isosteres listed in Table III. In 11 of the 14 instances for which data are at hand, the tripositive complexes, as expected, react more slowly, and for all five pairs the difference is most pronounced for reductions by Cr^{2+}. Thus, of the three inner-sphere metal-center reductants, Cr^{2+} is clearly the most sensitive to charge variation as well as to steric influences.[17]

We suspect that both effects arise from the same source. Alone among the three reducing centers, chromium(II) suffers a mismatch of symmetry between the metal orbital supplying the reducing electron (in the case of Cr^{2+}, a centrosymmetric e_g orbital) and the π orbitals of the bridging carboxyl group. This reductant requires, for inner-sphere transfer, a distortion of the reducing center that is unsymmetric with respect to the carboxyl plane in the precursor complex.[10] The burden of this distortion falls mainly on interaction with water molecules comprising the second coordination sphere. Hence, Cr^{2+} reductions are expected to be most sensitive to distrubances in this sphere. On one hand, large lipophilic groups on the periphery of the precursor will disfavor ordering in nearby solvent molecules. On the other, a positively charged substituent near the reaction center should increase ordering in the surrounding medium, but the ordering will be in the "wrong" direction; i.e., the oxygen ends of the water dipoles will point toward N^+ rather than toward the hydrogens of those water molecules in the primary sphere. The result will be the same in the two cases—a less effective secondary sphere.

An earlier observation appears also to be related to the special sensitivity of inner-sphere Cr(II) reductions to variations in the secondary coordination sphere. Liang[18] has reported that the reductions, by Cr^{2+}, of unsaturated carboxylato $(NH_3)_5Co^{III}$ complexes are substantially retarded by substitution of 1 M $HClO_4$ for 1 M $LiClO_4$ as a reaction medium. Since reactions of the same oxidants with V^{2+} and Eu^{2+} proceed at rates independent of acidity at unit ionic strength,[19] it may be inferred that the variations found with Cr^{2+} reflect a medium effect rather than one of the more usual kinetic acidity patterns. Here again, it may be argued that the strongly solvated hydrogen ions tend to orient the solvent dipoles so that their hydrogens, rather than their oxygens, face outward, thus weakening their interaction with the Cr(II)-bound water molecules constituting a portion of the primary coordination sphere of the precursor. (This reasoning, however, leaves unanswered the question as to why this medium-related retardation is observed for oxidants derived from olefinic acids but not for those from aromatic or saturated acids.)

Finally, it may be reasonably asked whether the marginal charge effects observed here for reductions by Eu^{2+} and V^{2+} suggest the need for revision of the widespread belief that rates of electron-transfer reactions are significantly charge sensitive. We feel such a veiw to be an overinterpretation of experiments which, in actuality, deal with only a small portion of the entire spectrum of such reactions. Note, moreover, that the reactions at hand are inner-sphere reactions, that their rates are generally determined jointly by the association constant of a precursor complex and the specific rate of internal electron transfer within the precursor, and that electron-attracting substituents (e.g., an additional positive charge) on the oxidant, while facilitating internal electron transfer,[20] also serve to destabilize the precursor. Hence, it is arguable that we are seeing a near cancellation of the two effects. At the same time, it must be remembered that the presumed sensitivity of outer-sphere reactions to charge type, although eminently reasonable, has not yet been experimentally demonstrated in a manner that bars the intervention of other important effects. Skepticism on this point is not unjustified.[21-23]

Registry No. II, 19173-62-7; III, 80327-80-6; IV, 33887-25-1; V, 40544-43-2; VI, 30931-78-3; VII, 80327-72-6; VIII, 68582-30-9; XI, 45127-13-7; XII, 31133-42-3; XIII, 55132-09-7; XIV, 61202-26-4; XV, 31133-39-8; XVI, 69421-16-5; XVII, 31133-44-5; CH_3COOCo^{III}, 16632-78-3; Cr, 7440-47-3; V, 7440-62-2; Eu, 7440-53-1; $Ru(NH_3)_6^{2+}$, 19052-44-9; RbH_2, 13345-95-4.

(17) As anticipated, the retarding action of the positive nitrogen toward reduction by Cr(II) becomes attenuated as the positive center is progressively removed from the site of reaction (compare k_{Cr} values for oxidants VIII, XIV, and XV). Somewhat surprisingly, no such trend is noted in the V(II) and Eu(II) series.
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(21) Two comments by reviewers deserve response. First, our view that the V^{2+} reductions at hand are predominantly inner sphere is based upon the report of Fan,[10] who has estimated the outer-sphere fraction for V^{2+} reactions of (carboxylato)cobalt(III) complexes of this type to fall between 0.003 and 0.09. A second reviewer has observed that plots of log k_{Cr} vs. log k_V are reasonably linear, as are plots of log k_{Cr} vs. log k_{Eu}. Relationships of this type were noted in earlier reports,[7b,22] which also pointed out that all three sets of log k values were linear functions of Taft's steric substituent constants.[23] These linear free-energy relationships are thought to reflect the circumstance that rate ratios in all three series are governed by nonbonded interactions within the precursor complex, augmented, in the case of Cr^{2+}, by distortions in the second coordination sphere (as described in the present text), which are also related to the bulk of substitutents on the carboxyl.
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Contribution from the Department of Chemistry, University of California, Davis, California 95616

Ambidentate Binding of Thiocyanate to Palladium. ^{31}P NMR Observation of the Distribution of Linkage Isomers in (diphosphine)$Pd(CNS)_2$ and (diphosphine)$_2Pd_2(CNS)_2$

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The distribution of linkage isomers of $[Ph_2P(CH_2)_nPPh_2]Pd(CNS)_2$ (n = 1-3), [*cis*-$Ph_2PCHCHPPh_2$]$Pd(CNS)_2$, and $(Ph_2PCH_2PPh_2)_2Pd_2(CNS)_2$ in a variety of solvents has been determined by ^{31}P NMR spectroscopy. Near 25 °C only a single broadened resonance due to time averaging over several environments is observed for each of these compounds, but at −40 to −60 °C, well-defined resonances assignable to the various possible linkage isomers can be observed. The resonances of the individual components have been identified by their spectral pattern and their line widths.

The ambidentate nature of the thiocyanate ligand, which may bind in a linear fashion A through the nitrogen atom or in a bent fashion B through the sulfur atom, is well recognized. It is known that a variety of factors including the nature of

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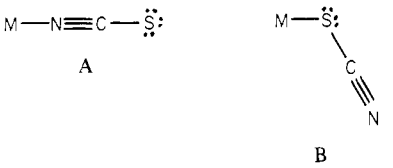
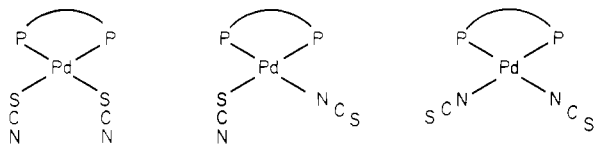


A B

the metal (particularly its polarizability; soft metal ions favor coordination mode B and hard metals prefer coordination mode A), the electronic structure of trans ligands, the steric properties of cis ligands, and medium effects (solid state, solvent) can influence the nature of the thiocyanate metal bond.[1]

While examples of linkage isomerization in metal thiocyanate compounds have been reported and many thiocyanate complexes have been structurally characterized by X-ray crystallography, there exists relatively little quantitative data dealing with equilibria between linkage isomers in solution.

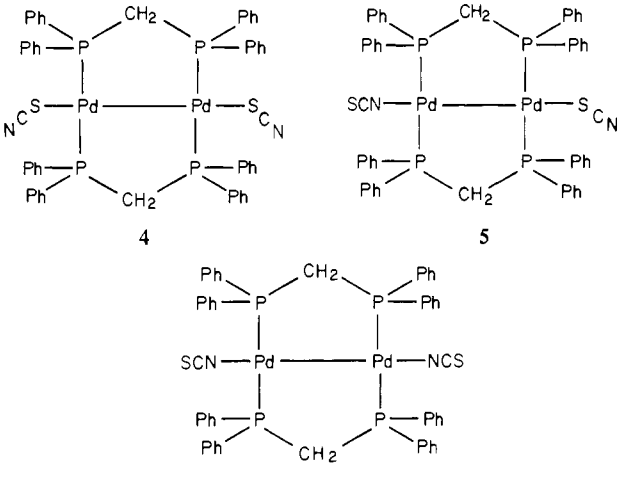
In this article we examine the behavior of several palladium(II) complexes containing a bidentate phosphine ligand and two cis thiocyanate ligands. Three linkage isomers **1–3** can



(dp)Pd(SCN)$_2$ (1) (dp)Pd(SCN,NCS) (2) (dp)Pd(NCS)$_2$ (3)

exist in this system, and we present evidence of their detection and identification by $^{31}P\{^1H\}$ NMR spectroscopy. The diphosphines utilized include bis(diphenylphosphino)methane (dpm), bis(diphenylphosphino)ethane (dpe), bis(diphenylphosphino)ethylene (dpv), and bis(diphenylphosphino)propane (dpp). The X-ray crystal structures of three coompounds (dpm)Pd(SCN)$_2$, (dpe)Pd(SCN,NCS), and (dpp)Pd(NCS)$_2$, are known.[2,3] The first, (dpm)Pd(SCN)$_2$, adopts structure **1** and the P–Pd–P and S–Pd–S angles are 73.33 (5) and 92.97 (7)°, respectively. In (dpe)Pd(SCN,NCS), which is present as isomer **2** in the solid state, the P–Pd–P and S–Pd–N angles are 85.1 (1) and 84.4 (3)°, respectively. For (dpp)Pd(NCS)$_2$, which exists as isomer **3** in the solid, the P–Pd–P and N–Pd–N angles are 89.32 (3) and 91.4 (1)°. Since the thiocyanate bonding mode changes regularly as the P–Pd–P bond angle increases in this series, it has been claimed that steric factors alone dictate the way a thiocyanate ligand binds. Although this view has been challenged,[4] the results from the X-ray analysis have been widely quoted in standard text books.[5,6] The distribution of isomeric forms of these complexes in solution has not been investigated. Although infrared measurements are capable of distinguishing between coordination through sulfur or through nitrogen for a single thiocyanate ligand, infrared spectroscopy generally cannot distinguish between the presence of the isomer 2 with mixed bonding modes and a mixture of **1** and **3**.

We have also examined the distribution of isomers for the palladium(I) dimer Pd$_2$(dpm)$_2$(CNS)$_2$. (The formula (CNS) is written whenever we do not wish to specify the specific mode(s) of thiocyanate bonding.) This compound can also exist in three isomeric forms **4–6**. Two different crystalline forms of this material have been isolated. The infrared data suggests that these are isomers **4** and **5**.[7]



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6

Experimental Section

Preparation of Compounds. The diphosphine ligands were purchased from Strem Chemicals. Pd$_2$(dpm)$_2$(CNS)$_2$ was prepared as described previously;[7] other complexes were prepared by the general route outline below.

General Preparation of (diphosphine)Pd(CNS)$_2$. A solution of Pd(SCN)$_4^{2-}$ was prepared by dissolving palladium chloride and 10 equiv of potassium thiocyanate in a 5:1 mixture of ethanol/water. The diphosphine (1 equiv) dissolved in dichloromethane was added and an immediate orange or yellow or pink precipitate formed. This was isolated by filtration and washed with ethyl ether. The infrared spectra and the color of the precipitate at this stage suggest that the material is a mixture of the constitutional isomers [(diphosphine)$_2$Pd][Pd(SCN)$_4$] and (diphosphine)Pd(CNS)$_2$. Complete conversion to (diphosphine)Pd(CNS)$_2$ was effected by dissolving the precipitate in a minimum volume of boiling *N,N*-dimethylformamide. The hot solution was immediately filtered. The filtrate was cooled, and the complex was precipitated by addition of water. The yellow solids which were obtained were washed with ethanol and ethyl ether and vacuum-dried. Further recrystallization from various solvents gave the solid forms noted in Table I.

Physical Measurements. $^{31}P\{^1H\}$ NMR spectra were recorded on a Nicolet-200 Fourier transform spectrometer at 81 MHz. Particular care was taken to ensure that the spectral intensities were not distorted due to relaxation effects. An external 85% phosphoric acid reference was used as chemical shift standard and the high-frequency-positive convention, recommended by IUPAC, has been used in reporting chemical shifts. Spectral analysis and deconvolution was carried out with the analysis routine available with the Nicolet software. Infrared spectra were recorded from Nujol mulls on a Perkin-Elmer 180 spectrometer.

Results

The study of the (diphosphine)palladium(II) thiocyanate complexes is complicated by the formation of two constitutional isomers: the salt, [(diphosphine)$_2$Pd][Pd(SCN)$_4$] and the neutral compound, (diphosphine)Pd(CNS)$_2$. We find that the usual preparative route of adding the appropriate diphosphine to Pd(SCN)$_4^{2-}$ produces a mixture of these constitutional isomers.[2,8-10] This mixture generally has poor solubility in organic solvents and the portion which dissolves appears to be largely (diphosphine)Pd(CNS)$_2$. In agreement with the results of Meek et al.[8] on [Pd(dpe)$_2$][Pd(SCN)$_4$], we find that this mixture can be converted entirely to (di-

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Table I. Infrared Spectra of Thiocyanate Complexes

compd	color	recrystn solvent(s)	ν(SCN), cm^{-1} [a]	linkage isomer
(dpm)Pd(CNS)$_2$	deep yellow	hot (CH$_3$)$_2$NCOH/H$_2$O	2116 (s, sh)	Pd(SCN)$_2$
(dpe)Pd(CNS)$_2$	yellow	hot (CH$_3$)$_2$NCOH/H$_2$O	2116 (s, sh), 2073 (s, br)	Pd(SCN,NCS)
(dpv)Pd(CNS)$_2$	yellow	hot (CH$_3$)$_2$NCOH/H$_2$O	2108 (s, sh), 2076 (s, br)	Pd(SCN,NCS)
(dpp)Pd(CNS)$_2$	white	hot (CH$_3$)$_2$CO	2076 (s, br)	Pd(NCS)$_2$
	pale yellow	CH$_2$Cl$_2$/(C$_6$H$_5$)$_2$O	2109 (w, sh), 2078 (s, br)	mixture
	pale yellow	hot (CH$_3$)$_2$CO/H$_2$O	2078 (s, br)	Pd(NCS)$_2$
	yellow	hot (CH$_3$)$_2$NCOH/H$_2$O	2107 (s, sh), 2079 (s, br)	Pd(SCN,NCS)
(dpm)$_2$Pd$_2$(CNS)$_2$	orange	CH$_2$Cl$_2$/(C$_6$H$_5$)$_2$O	2102 (s), 2094 (s)	Pd(SCN)$_2$

[a] Recorded as Nujol mulls. Key: br = broad, s = strong, sh = sharp, w = weak.

phosphine)Pd(CNS)$_2$ by dissolving it in boiling *N,N*-dimethylformamide and reprecipitating the nonionic form through the addition of water. Analysis of the ^{31}P{^{1}H} NMR spectra (vide infra) of the materials at this stage indicates that they are entirely converted to (diphosphine)Pd(CNS)$_2$. That is, the (diphosphine)$_2$Pd^{2+} cations are not detected by ^{31}P NMR spectroscopy[11] in these samples.

As was reported earlier for (dpm)$_2$Pd$_2$(CNS)$_2$,[7] recrystallization of the (diphosphine)Pd(CNS)2 from different solvents can produce solids containing different linkage isomers (as determined by the infrared spectra of the solids).

Representative data for these thiocyanate complexes as solids are recorded in Table I. Sulfur-bound thiocyanate generally exhibits structurally diagnostic infrared absorptions at 2130–2100 and 720–680 cm^{-1} while nitrogen-bound thiocyanate has corresponding absorptions at 2100 or below and 860–780 cm^{-1}. With use of these criteria, the linkage isomers likely to be present in the solids have been assigned in Table I. Of particular significance is (dpp)Pd(CNS)2 which, like (dpm)$_2$Pd$_2$(CNS)$_2$, can be isolated in differnt forms depending on the solvent system used for recrystallization. Our observations run parallel to those of Flutz et al.,[12] who reported, while this paper was in preparation, the isolation of the following pairs of linkage isomers: (dpp)Pd(SCN,NCS) and (dpp)Pd(NCS)$_2$; (dpm)Pd(SCN)$_2$ and (dpm)Pd(SCN,NCS). We have not examined the last compound.

^{31}P NMR Spectra. At room temperature, the ^{31}P{^{1}H} NMR spectra of all of the palladium complexes show only a single line due to rapid interconversion of the various isomeric forms present. Similar observations have been reported for other palladium thiocyanate complexes.[13,14] On cooling, the spectra of the individual isomers become resolved, consequently most of our data are reported at temperatures below −40 °C.

Figure 1 shows the effect of cooling a sample of Pd$_2$(dpm)$_2$(CNS)$_2$. The single line observed at room temperature broadens and shifts, and at low temperature a deceptively simple A_2B_2 pattern due to isomer **5** and a singlet due to isomer **4** or **6** become clearly resolved. The temperature dependence of the spectrum obtained for solutions of two different concentrations (1.3 and 3.9 mM) are identical. Consequently the isomerization process is intramolecular.

The ^{31}P{^{1}H} NMR spectrum of (dpv)Pd(CNS)$_2$ in *N,N*-dimethylformamide at −50 °C is shown in Figure 2. Six resonances are clearly seen. The AB quartet is immediately assignable to linkage isomer **2**. The P–P coupling constant of 10 Hz is consistent with the presence of inequivalent, cis phosphorus donors. Note the difference in peak heights caused by the broadening of the pair of lines at low frequency. We ascribe this selective broadening to unresolved coupling with the ^{14}N of an N-bound thiocyanate ligand. Since trans-coupling constants are usually 1 order of magnitude larger than cis-coupling constants in metal complexes,[15] we assign the doublet of 77.0 ppm to the phosphorus atom trans to an N-bound thiocyanate ligand and the doublet at 78.7 ppm to a phosphorus atom trans to an S-bound thiocyanate ligand. Consideration of the line widths of the two singlets also allows them to be assigned. The singlet at 79.2 ppm has a line width of 3 Hz while the singlet at 78.2 ppm has a corresponding line

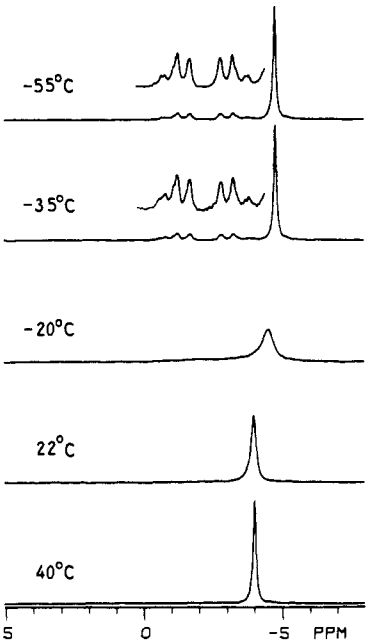

Figure 1. ^{31}P{H} NMR spectrum of Pd$_2$(dpm)$_2$(CNS)$_2$ in dichloromethane-d_2 as a function of temperature. With cooling, two of the linkage isomers, Pd$_2$(dpm)$_2$(SCN)$_2$ and Pd$_2$(dpm)$_2$(SCN,NCS), become resolved.

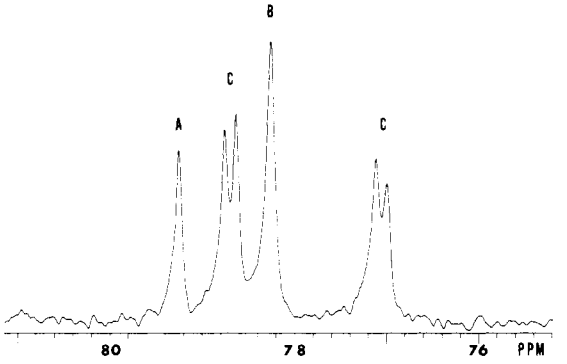

Figure 2. ^{31}P{^{1}H} NMR spectrum of (dpv)Pd(CNS)$_2$ in *N,N*-dimethylformamide-d_7 at −50 °C. The three linkage isomers are easily identified: (A) (dpv)Pd(SCN)$_2$, (B) (dpv)Pd(NCS)$_2$, and (C) (dpv)Pd(SCN,NCS).

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Table II. $^{31}P\{^1H\}$ NMR Parameters for Palladium Thiocyanate Complexes

compd[a]	T, °C	δ(SCN)$_2$ (width, Hz)	δ(SCN) (width, Hz)	δ(NCS) (width, Hz)	J_{P-P}, Hz	δ(NCS)$_2$ (width, Hz)
$Pd_2(dpm)_2(CNS)_2$[b]	−55	−4.2 (3)	−0.7[c]	−2.6[d]	39	
$Pd(dpm)(CNS)_2$	−45	−37.0 (7)	−46.5 (4)	−41.5 (29)	82	−51.3 (29)
$Pd(dpe)(CNS)_2$	−50	70.2 (3)	67.4 (5)	69.5 (10)	2	69.4 (10)
$Pd(dpv)(CNS)_2$	−45	78.2 (4)	77.6 (4)	76.2 (17)	10	77.3 (17)
$Pd(dpp)(CNS)_2$	−70	11.6 (3)	8.2 (2)	13.4 (10)	28	12.9 (9)

[a] Solvent is acetone unless otherwise noted. [b] Solvent is chloroform. [c] The line widths are unresolved due to the complex splitting pattern and low concentration of this isomer. Since the line widths are unresolved, these chemical shift assignments are tentative and may be interchanged.

width of 15 Hz. Consequently, the resonance at 79.2 ppm is assigned to isomer **1** with a sulfur atom trans to each phosphorus, and the resonance at −78.2 ppm is assigned to isomer **3** with a nitrogen atom trans to each phosphorus. These factors hold for spectra recorded for samples in other solvents as well. For example, the line widths in acetone are 4 and 17 Hz for the phosphorus nuclei opposite the sulfur and nitrogen, respectively. Note that the line widths of the NMR signals of the phosphorus atoms trans to N-bound thiocyanate are 2–4 times larger than the line widths of the NMR signals of the phosphorus atoms trans to S-bound thiocyanate.

The $^{31}P\{^1H\}$ NMR data for these palladium complexes are Tabulated in Table II. Although spectra have been obtained in a variety of solvents, data are given only for a representative one, acetone. The variation in parameters from solvent to solvent is small. Assignments of resonances to isomers are based on the unique spectral pattern (AB or A_2B_2) of the mixed-species **2** or **5** and on the relative line widths of isomers **1** and **3** as outlined above for $(dpv)Pd(CNS)_2$. Notice how uniform the line widths for the two situations are. For our assignment of a phosphorus atom trans to S-bound thiocyanate, the line widths fall in the range 2–9 Hz, while for a phosphorus atom trans to an N-bound thiocyanate the line widths are 5–29 Hz.

The P–P coupling constants for isomer **2** are all in the range expected for cis phosphorus atoms. The variation of the cis coupling constant, as a function of the number of methylene groups between the two phosphorus atoms, follows the same order, dpm > dpp > dpe, which we have observed for other complexes.[11,16]

The phosphorus chemical shifts for these complexes depend on the identity of the phosphine ligand and correlate with the chemical shifts found for the corresponding $(diphosphine)PdX_2$ (X = halide) complexes. For comparison, the chemical shifts of $(dpm)PdCl_2$, $(dpe)PdCl_2$, $(dpp)PdCl_2$, and $(dpm)_2Pd_2Cl_2$ are −53.7, 64.2, 11.9, and −2.5 ppm, respectively. The unusual shift of $(dpm)PdX_2$ to low frequency has been noted previously.[11] The chemical shifts of the individual thiocyanate linkage isomers do not follow any characteristic pattern. For example, in Figure 2 it is readily seen that the chemical shift difference between the two inequivalent phosphorus atoms of the mixed-isomer **2** is larger than the difference between **1** and **3**. The pattern of relative chemical shifts differs from complex to complex. For example, the highest frequency resonance is not uniquely assigned to a particular isomer. Consequently, it is not possible to use the chemical shift data to establish the structure of the isomers.

The relative abundance of the individual linkage isomers of these palladium complexes, as determined by deconvolution and integration of the $^{31}P\{^1H\}$ NMR spectra, are presented in Table III. Data are reported for *N*,*N*-dimethylformanide, acetone, dichloromethane, and in some cases for chloroform solution. The solvent has a significant effect on the distribution of isomers. In all cases except for the dimer, $Pd_2(dpm)_2(CNS)_2$, all three isomeric forms are present in detectable concentrations.

Table III. Relative Ratios of Isomeric Forms of Palladium Thiocyanate Complexes

compd	solvent	T, °C	rel ratios[a] (SCN)$_2$	(NCS)$_2$
$Pd_2(dpm)_2(CNS)_2$	$CDCl_3$	−55	20	
	$(CD_3)_2NCOD$	−52	18	
$Pd(dpm)(CNS)_2$	$CDCl_3$	−55	75	
	CD_2Cl_2	−40	53	0.4
	$(CD_3)_2NCOD$	−45	16	2
	$(CD_3)_2CO$	−45	18.7	2.5
$Pd(dpe)(CNS)_2$	CD_2Cl_2	−70	8.1	1.3
	$(CD_3)_2NCOD$	−45	3.3	3.3
	$(CD_3)_2CO$	−50	3.3	3.3
$Pd(dpv)(CNS)_2$	CD_2Cl_2	−70	7.5	1.7
	$(CD_3)_2NCOD$	−50	2.5	4.9
	$(CD_3)_2CO$	−45	3.4	5.5
$Pd(dpp)(CNS)_2$	CD_2Cl_2	−50	0.8	1.1
	$(CD_3)_2NCOD$	−45	0.3	4
	$(CD_3)_2CO$	−70	0.3	4

[a] Relative ratio of (SCN,NCS) is assigned as 10.

Discussion

The present results indicate that the linkage isomers of $(diphosphine)Pd(CNS)_2$ and $(dpm)_2Pd_2(CNS)_2$ exist as a rapidly interconverting, equilibrated mixture in solution. It has been established that this is an intramolecular process for $(dpm)_2Pd_2(CNS)_2$, and it is likely that intramolecular processes pertain in all cases.

It is informative to compare this linkage isomerization with the scrambling of terminal halides shown in eq 1. We have

$$(diphosphine)PdX_2 + (diphosphine)PdY_2 \rightleftharpoons 2(diphosphine)PdXY \quad (1)$$

examined this reaction for bis(diphenylphosphino)methane and X = Cl, Br, and I. Although a nearly statistical distribution of species is rapidly obtained upon mixing the reactants, nevertheless the $^{31}P\{^1H\}$ NMR spectra recorded at 25 °C show well-resolved resonances for each individual species.[16] Similar chemical shift differences are involved in both cases, suggesting that terminal halide exchange, which must be intermolecular in nature, is somewhat slower than the interconversion of thiocyanate linkage isomers.

It is interesting to note that while these and other thiocyanate[14] complexes of chelating diphosphines undergo isomerization which is rapid on the NMR time scale at 25 °C, that complexes of monodentate phosphines of the type $(R_3P)_2Pd(CNS)_2$ give ^{31}P NMR spectra at 25 °C in which the individual linkage isomers can be distinguished for both cis and trans arrangements of the phosphines.[17,18] For analogous platinum(II) complexes, where metal ligand bonding changes

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are expected to be slower, individual linkage isomers have been detected in solution at ambient temperature by ^{31}P NMR spectroscopy.[13,14,19-21]

The results summarized in Table III clearly indicate that all three linkage isomers, **1-3**, can be detected in appreciable concentrations for solutions of complexes of the type (diphosphine)$Pd(CNS)_2$ at low temperatures. For the dimer $(dpm)_2Pd_2(CNS)_2$, only two linkage isomers **4** and **5** are detectable in solution at low temperature.

There are significant solvent effects on the proportions of linkage isomers in solution. For the (diphosphine)$Pd(CNS)_2$ complexes, the all-sulfur-bound linkage isomer **1** is present in greater proportions in the chlorinated solvents than in the carbonyl containing solvents. Conversely the all-nitrogen-bound linkage isomer **3** is found in greater relative quantities in the carbonyl containing solvent than in the chlorinated solvents. For $(dpm)_2Pd_2(CNS)_2$, the effect of solvent on the proportions of linkage isomers is less marked, and in no solvent is a detectable amount of the all nitrogen bound isomer **6** present.

Notice that the solvent effects observed for the (diphosphine)$Pd(CNS)_2$ complexes are opposite those reported earlier for $(Ph_3P)_2Pd(CNS)_2$ and some other palladium(II) thiocyanate complexes.[22] From infrared spectral measurements it was noted that *N,N*-dimethylformamide (along with dimethyl sulfoxide) was one of several solvents favoring sulfur coordination while chlorocarbon solvents stabilized nitrogen coordination. On the other hand studies of *cis*-$(R_3P)_2Pt(CNS)_2$ have shown that the proportion of NS linkage isomer relative to NN isomer is larger in dichloromethane than in dimethyl sulfoxide.[19,20] The linkage isomerization of the thiocyanate ligand is object to many subtle effects, and a consistent pattern of some of these has yet to emerge. It is clear from the distribution of isomers in solution and the ability to selectively crystallize certain linkage isomers by the choice of solvent system that not only are steric effects operative in altering the balance between isomers but electronic and environmental effects all contribute to the stability of the individual isomers.

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Registry No. $Pd_2(dpm)_2(SCN)_2$, 68079-56-1; $Pd_2(dpm)(SCN)(NCS)$, 68447-96-1; $Pd(dpm)(SCN)_2$, 51320-63-9; Pd(dpm)(SCN)(NCS), 76793-83-4; $Pd(dpm)(NCS)_2$, 80293-85-2; $Pd(dpe)(SCN)_2$, 19998-22-2; Pd(dpe)(SCN)(NCS), 29893-44-5; $Pd(dpe)(NCS)_2$, 69237-91-8; $Pd(dpv)(SCN)_2$, 41278-37-9; Pd(dpv)(SCN)(NCS), 80293-86-3; $Pd(dpv)(NCS)_2$, 80293-87-4; $Pd(dpp)(SCN)_2$, 80293-88-5; Pd(dpp)(SCN)(NCS), 76793-82-3; $Pd(dpp)(NCS)_2$, 51886-81-8.

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Contribution from the Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich, Switzerland

Correlation between NMR Coupling Constants and Molecular Structure. Synthesis and ^{31}P NMR Measurements of $[HgX_2(cis\text{-}Ph_2PCH{=}CHPPh_2)]$ and X-ray Crystal Structures of $[HgBr_2(cis\text{-}Ph_2PCH{=}CHPPh_2)]$, $[Hg(NO_3)_2(PPh_3)_2]$, and $[Hg(CN)_2(PPh_3)_2]$

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The complexes $[HgX_2(cis\text{-}Ph_2PCH{=}CHPPh_2)]$ (X = ac, Cl, Br, I, CN, $(EtO)_2PO$) have been synthesized and studied by ^{31}P NMR methods. Results of the X-ray structure analyses of $[Hg(CN)_2(PPh_3)_2]$ (I), $[Hg(NO_3)_2(PPh_3)_2]$ (II), and $[HgBr_2(cis\text{-}Ph_2PCH{=}CHPPh_2)]$ (III) are presented. Changes of $^1J(^{199}Hg,^{31}P)$ (2.6-5.9 kHz) in complexes of the general type $[HgX_2P_2]$ are correlated to changes in the bond angles $\theta(P,Hg,P)$ (80-150°) and $\theta(X,Hg,X)$ (70-113°). A two-dimensional function $^1J(^{199}Hg,^{31}P) = f[\theta(P,Hg,P),\theta(X,Hg,X)]$ is presented, whose general form was investigated by EHMO calculations on the model compound $[HgCl_2(PH_3)_2]$, whereas its numerical parameters were derived from the available structural and spectroscopic data by linear regression. Chemical formula, lattice constants (esd), crystal system, space group, and Z for compounds I, II, and III are as follows: $C_{38}H_{30}HgN_2P_2$, 18.023 (5) Å, 18.262 (4) Å, 10.032 (3) Å, orthorhombic, $Pn2_1a$, 4; $C_{36}H_{30}HgN_2O_6P_2$, 13.415 (3) Å, 14.004 (4) Å, 17.874 (3) Å, 91.72 (2)°, monoclinic, $C2/c$, 4; $C_{26}H_{22}Br_2HgP_2$, 8.773 (5), 18.952 (2), 7.710 (2) Å, 101.77 (3)°, monoclinic, $P2_1/m$, 2.

Introduction

There have been a number of recent studies concerned with the effects of coordination number and anion on ^{31}P NMR parameters for the complexes $[HgX_2(PR_3)_2]$,[2] $[HgX_2PR_3]$,[3,4] and $[HgXPR_3]^+$,[5] where X is an anion and PR_3 stands for a tertiary phosphine. These reports have considered changes in $\delta(^{31}P)$ and $^1J(^{199}Hg,^{31}P)$ primarily in terms of changes in electronic properties. Using solid-state data, we have shown for some complexes $[HgX_2(PPh_3)_2]$ that marked deviations in molecular structure from ideal tetrahedral bond angles and standard bond distances may occur.[6] A juxtaposition of the

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