase in temperature. To explain these results two processes are considered. For the nickel(II) compounds, fast halide exchange appears to be responsible. For the palladium(II) and platinum(II) compounds, C⋯N partial double bond rotation appears to produce the magnetic equivalences observed at high temperatures. The $\Delta G^{\ddagger}$ values for the latter process range from 20.6 to 21.9 kcal/mol, some 5–10 kcal/mol higher than the rotational barrier found for the octahedral dithiocarbamato complexes of Fe(II), -(III), and -(IV).

Introduction

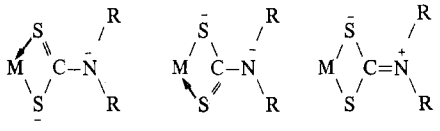
The preparation of several unsymmetrical square-planar halo(dithiocarbamato)phosphinenickel(II) complexes, $Ni(S_2CNR_2)(PR'_3)X$ (R = ethyl, R′ = alkyl or aryl, X = halide), has been reported by Maxfield.[2] However, few physical data were reported, and prior to our initiation of this study no analogous palladium(II) and platinum(II) complexes had been described.[3,4] Allison et al.[5] recently cited some results obtained by McCleverty on the ^{1}H NMR spectra of Maxfield's compounds which showed that the unsymmetrical $Ni(S_2CNR_2)(PR'_3)X$ complexes have equivalent dithiocarbamate alkyl groups. On the basis of this observation the statement was made that in $Pt(S_2CNR_2)_2(PR'_3)$ (I) "the atoms (S and



I

P) inducing the magnetic inequivalence in R^3 and R^4 are well removed (six bonds) from these groups so that the separation between the R^3 and R^4 resonances may well be too small to be resolved". However, ^{1}H NMR spectra of unsymmetrical nickel(II) complexes,[6,7] $Ni(AA)(PR_3)R$ (AA = acetylacetonate; R = CH_3, C_2H_5), showed that the two methyl groups on the acetylacetonate ligand are magnetically nonequivalent at room temperature in acetone-d_6. Thus we felt that the statement of Allison et al.[5] needed careful scrutiny.

The partial double bond character of the C⋯N bond in dithiocarbamatometal complexes has been known from both infrared spectroscopic studies[8-12] and x-ray structural data.[13-22] Chatt et al.[8] have discussed the C⋯N partial double bond in terms of the canonical structures IIa–c. It has been

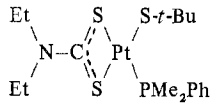


IIa IIb IIc

shown[8,23,24] that when electron-withdrawing groups are coordinated to the metal, the C⋯N stretching frequency may be increased due to increased contributions of form IIc.

Recently, Pignolet and co-workers[25-29] have examined the rotation about the C⋯N bond in octahedral dithiocarbamato complexes of Fe(II), -(III), and -(IV), Co(III), and Rh(III) using ^{1}H NMR and infrared spectroscopy. A correlation was found between increasing oxidation state, the C⋯N stretching frequency, and the free energy of activation ($\Delta G^{\ddagger}$) associated with bond rotation.[27] The Fe(IV) complexes displayed the largest C⋯N stretching frequencies and highest $\Delta G^{\ddagger}$ values. The barrier to C⋯N bond rotation in Fe(IV) complexes was found to be similar to that of *N,N,N′,N′*-tetramethylthiuram disulfide and *N,N,N′,N′*-tetramethyldithiocarbamate esters. The C⋯N bond distances also were compared. It was shown that long C⋯N bond distances are associated with small $\Delta G^{\ddagger}$ values.[29]

While investigating the interaction of phosphines with the mercapto-bridged dimer $[Pt(S_2CNEt_2)(S\text{-}t\text{-}Bu)]_2$, one of us[30] noted that there are two distinct types of ethyl groups in the ^{1}H NMR spectrum of the 1:1 adduct. The spectrum is temperature independent from −50 to +100 °C in $CHCl_3$ or $CHBr_3$. Although adduct interaction conceivably[30] could produce the observed NMR result, formation of the monomer III appeared likely. However, this interpretation assumed



III

magnetically nonequivalent R groups on the dithiocarbamato ligand (low temperatures) and a higher barrier to C⋯N (thioureide) bond rotation in this planar d^8 complex than in the octahedral iron complexes.

With planar d^8 complexes, no kinetic parameters for C⋯N bond rotation have been reported. Here we present the preparation and investigation of some unsymmetrical square-planar d^8 complexes of the type $M(S_2CNR_2)(PR'_3)X$, where M = Ni, Pd, or Pt, R = alkyl, and R′ = alkyl or aryl (Me = CH_3, Et = C_2H_5, *i*-Bu = C_4H_9, *t*-Bu = C_4H_9, Ph = C_6H_5, Bzl = C_7H_7). By use of ^{1}H NMR spectroscopy quantitative kinetic parameters for the C⋯N bond rotation

in these and related planar complexes have been obtained.

Experimental Section

Physical Measurements. Melting points were determined on a Laboratory Devices Mel-Temp melting point block and are reported uncorrected. Nuclear magnetic resonance measurements were obtained on both Varian A-60A and a Varian XL-100 NMR spectrometers equipped with variable-temperature probes. Variable-temperature spectra were all recorded on the XL-100 spectrometer. Temperatures were measured by a thermocouple mounted in the probe which was calibrated with ethylene glycol and methanol.[31] Infrared spectra were recorded on the Beckman IR-9 spectrophotometer. Solution molecular weights were determined using a Mechrolab vapor-phase osmometer calibrated with benzil.

Preparation of Compounds. All chemicals were used as purchased unless otherwise specified. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Anal. Calcd for $[Pd(S_2CN(i\text{-}Bu)_2)Cl]_2$: C, 31.2; H, 5.2. Found: C, 31.2; H, 5.2. Calcd for $[Pd(S_2CN(i\text{-}Bu)_2)Br]_2$: C, 27.7; H, 4.7. Found: C, 27.8; H, 4.6. Calcd for $[Pd(S_2CN(i\text{-}Bu)_2)I]_2$: C, 24.7; H, 4.2; N, 3.2. Found: C, 24.7; H, 4.4; N, 3.0. Calcd for $[Pd(S_2CN(i\text{-}Bu)_2)SEt]_2$: C, 35.5; H, 6.3. Found: C, 35.7; H, 6.1. Calcd for $[Pd(S_2CNEt_2)(S\text{-}t\text{-}Bu)]_2$: C, 31.5; H, 5.5. Found: C, 30.4; H, 5.6. Calcd for $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Cl$: C, 53.3; H, 5.5; N, 2.3. Found: C, 53.2; H, 5.5; N, 2.3. Calcd for $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Br$: C, 49.7; H, 5.1; N, 2.2. Found: C, 49.5; H, 5.2; N, 2.2. Calcd for $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)I$: C, 46.3; H, 4.8; N, 2.0. Found: C, 46.3; H, 4.8; N, 2.0. Calcd for $Pd(S_2CN(i\text{-}Bu)_2)(PMe_2Ph)Cl$: C, 42.2; H, 6.1; N, 2.9. Found: C, 42.2; H, 6.1; N, 2.8. Calcd for $[Pt(S_2CNMePh)(PMe_2Ph)_2](BPh_4)$: C, 46.4; H, 6.7; N, 3.2. Found: C, 46.2; H, 6.7; N, 3.0. Calcd for $Ni(S_2CNEt_2)(PPh_3)I$: C, 46.3; H, 4.2. Found: C, 46.2; H, 4.3. Calcd for $Ni(S_2CNEt_2)(PMe_2Ph)Cl$: C, 41.0; H, 5.6. Found: C, 41.2; H, 5.7. Calcd for $Ni(S_2CNEt_2)(PMe_2Ph)I$: C, 33.1; H, 4.5. Found: C, 33.2; H, 4.6. Calcd for $Ni(S_2CNEt_2)(PMe_2Ph)(SCN)$: C, 41.5; H, 5.2. Found: C, 41.6; H, 5.2.

Bis-μ-(*tert*-butylthio)-bis(*N,N*-diethyldithiocarbamato)dipalladium(II). Excess diethylamine (5 ml) was added to a methylene chloride solution of $[Pd(S_2CS\text{-}t\text{-}Bu)\text{-}\mu\text{-}(S\text{-}t\text{-}Bu)]_2$. The solvent was evaporated in air leaving orange crystals. The product was recrystallized in the same manner as other[32] mercaptide-bridged complexes; mp 227–229 °C; mol wt calcd 686, found 705.

Di-μ-chloro-bis(*N,N*-diisobutyldithiocarbamato)dipalladium(II). Method A. In 200 ml of H_2O–acetone (1:1 by volume), 0.70 g of $Pd(S_2CN(i\text{-}Bu)_2)_2$ was mixed with 0.45 g of K_2PdCl_4. The resultant solution was warmed and stirred for 1 h. Orange-red crystals precipitated. After cooling of the mixture in a refrigerator for 10 min the crystals were filtered off and washed with acetone; mp 256–257 °C dec after recrystallization from CH_2Cl_2.

Method B. $NaS_2CN(i\text{-}Bu)_2\cdot 3H_2O$ (1.0 g) in 100 ml of acetone was treated with 1.43 g of K_2PdCl_4 in 250 ml of water. The solution was stirred for 1 h. A brown solid was filtered off. After being washed with acetone, orange-red crystals were obtained by recrystallization from dichloromethane.

Di-μ-bromo-bis(*N,N*-diisobutyldithiocarbamato)dipalladium(II). A suspension of the chloro compound in acetone was treated with an excess of NaBr. This mixture was stirred for 1 h and allowed to stand overnight. The orange-red solid was filtered off and washed with water and acetone several times. Recrystallization from dichloromethane and hexane yielded the compound with mp 257–259 °C.

Di-μ-iodo-bis(*N,N*-diisobutyldithiocarbamato)dipalladium(II). The preparation was similar to that used for the bromo compound using KI instead of NaBr. The product is purple black with mp 282–284 °C. The molecular weight obtained crystallographically is 874.8, compared to 875.4 calculated.

Bis-μ-(ethylmercapto)-bis(*N,N*-diisobutyldithiocarbamato)dipalladium(II). In 5 ml of acetone, 0.2 g of the chloro dimer was treated with 2 ml of ethanethiol. The resultant solution was stirred for 5 min. Slow evaporation gave orange crystals. These were recrystallized from benzene–heptane and vacuum-dried; mp 176–178 °C.

Di-μ-chloro-bis(*N,N*-diisobutyldithiocarbamato)diplatinum(II). The compound was prepared in a manner similar to that used for the palladium compound, except that the temperature was kept at 50 °C while the mixture was stirred for more than 24 h; mp 270 °C dec.

Chloro(*N,N*-diisobutyldithiocarbamato)triphenylphosphinepalladium(II). In 5 ml of acetone, 0.2 g of $[Pd(S_2CN(i\text{-}Bu)_2)Cl]_2$ was treated with a 2:1 molar excess of PPh_3. After all of the solid went into the solution, a large amount of diethyl ether was added and the solution was cooled in an ice bath. Yellow needles were precipitated. These were filtered off and washed with diethyl ether several times. Recrystallization from benzene–hexane gave yellow-orange crystals, mp 220–222 °C; mol wt in chloroform 609 calcd, 625 found.

Bromo(*N,N*-diisobutyldithiocarbamato)triphenylphosphinepalladium(II). Method A. This compound can be prepared in a manner similar to the preparation of the chloro compound by the addition of a 2:1 molar excess of PPh_3 to $[Pd(S_2CN(i\text{-}Bu)_2)Br]_2$ in acetone.

Method B. $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Cl$ was dissolved in a NaBr-saturated acetone solution. The resultant solution was allowed to stand overnight and was evaporated to dryness. The residues were washed with distilled water several times and recrystallized from benzene–hexane; mp 223–224 °C; mol wt in chloroform 700 calcd; 712 found.

Iodo(*N,N*-diisobutyldithiocarbamato)triphenylphosphinepalladium(II). The preparation was identical with the preceding preparation of the bromo compound except that the iodo dimer was used in method A and KI was used instead of NaBr in method B. Dark red crystals were obtained with mp 224–225 °C.

Ethylmercapto(*N,N*-diisobutyldithiocarbamato)triphenylphosphinepalladium(II). The compound was prepared by a method similar to that for the chloro compound. Yellow-orange crystals were obtained; mp 153–155 °C.

Chloro(*N,N*-diisobutyldithiocarbamato)dimethylphenylphosphinepalladium(II). To 10 ml of a benzene solution of 0.2 g of the chloro-bridged dimer, 0.075 g of dimethylphenylphosphine in 2 ml of benzene was slowly added with stirring. The resultant solution was filtered to remove any unreacted chloro dimer. Upon addition of *n*-heptane, yellow crystals were obtained; mp 122–124 °C.

(*N,N*-Methylphenyldithiocarbamato)bis(dimethylphenylphosphine)platinum(II) Tetraphenylborate. To 0.52 g of $Pt(PMe_2Ph)_2Cl_2$ in 10 ml of 95% alcohol, 0.20 g of $NaS_2CNMePh\cdot 3H_2O$ in 25 ml of 95% alcohol was slowly added with stirring. After the addition, the solution was filtered to remove unreacted material. To this solution, 0.33 g of $NaBPh_4$ was added. A white precipitate was isolated, which was recrystallized from methanol; mp 158–160 °C.

(*N,N*-Diisobutyldithiocarbamato)bis(triphenylphosphine)platinum(II) Chloride. Reacting the chloroplatinum(II) dimer with ethyl mercaptan did not give the mercaptide dimer. After the platinum(II) dimer was treated with a 4:1 molar excess of PPh_3 in CH_2Cl_2, a white precipitate was obtained upon addition of diethyl ether to the solution. Recrystallization from CH_2Cl_2 gave white crystals, mp 152–154 °C.

Chloro(*N,N*-diethyldithiocarbamato)triphenylphosphinenickel(II). A mixture of 1.2 g of nickel chloride hexahydrate, 1.3 g of triphenylphosphine, and 1.2 g of sodium diethyldithiocarbamate trihydrate in 25 ml of absolute ethanol was heated at 50 °C for 1 h with stirring. The purple crystals were filtered when the solution was still warm. After being dried thoroughly under vacuum, these were recrystallized from acetone (dried over molecular sieves) in the presence of a small amount of LiCl and PPh_3. Large, dark purple crystals were obtained; mp 162–165 °C.

Iodo(*N,N*-diethyldithiocarbamato)triphenylphosphinenickel(II). In 5 ml of dried acetone, 0.5 g of the chloro compound $Ni(S_2CNEt_2)(PPh_3)Cl$ was treated with excess KI. The resultant solution was stirred for 1 h and evaporated under vacuum. The product was washed with water and dried under vacuum. Recrystallization from dry acetone in the presence of a small amount of KI and PPh_3 gave dark purple crystals, mp 158–162 °C.

Iodo(*N,N*-diethyldithiocarbamato)triphenylphosphinenickel(II). In 5 ml of dried acetone, 0.5 g of the chloro compound $Ni(S_2CNEt_2)(PPh_3)Cl$ was treated with excess KI. The resultant solution was stirred for 1 h and evaporated under vacuum. The product was then washed with water and dried under vacuum. Recrystallization from dry acetone in the presence of a small amount of KI and PPh_3 gave dark purple crystals, mp 158–162 °C.

Chloro(*N,N*-diethyldithiocarbamato)dimethylphenylphosphinenickel(II). A mixture of 1.30 g of nickel chloride hexahydrate, 1.24 g of dimethylphenylphosphine, and 1.36 g of sodium diethyldithiocarbamate trihydrate in 25 ml of absolute ethanol was heated at 50 °C for 1 h under nitrogen. This was evaporated to dryness under vacuum and washed with absolute ether several times. Recrystallization from dry acetone in the presence of LiCl gave dark purple crystals, mp 143–145 °C.

The following compounds were prepared by the metathetical reaction of $Ni(S_2CNEt_2)(PMe_2Ph)Cl$ with the appropriate salt in dry acetone: **iodo(*N,N*-diethyldithiocarbamato)dimethylphenylphosphinenickel(II),** dark red crystals, mp 132–134 °C; **thiocyanato-(*N,N*-diethyldithiocarbamato)dimethylphenylphosphinenickel(II),** dark brown crystals, mp 107–109 °C.

Line Shape Analysis. The kinetic line-shape analysis of the palladium complexes in this study is a two-site exchange problem as shown in Figure 4 for the $-CH_2$ resonances of $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Cl$. Rapid C⋯N bond rotation results in random scrambling of these two $-CH_2$ resonances. Line shapes were simulated using a modified Binsch DNMR 3 computer program.[33] The best fit to experimental line shapes was determined visually and the resulting values of k at various temperatures were taken to be the rate constants for C⋯N bond rotation.

The kinetic parameter $\Delta H^{\ddagger}$ was determined by a linear plot of ln (k/T) vs. $1/T$ in which the slope is $-\Delta H^{\ddagger}/R$. The $\Delta G^{\ddagger}$ values can be calculated by the Eyring equation, eq 1. Activation energies, E_a,

$$k = \overline{K}(K_B T/h)\exp(-\Delta G^{\ddagger}RT) \quad (1)$$

were determined by the linear plot of ln k vs. $1/T$, in which the slope is $-E_a/R$.

Results and Discussion

Preliminary Observations. An attempt to prepare a phosphine adduct of $Pd(S_2CS\text{-}t\text{-}Bu)_2$ by adding PPh_2Me to a tetrahydrofuran solution of the complex proved unsuccessful. Instead, a change occurred in the visible spectrum which was characteristic of the spectral change observed in the carbon disulfide elimination reaction.[32] The rate of the reaction in the presence of PPh_2Me was approximately 10 times the rate observed without PPh_2Me. The appearance of the peak at τ 8.01 (*tert*-butyl mercaptide) and the decrease in the peak at τ 8.55 (trithiocarbonate ligand) in the ^1H NMR spectrum are consistent with this interpretation.

The product of the carbon disulfide elimination reaction in the presence of PPh_2Me has a ^1H NMR spectrum identical with the spectrum obtained by adding PPh_2Me to $[Pd(S_2CS\text{-}t\text{-}Bu)\text{-}\mu\text{-}(S\text{-}t\text{-}Bu)]_2$ in a ratio of 2 mol of phosphine to every mole of complex. The ^{31}P–^1H coupling constant found in the spectra obtained by both methods is 11 Hz. This coupling constant is characteristic of tetrahedral phosphorus[34] and suggests that the PPh_2Me has reacted with the complex. When PPh_2Me is added to a solution of $[Pt(S_2CS\text{-}t\text{-}Bu)\text{-}\mu\text{-}(S\text{-}t\text{-}Bu)]_2$, the ^1H NMR spectrum contains a six-line multiplet for the phosphine methyl group. The additional lines are attributed to a coupling between the proton and the ^{195}Pt nucleus. From this coupling it was concluded that the phosphine was bound to the central metal atom. The NMR spectra of these phosphine adducts showed no change with temperature over a range of −50 to +50 °C. Attempts to isolate these adducts in crystalline form were unsuccessful.

The bridged dithiocarbamato complex $[Pt(S_2CNEt_2)\text{-}\mu\text{-}(S\text{-}t\text{-}Bu)]_2$ also shows evidence for the formation of a phosphine adduct in solution. A six-line multiplet at τ 7.92 in the spectrum indicates that the phosphine is interacting with the central metal atom. The presence of two distinct types of ethyl groups on the dithiocarbamate ligands also is observed, while the complex without phosphine shows only one type of ethyl group. Only one *tert*-butyl peak is found with or without the phosphine. The chemical shift difference between the methylene groups in the nonequivalent ethyl groups of the phosphine adduct is 12 Hz. The ^1H NMR spectrum of this adduct remained unchanged over a temperature range from −50 to +100 °C in $CHCl_3$ and $CHBr_3$. This adduct, as those mentioned above, could not be isolated in crystalline form.

Proton Magnetic Resonance Studies of $M(S_2CNR_2)(PR'_3)X$. ^1H NMR spectra of $Pd(S_2CNR_2)(PR'_3)X$ (R = *i*-Bu; PR'_3 = PMe_2Ph, PPh_3; X = Cl, Br, I, SEt) complexes in $CDCl_3$ at 37 °C reveal two different types of isobutyl groups. Figure 1 shows the spectrum of $Pd(S_2CNR_2)(PPh_3)Cl$ in which two doublet methylene protons (the doublet is due to the coupling between methine protons and methylene protons) are separated by 0.17 ppm and the two doublet methyl protons (due to $^3J_{CH_3\text{-}CH}$) are separated by 0.07 ppm. A similar result was observed when 2 mol of $PMePh_2$ was added to 1 mol of mercaptide-bridged dimer $[M(S_2CNEt_2)\text{-}\mu\text{-}(S\text{-}t\text{-}Bu)]_2$, M = Pd, Pt. The ^1H NMR spectra show two distinctive ethyl proton resonances. Table I shows the chemical shift differences of the nonequivalent alkyl groups observed in several unsymmetrical square-planar palladium complexes.

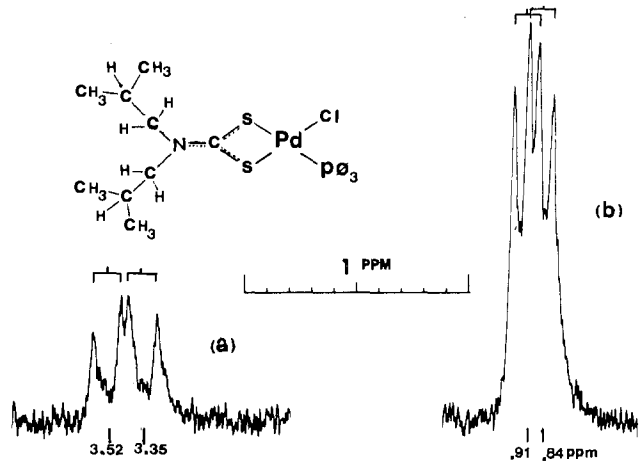


Figure 1. ^1H NMR spectrum of $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Cl$ at 37 °C, 60 MHz in $CDCl_3$: (a) methylene region; (b) methyl region.

Table I. Proton Chemical Shifts of $Pd(S_2CNR_2)(PR'_3)X$ Complexes at 37 °C Relative to TMS in Ppm

Compd	δ(N–CH₂)	Δδ (CH₂)	δ(N–CH₃)	Δδ (CH₃)	Solvent
$Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Cl$	3.69, 3.48	0.21	0.95, 0.82	0.13	$C_6D_5NO_2$
	3.52, 3.35	0.17	0.91, 0.84	0.07	$CDCl_3$
$Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Br$	3.68, 3.47	0.21	0.95, 0.82	0.13	$C_6D_5NO_2$
	3.52, 3.35	0.17	0.91, 0.84	0.07	$CDCl_3$
$Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)I$	3.67, 3.45	0.22	0.93, 0.83	0.10	$C_6D_5NO_2$
	3.53, 3.34	0.18	0.92, 0.86	0.06	$CDCl_3$
$Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)(SEt)$	3.61, 3.48	0.13	0.94, 0.87	0.07	$CDCl_3$
$Pd(S_2CN(i\text{-}Bu)_2)(PMe_2Ph)Cl$	3.65, 3.57	0.08	0.92, 0.87	0.05	$C_6D_5NO_2$
$Pd(S_2CNEt_2)(PMePh_2)(S\text{-}t\text{-}Bu)$	3.79, 3.61	0.18	1.25, 1.15	0.10	$CDCl_3$

We have considered the following possible causes of the observation of two different R groups on the dithiocarbamate ligands: (1) the formation of a dimeric adduct of the dimer used to synthesize the complex, thereby producing a nonequivalence of the dithiocarbamate ligands; (2) an orientational nonequivalence of the monomer due to N–C single-bond rotation; (3) a magnetic nonequivalence of the monomer induced by atoms (P, Cl, Br, I, S) six or more bond distances away with restricted thioureide C⋯N bond rotation.

(1) Molecular weight determinations showed that the complexes are monomeric. This ruled out the first possibility.

(2) Examples of the second possibility are found in $Ni(S_2CNR_2)_2$ and $Co(S_2CNR_2)_3$ (R = *i*-Pr) complexes.[35] The methyl groups on the dithiocarbamate ligands are nonequivalent below −54 °C, this being attributed to the slow N–C single-bond rotation. To examine this possibility the ^1H NMR spectrum of $Pd(S_2CN(i\text{-}Bu)_2)_2$ was taken at 37 °C, the temperature at which the nonequivalent isobutyl groups can be observed in the $Pd(S_2CNR)(PR'_3)X$ complexes. At this temperature there is only one set of magnetically equivalent

isobutyl groups. Thus the N–C single-bond rotation is relatively fast at ~37 °C.

(3) We are left with the conclusion that the observed *magnetic nonequivalence is induced by atoms (P, Cl, Br, I, S) six or more bond distances away from the resonating nucleus in these square-planar compounds.* Substantial chemical shift differences of the respective $-NR_2$ groups have been observed at low temperatures in the dithiocarbamate esters studied by Holloway and Gitlitz.[36]

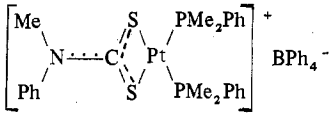
The proton chemical shifts of $M(S_2CNR_2)(PR'_3)X$ complexes are solvent dependent. In nitrobenzene-d_5 the two magnetically nonequivalent methylene protons (N^α protons) were both shifted downfield relative to the chemical shifts in $CDCl_3$, and the two nonequivalent methyl protons (N^γ protons) were shifted in both directions—the downfield methyl protons were shifted downfield while the upfield methyl protons were shifted upfield (Table I).

When the NMR spectrum of an *N,N*-dimethylamide in benzene is compared with the spectrum in nonaromatic solvents, it is seen that the resonances of both *N*-methyl groups are upfield in benzene. Hatton and Richards[37,38] proposed that the benzene shift was caused by a specific interaction between the π electrons of benzene and the positively charged amide nitrogen atom. Stereospecific interactions between benzene and bis(*N,N*-dialkyldithiocarbamato)dimethyltin and bis(*N,N*-dimethyldithiocarbamato)methyltin halides have been reported[39] in which the N^α protons were found to be shifted upfield while the tin methyl protons were shifted downfield. This was interpreted to mean that the methyl protons attached to the tin atom are on the average located in the paramagnetic region and the N^α protons in the diamagnetic region of the aromatic solvent. A similar observation was also reported for $(CH_3)_2Au(XYCNEt_2)$ (X = S, Y = Se) complexes.[40]

In nitrobenzene the N^α proton resonances of our compounds are shifted downfield. The electron withdrawing group, $-NO_2$, in the nitrobenzene may prevent the interaction of phenyl π electrons with the nitrogen on the dithiocarbamate. Hence a specific aromatic solvent–solute interaction different from that in benzene occurs.

Magnetic Resonance Studies of $[M(S_2CNR_2)(PR'_3)_2]X$. A series of compounds with the formula $M(S_2CNR_2)(PR'_3)_2X$ (M = Pd(II), Pt(II); R = Me, Et; PR_3 = PPh_3, $PMePh_2$, PMe_2Ph; X = Cl, BPh_4, Me_2SnCl_3) was reported.[5,41] Conductivity measurements indicate that the complexes are 1:1 electrolytes in solution. Results of IR and ^1H NMR studies suggest that the cation assumes a planar configuration. The phosphine methyl proton signal of $Pt(S_2CNR_2)(PMe_2Ph)_2X$ is a triplet (1:4:1) of doublets (1:1) six-line pattern (the two outer satellites are due to $^3J_{^{195}Pt-P-C-H}$, $I = {}^1/_2$, natural abundance 33%). ^1H NMR spectra of selenothiocarbamato complexes, $M(SeSCNR_2)(PR'_3)_2X$, showed two overlapping phosphine methyl proton signals. These nonequivalent proton resonances were attributed to the different atoms (S, Se) in trans positions.

The ^1H NMR spectrum of (*N,N*-methylphenyldithiocarbamato)bis(dimethylphenylphosphine)platinum(II) tetraphenylborate (IV) shows that the $P-CH_3$ protons are two



IV

overlapping six-line multiplets separated by 0.08 ppm in $CDCl_3$. The two sets of phosphine protons observed on the complex are due to the different substituents on the dithiocarbamate ligand, namely, methyl and phenyl groups. In this case, the protons on the phosphine methyls are seven bond distances away from the $-CH_3$ and $-C_6H_5$ groups.

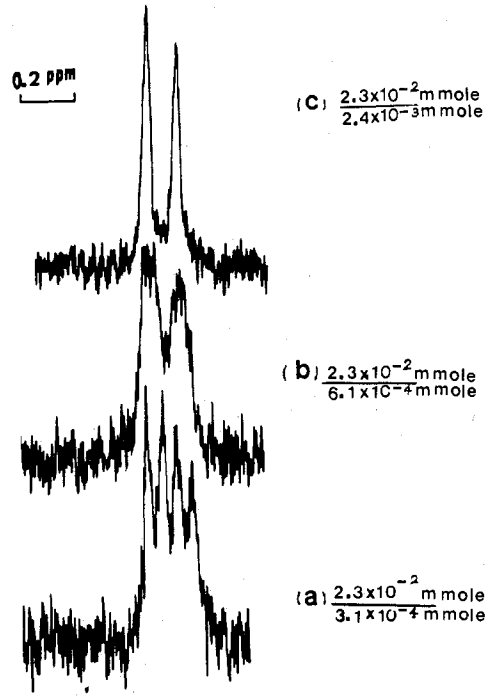
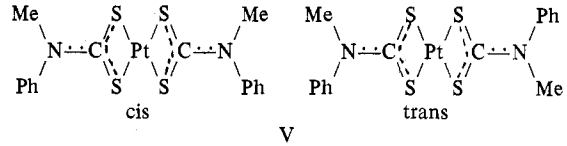


Figure 2. $Pd(S_2CN(i\text{-}Bu)_2)PPh_3Cl$ in the methylene region with different amounts of PPh_3 in $CDCl_3$ solution. The values indicate the complex:PPh_3 ratios.

***cis*- and *trans*-$Pt(S_2CNMePh)_2$.** The ^1H NMR spectrum of $Pt(S_2CNMePh)_2$ obtained at 0 °C in $CDCl_3$ using the Fourier transform mode shows that there are two methyl resonances separated by 0.02 ppm with approximately equal intensity. This observation is consistent with the presence of both cis and trans isomers (V) in solution.



V

It is apparent from these results that induced magnetic nonequivalences occur over rather long distances in these dithiocarbamates. However, as we now describe, magnetic equivalence of the R groups can be produced under a variety of circumstances.

^1H NMR Studies of $Pd(S_2CNR_2)(PPh_3)Cl$ in the Presence of Free Phosphine. When a trace amount of triphenylphosphine was added to a $CDCl_3$ solution of $Pd(S_2CNR_2)(PPh_3)Cl$, the ^1H NMR spectrum showed no appreciable line shape change. On increasing the amount of added triphenylphosphine, the two doublets for the methyl and methylene protons collapsed to a doublet in both regions. The line shape changes of $Pd(S_2CNR_2)(PPh_3)Cl$ induced by adding different amounts of triphenylphosphine are shown in Figure 2. This observation is explained by recognizing the existence of the equilibrium reaction, eq 2. The bis(phosphine)-sub-

$$Pd(S_2CNR_2)(PPh_3)Cl + PPh_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd(S_2CNR_2)(PPh_3)_2{}^+Cl^- \qquad (2)$$

stituted dithiocarbamato complex $Pd(S_2CNR_2)(PPh_3)_2Cl$ has equivalent R groups. The isolation of $M(S_2CNR_2)(PR'_3)_2X$ complexes (M = Pd, Pt; R = methyl, ethyl, isobutyl; R′ = alkyl, aryl; X = Cl, $BPPh_4$, PF_6) has been reported.[5,41] A rapid equilibrium reaction will collapse the nonequivalent R groups in $Pd(S_2CNR_2)(PPh_3)Cl$, with the observed rates being dependent on the concentration of phosphine.

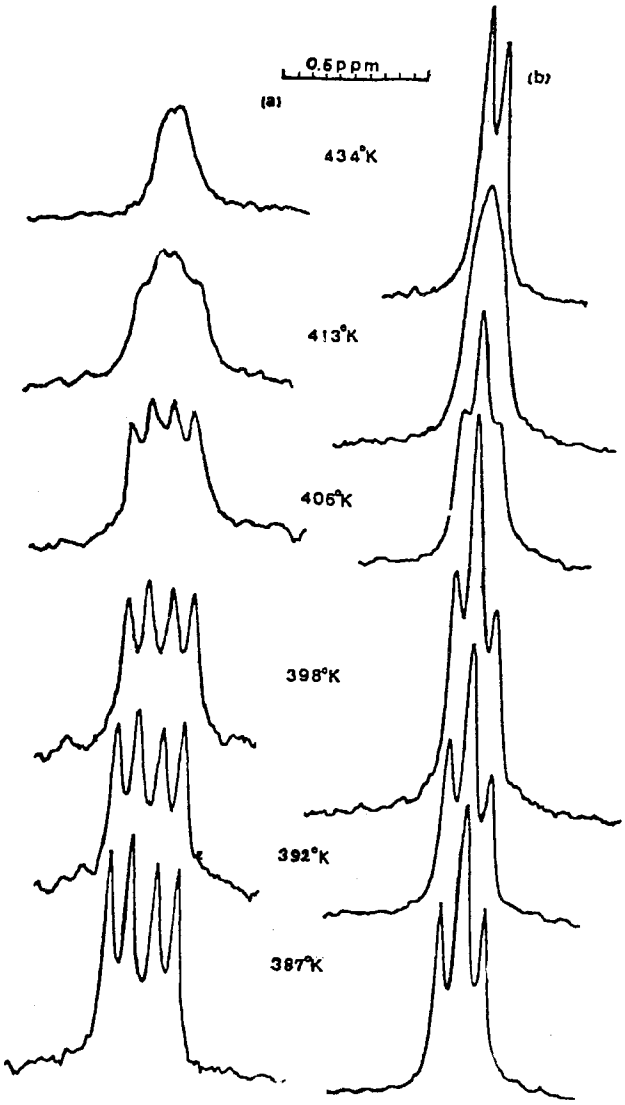


Figure 3. Variable-temperature ^{1}H NMR spectra of $Pd(S_2CN(i\text{-}Bu)_2)PPh_3Cl$ in $C_6H_5NO_2$: (a) methylene region; (b) methyl region.

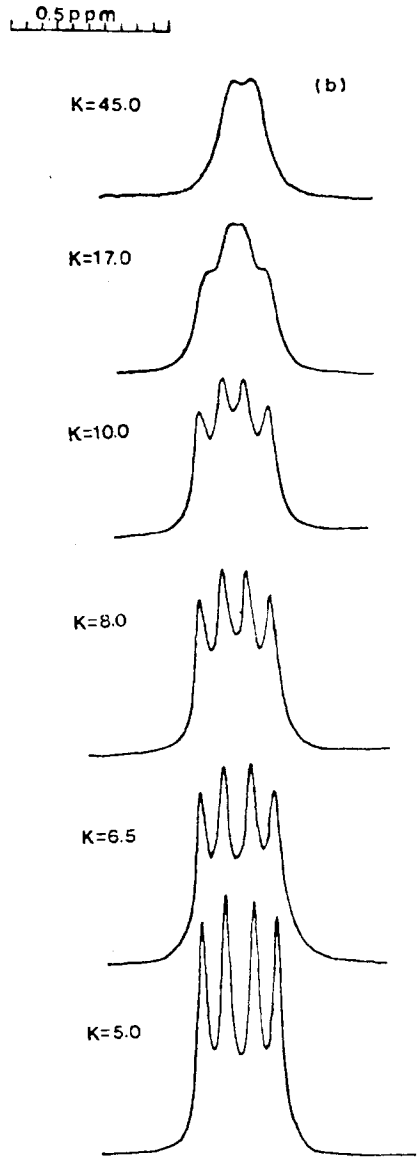


Figure 4. Calculated ^{1}H NMR spectra of $Pd(S_2CN(i\text{-}Bu)_2)PPh_3Cl$ in the methylene region.

Variable-Temperature ^{1}H NMR Studies. The Palladium(II) Complexes $Pd(S_2CN(i\text{-}Bu)_2)(PR'_3)X$. ^{1}H NMR spectra of $Pd(S_2CNR_2)(PPh_3)Cl$ in nitrobenzene-d_5 up to temperatures of 100 °C show no appreciable line broadening for the two methyl and methylene doublets. At 120 °C the methyl and methylene signals finally broaden (the methine protons will not be discussed because of their complicated multiplets and low intensity). At 180 °C equivalent isobutyl signals are observed. *The process is reversible.* A similar line shape change with increasing temperature was observed for the corresponding bromide and iodide compounds. Figure 3 shows the variable-temperature spectra of the chloride complex in the methyl and methylene regions. Figure 4 presents the calculated spectrum in the methylene region.

Several processes may lead to the equivalent isobutyl groups in these complexes. We have considered the following: (1) bimolecular association; (2) phosphine dissociation; (3) square planar ⇄ tetrahedral ⇄ square planar twisting about the metal center; (4) a ligand-exchange process involving either the halides or the dithiocarbamate ligand; (5) dissociation of one Pd–S bond followed by internal rotation in the temporarily unidentate dithiocarbamate ligand with the formation of a new Pd–S bond; (6) rotation about the C⋯N thioureide bond.

(1) At the temperature of coalescence of the methyl protons in the $Pd(S_2CNR_2)(PPh_3)Br$ complex, the rate of exchange of the nonequivalent isobutyl groups was found to be concentration independent over fourfold dilution in nitrobenzene-d_5. This observation excludes the possibility of a bimolecular process.

(2) The phosphine dissociation process was eliminated by preparing the dimethylphenylphosphine complexes $Pd(S_2CNR_2)(PMe_2Ph)Cl$, R = isobutyl. Fast phosphine dissociation would collapse the signal of the phosphine methyl protons.[42–45] Since the coupling constant, $^2J_{P\text{-}C\text{-}H}$ ($\simeq$−11 Hz) remains unchanged even in the fast-exchange region of the R groups on the dtc, the phosphine dissociation process is slow.

(3) For a number of Ni(II) complexes the planar (S = 0) ⇄ tetrahedral (S = 1) configurational equilibrium has been well established.[46] Eaton[47] using symmetry rules[48,49] predicted that square-planar cis–trans isomerizations are thermally disallowed, but square planar to tetrahedral reactions are allowed. This conclusion was criticized by Whitesides,[50] who showed that neither square-planar isomerizations nor tetrahedral racemizations are thermally allowed processes if the mechanism involves a tetrahedral–square planar interconversion. Consequently, although nonequivalent R groups on the unsymmetrical square-planar $Pd(S_2CNR_2)PR'_3X$ complexes can become equivalent by going through a tetrahedral

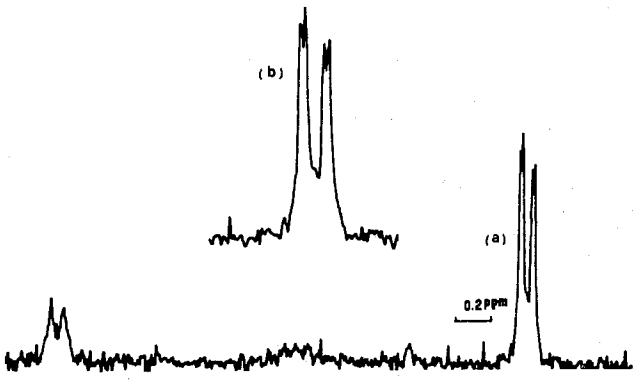


Figure 5. (a) The 170 °C ^{1}H NMR spectrum of a mixture of $Pd(S_2CN(i\text{-}Bu)_2)PPh_3Cl$ and $Pd(S_2CN(i\text{-}Bu)_2)PPh_3I$ in $C_6D_5NO_2$ in the methylene and methyl regions. (b) The methyl region with twice the scale of (a).

transition state, this process is energetically unfavorable. No stable tetrahedral configuration has been found to date in Pd(II) and Pt(II) complexes.

Further support for the kinetic absence of the third process was obtained from variable-temperature ^{1}H NMR studies of a mixture of cis–trans isomers of $Pd(S_2P(OEt)Ph)_2$[51] in nitrobenzene-d_5 at temperatures up to 140 °C (the temperature at which the nonequivalent alkyl groups on the dtc of unsymmetrical palladium(II) complexes broadened and collapsed). The line shapes of the cis–trans mixture are essentially invariant over this temperature range. This observation suggests that a metal-centered twist mechanism is not responsible for the magnetically equivalent R groups observed at high temperature.

(4) The intermolecular ligand-exchange mechanism (either halide or dtc) was ruled out by the following experimental result: ^{1}H NMR spectra of both $Pd(S_2CNR_2)(PPh_3)Cl$ and $Pd(S_2CNR_2)(PPh_3)I$ (R = isobutyl) show one set of sharp methyl proton signals at 170 °C in nitrobenzene-d_5, an indication of fast exchange between the two nonequivalent alkyl groups in each compound. Upon mixing of the chloride and iodide complexes, the ^{1}H NMR spectrum at 172 °C in nitrobenzene-d_5 shows two sets of methyl signals as expected for two species (see Figure 5). Since fast halide (or dtc) exchange should average the two methyl signals, the observation of distinct methyl resonances in the chloride and iodide complexes indicates that the rates of intramolecular rearrangement are faster than the rates of ligand exchange for the four coordinated species, at least at the concentrations used here.

(5) The dithiophosphonate study mentioned above also militates against an M–S bond rupture mechanism. While the three-coordinate palladium(II) intermediate cannot be ruled out conclusively, its presence alone does not produce equivalent R groups. Either C⋯N thioureide bond rotation or cis–trans isomerization at the metal center must follow. Both of these processes, however, are expected to occur once Pd–S bond rupture takes place. The strongest evidence that Pd–S bond rupture in the dithiocarbamates is slow comes from the generally similar behavior of these materials compared to that of the dithiophosphates. A unimolecular bond rupture mechanism would have a rather high activation energy.[52]

(6) The most reasonable explanation for the reversible formation of magnetically equivalent alkyl groups in palladium(II) compounds at 180 °C assumes a C⋯N bond rotation. Numerous kinetic analyses of C⋯N bond rotation[25–29,36,53–56] on substituted amides, thioamides, thiocarbamates, dithiocarbamate esters, thiuram disulfides, and tris(dithiocarbamato)metal complexes using NMR spectroscopy have been published.

Table II. Kinetic Parameters for the C⋯N Bond Rotation and Corresponding ν(C⋯N) Stretching Frequencies

Compd	ν(C⋯N), cm^{-1}	$\Delta G^{\ddagger}$,[d] kcal/mol (T, K)
$Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Cl$	1517[a]	21.9 ± 1.0 (3.98)[e]
$Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Br$	1516[a]	21.8 (398)[c]
$Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)I$	1509[a]	21.5 (398)[c]
$Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)(SEt)$	1506[a]	
$Pd(S_2CN(i\text{-}Bu)_2)(PMe_2Ph)Cl$	1509[a]	21.7 (398)[c]
$Pt(S_2CNMePh)(PMe_2Ph)_2(BPh_4)$	1506[a]	20.6 (393)[c]
$Fe(S_2CNEt_2)_2phen$[27]	1482[b]	8.8 (202)[c]
$(S_2CNEt_2)_2$[57]	1487	15.4 (300)[c]

[a] KBr pellets. [b] CH_2Cl_2 solution. [c] Calculated at the coalescence temperature. [d] All of the values obtained in this work are in $C_6D_5NO_2$ solvent. The $\Delta G^{\ddagger}$ value for $(S_2CNEt_2)_2$[57] in $CDCl_3$ is 15.0 kcal/mol. [e] $\Delta H^{\ddagger} = 14.9 \pm 1.0$ kcal/mol, $\Delta S^{\ddagger} = -17.5 \pm 2.0$ eu, and $E_a = 15.8 \pm 1.0$ kcal/mol.

Table II lists the kinetic parameters for C⋯N bond rotation along with the frequency of the C⋯N stretching vibration in several dithiocarbamate derivatives. The ν(C⋯N) decreases in the following order: $Pd(S_2CNR_2)(PPh_3)Cl \simeq Pd(S_2CNR_2)(PPh_3)Br > Pd(S_2CNR_2)(PPh_3)I \simeq Pd(S_2CNR_2)(PPhMe_2)Cl > Pd(S_2CNR_2)(PPh_3)(SEt)$. This trend suggests a correlation between the electron-withdrawing behavior of the halide and the C⋯N bond order (or the ν(C⋯N) stretch). A similar argument has been used for the compounds $Au(S_2CNMe_2)L_2$[23] (L_2 = MeMe, BrBr) and $Sn(S_2CNMe_2)_2L_2$[24] (L_2 = ClCl, MeCl, MeBr, MeI, MeMe). However, considering the small differences in $\Delta G^{\ddagger}$ values observed, no correlation between the kinetic parameter ($\Delta G^{\ddagger}$) and the ν(C⋯N) can be made from our work.

By comparing kinetic parameters with those for iron complexes,[27] it is noticed that $\Delta G^{\ddagger}$ is higher for the planar palladium(II) compounds. Long ago Chatt[9] pointed out that the ν(C⋯N) stretching frequency is dependent on the stereochemical arrangement around the central metal roughly in the order of planar > octahedral. Chatt, however, did not consider the influence of the formal oxidation state. Both the formal oxidation state of the metal ion and its stereochemical arrangement appear to influence the relative ν(C⋯N) stretching frequencies. Assuming resonance form IIc increases with ν(C⋯N), it should dominate in high oxidation state cases when the metal ion is coordinately unsaturated or formally contains fewer than 18 valence electrons. Thus resonance form IIc is expected to contribute more in $Fe^{IV}(S_2CNR_2)_3^+$ than in $Fe^{III}(S_2CNR_2)_3$ or $Fe^{II}(S_2CNR_2)_2phen$. Thus it is not surprising that $\Delta G^{\ddagger}$ is larger for the palladium(II) compounds reported here than it is for the iron compounds studied by Pignolet.[25–27,46]

$[Pt(S_2CNMePh)(PMe_2Ph)_2](BPh_4)$. Variable-temperature ^{1}H NMR studies in nitrobenzene-d_5 show that upon increasing the temperature to 120 °C the pattern of two sets of six lines for the phosphine methyl groups collapses. At 150 °C they merge together. The process which produces magnetically equivalent phosphine methyl protons is assumed to be C⋯N thioureide bond rotation. The $\Delta G^{\ddagger}$ value calculated near the coalescence temperature (120 °C) is close to the value found in the palladium(II) complexes.

Martin et al.[58–60] have studied the influence of substituents on the contribution of resonance form IIc. They rationalized the substituent effects in terms of electronic and steric influences. Nakamoto[61] suggested that the ν(C⋯N) frequency and hence its partial double bond character decreases in the order Pt > Pd > Ni. Since various effects apparently balance things out, a comparison of the $\Delta G^{\ddagger}$ of $[Pt(S_2CNMePh)(PMe_2Ph)_2](BPh_4)$ with that of the $Pd(S_2CN(i\text{-}Bu)_2)(PR'_3)X$ complexes gives no further insight into the relative effect the two metal ions have on the C⋯N bond.

Table III. ^{1}H NMR Data of $Ni(S_2CNEt_2)(PR'_3)X$ at 37 °C

Compd	$\delta(CH_2)$, ppm	$J_{CH_2-CH_3}$, Hz	$\delta(CH_3)$, ppm	$\delta(P-CH_3)$, ppm	J_{P-C-H}, Hz
$Ni(S_2CNEt_2)_2$ [a]	3.65	7.0	1.23		
$Ni(S_2CNEt_2)(PPh_3)Cl$ [b]	3.58	7.0	1.17		
$Ni(S_2CNEt_2)(PPh_3)I$ [b]	3.62	7.0	1.17		
$Ni(S_2CNEt_2)(PMe_2Ph)Cl$ [b]	3.62	7.0	1.20	1.55	11.0
$Ni(S_2CNEt_2)(PMe_2Ph)I$ [b]	3.62	7.0	1.21	1.75	10.0
$Ni(S_2CNEt_2)(PMe_2Ph)(SCN)$ [b]	3.65	7.0	1.22	1.71	11.0

[a] $CDCl_3$ solvent. [b] $CDCl_3$-$(CD_3)_2CO$ solvent.

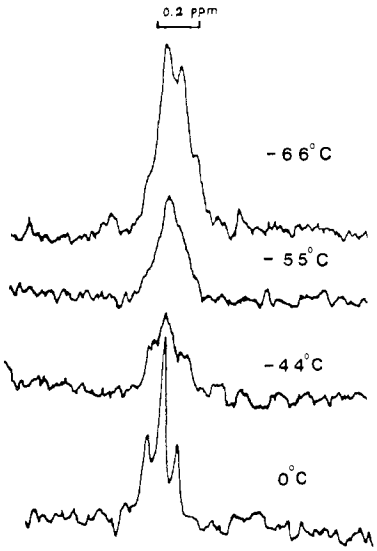


Figure 6. Variable-temperature ^{1}H NMR spectra of $Ni(S_2CNEt_2)(PPh_3)I$ in $(CH_3)_2CO$ and $CDCl_3$ (2:1 v/v) mixed solvent.

The Nickel(II) Complexes $Ni(S_2CNEt_2)(PR_3)X$. Although ^{1}H NMR data can distinguish magnetically nonequivalent alkyl groups on the dithiocarbamate ligand in the unsymmetrical $Pd(S_2CNR_2)(PR'_3)X$ complexes, the room-temperature spectra of the analogous nickel(II) complexes, $Ni(S_2CNEt_2)(PR_3)X$ (R = alkyl, aryl; X = Cl, I, SCN), show equivalent alkyl groups in a mixture of the solvents $CDCl_3$ and $(CD_3)_2CO$. The chemical shifts and coupling constants of these compounds are listed in Table III.

McCleverty's[5] ^{1}H and ^{13}C NMR results indicated that only one alkyldithiocarbamate resonance was observed at −60 to −70 °C for $Ni(S_2CNR_2)(PR'_3)X$. We find, however, that at −60 °C two different R resonances are observed for all of the unsymmetrical nickel(II) compounds we prepared. The spectra are temperature dependent. At room temperature only one R resonance is observed, while when the temperature is decreased, the resonance broadens and collapses, and at −65 °C two overlapping R resonances are observed. Figure 6 shows the variable-temperature ^{1}H NMR spectra of $Ni(S_2CNEt_2)(PPh_3)I$ in the methyl region.

Dynamical planar (diamagnetic) ⇌ tetrahedral (paramagnetic) interconversions in four-coordinate nickel(II) complexes are well known.[41] The planar–tetrahedral interconversion was found to be so rapid on the NMR time scale that for a given nucleus only a single resonance was observed at a weighted average frequency which indicates that the diamagnetic planar species and the paramagnetic tetrahedral complex are in rapid equilibrium. However, in this case there is no evidence for a chemically shifted paramagnetic species. The two R resonances arise from *two magnetically nonequivalent R groups on the dithiocarbamate ligand in diamagnetic complexes.*

The temperature of coalescence for the ethyl resonances in $Ni(S_2CNEt_2)(PPh_3)I$ and, hence, the rate of exchange are concentration dependent. Upon fivefold dilution the exchange rate increases slightly. This observation argues against a bimolecular mechanism but implicates an equilibrium involving a dissociative process. In order to eliminate the possibility of phosphine exchange, complexes containing dimethylphenylphosphine, $Ni(S_2CNEt_2)(PMe_2Ph)X$ (X = Cl, I, SCN), were prepared. Since $^2J_{P-C-H} = -11$ Hz was retained from −60 to +40 °C, phosphine dissociation must be slow below +40 °C.

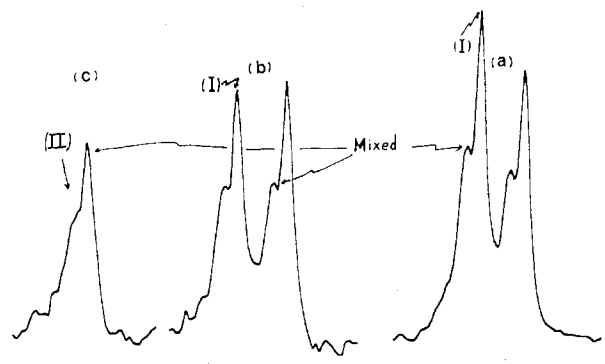


Figure 7. ^{1}H NMR spectrum of a mixture of $Ni(S_2CNBzl_2)_2$ (I) and $Ni(S_2CN(i\text{-}Bu)_2)_2$ (II) in $CDCl_3$ at 37 °C: (a) and (b) N^α and N^γ protons of the isobutyl groups, respectively; (c) $N-CH_2$ protons from benzyl groups.

At room temperature, proton signals for the ethyl groups in $Ni(S_2CNEt_2)(PPh_3)Cl$ are upfield relative to $Ni(S_2CNEt_2)(PPh_3)I$ in $CDCl_3$. When the chloride and iodide complexes are mixed together in $CDCl_3$, only one set of ethyl proton resonances is observed. This suggests that fast intermolecular ligand exchange takes place at room temperature between the two complexes.

In order to ascertain the probability of dtc ligand exchange, we mixed $Ni(S_2CNBzl_2)_2$ and $Ni(S_2CNR_2)_2$ (R = *i*-Bu) in $CDCl_3$ and looked for the mixed-ligand complex. A new R resonance appeared at ~37 °C (see Figure 7). This suggests that an equilibrium (eq 3) is established. This ligand-exchange

$$Ni(S_2CNBzl_2)_2 + Ni(S_2CNR_2)_2 \rightleftharpoons 2Ni(S_2CNBzl_2)(S_2CNR_2) \quad (3)$$

process, however, is much slower than the exchange process observed in $Ni(S_2CNR_2)(PPh_3)X$, since at 37 °C only one R resonance is observed for the latter species. For the mixed bis(dithiocarbamato)nickel(II) complexes separate signals are observed. We conclude therefore that the ligand exchange observed in $Ni(S_2CNR_2)(PPh_3)X$ complexes is a halide exchange.

When methanol, ethanol, or water was added to an acetone solution of the nickel complexes, the purple-red color changed immediately to greenish yellow. After the mixture stood overnight, a deep green precipitate formed. The precipitate was identified as $Ni(S_2CNEt_2)_2$ by comparing its melting point and ^{1}H NMR spectra with those of an authentic sample. As expected for a ligand dissociation process, the compounds were sensitive to the nature of the solvents present.

Acknowledgment. The primary support for this work was received from the National Institutes of Health, Grant GM19050. Funding also was obtained from the National Science Foundation, Grant GP-40689X, for structural studies related to this investigation.

Registry No. $Pd(S_2CN(i\text{-}Bu)_2)(PMe_2Ph)Cl$, 61026-14-0; $[Pt(S_2CNMePh)(PMe_2Ph)_2](BPh_4)$, 61026-16-2; $Ni(S_2CNEt_2)(PPh_3)I$, 59560-58-6; $Ni(S_2CNEt_2)(PMe_2Ph)Cl$, 61025-68-1; $Ni(S_2CNEt_2)(PMe_2Ph)I$, 61025-69-2; $Ni(S_2CNEt_2)(PMe_2Ph)(SCN)$, 61025-70-5; $[Pd(S_2CN(i\text{-}Bu)_2)Cl]_2$, 61025-71-6; $[Pd(S_2CN(i\text{-}Bu)_2)Br]_2$, 61025-72-7; $[Pd(S_2CN(i\text{-}Bu)_2)I]_2$, 61062-64-4; $[Pd(S_2CN(i\text{-}Bu)_2)SEt]_2$, 61025-74-9; $[Pd(S_2CNEt_2)(S\text{-}t\text{-}Bu)]_2$, 61025-75-0; $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Cl$, 61025-76-1; $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)Br$, 61025-77-2; $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)I$, 61025-78-3; $[Pd(S_2CS\text{-}t\text{-}Bu)\text{-}\mu\text{-}(S\text{-}t\text{-}Bu)]_2$, 35594-96-8; $[Pt(S_2CN(i\text{-}Bu)_2)Cl]_2$, 61025-82-9; $Pd(S_2CN(i\text{-}Bu)_2)(PPh_3)(SEt)$, 61025-79-4; $[Pt(S_2CN(i\text{-}Bu)_2)(PPh_3)_2]Cl$, 61025-80-7; $Pd(S_2CN(i\text{-}Bu)_2)_2$, 52613-84-0; K_2PdCl_4, 10025-98-6; $Pt(PMe_2Ph)_2Cl_2$, 30759-88-7; $Pd(S_2CNEt_2)(PMePh_2)(S\text{-}t\text{-}Bu)$, 61025-81-8; $Ni(S_2CNEt_2)_2$, 14267-17-5; $Ni(S_2CNEt_2)(PPh_3)Cl$, 30052-07-4; $Ni(S_2CNBzl_2)_2$, 38542-61-9; $Ni(S_2CN(i\text{-}Bu)_2)_2$, 28371-07-5.

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