would be expected to be higher, with assumption of similar geometry and bonding, since the weighted average for the chemical shift involves one less terminal hydrogen. These calculations show that the change in chemical shift for the borane hydrogens upon complexation to metals with phenylphosphine ligands is most likely due to a combination of inductive and anisotropic effects, since the calculations are for the probable upper limit of the anisotropic effects. This makes it difficult to assess the magnitude of the inductive effects for individual cases. The calculations do suggest, however, that the inductive effects and the metal–anion interactions are not vastly different for the bis(phosphine) complexes compared to their bis(phosphite) counterparts, a conclusion supported by the infrared spectra of these complexes. Further supporting evidence that the borane hydrogens may be experiencing an anisotropic effect comes from the neutron diffraction results on $(MePh_2P)_3CuBH_4$[14] in which one of the terminal hydrogen distances is distinctly longer than the other B–H distance, and indeed, one could envision that in solution interaction with the phenyl rings might be present.

^{11}B Chemical Shifts. The ^{11}B NMR spectra of the phosphine and phosphite complexes generally consist of a somewhat broadened quartet. Chemical shift values (Table II) indicate considerable inductive deshielding of the boron nucleus (on the assumption that the paramagnetic contribution to the chemical shift is small because of the upfield shift of some of the complexes compared to the free ligands). This may be a consequence of inductive effects through the bridging hydrogens or some direct bonding between the boron and the metal or both. Some direct Cu–B bonding has been considered as a possible explanation for the large P–Cu–P′ angle in the complex $(Ph_3P)_2CuBH_4$,[12] and neutron diffraction data on unidentate $(MePh_2P)_3CuBH_4$ suggests that the overlap pattern in the Cu–H–B bond is "closed".[14] The ^{11}B chemical shift of bis(phosphine) complexes is apparently not significantly affected by anisotropic deshielding by the phosphines, more than likely due to its distance from the phenyl rings.

Summary. We have shown that these phosphite and phosphine complexes exhibit various equilibria which are dependent on temperature, the particular phosphorus-containing ligand, and the hydroborate ligand. That the (ethoxycarbonyl)trihydroborate is completely replaceable by a phosphite even at ambient temperature is not surprising since previous studies have shown that the trihydroborate possesses a weaker M–H–B linkage than tetrahydroborate. Reduction of temperature resulting in a shift in equilibrium with a concomitant slowing down of the dynamic equilibrium process allows both the tri- and tetrahydroborate phosphite and phosphine complex equilibria to be observed. The fact that the equilibria are observed at higher temperatures for the phosphine than the phosphite may reflect the differences in basicity as well as equilibria temperature dependence.

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Registry No. $[(MeO)_3P]_2CuBH_4$, 67784-66-1; $[(MeO)_3P]_3CuBH_4$, 76986-54-4; $[(MeO)_3P]_4Cu^+BH_4^-$, 76986-53-3; $[(EtO)_3P]_2CuBH_4$, 76986-52-2; $[(EtO)_3P]_3CuBH_4$, 76986-73-7; $(MePh_2P)_3CuBH_4$, 63371-86-8; $(MePh_2P)_4Cu^+BH_4^-$, 76986-72-6; $[(MeO)_3P]_2CuH_3BCOOC_2H_5$, 76986-71-5; $[(MeO)_3P]_4Cu^+H_3BCOOC_2H_5^-$, 76986-70-4; $[(EtO)_3P]_2CuH_3BCOOC_2H_5$, 76986-69-1; $[(EtO)_3P]_4Cu^+H_3BCOOC_2H_5^-$, 76986-68-0.

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Nitrogen-14 Nuclear Quadrupole Resonance Study of Coordinated Thiocyanate[1]

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A series of twenty palladium(II) thiocyanate complexes have been synthesized and their ^{14}N nuclear quadrupole resonance (NQR) spectra recorded by using the recently developed technique of adiabatic demagnetization in the laboratory frame–double resonance level crossing (ADLF–drlc). A clearly definitive trend for determining the mode of coordination of the thiocyanate moiety, via its ^{14}N nuclear quadrupole coupling constant, has been established. The field gradients at nitrogen are found to be largest in sulfur-bound thiocyanates and smallest in nitrogen-bound thiocyanates, while ionic thiocyanates have field gradients of intermediate values. The asymmetry parameter does not vary consistently with the mode of attachment but, on the average, increases in the order $NCS^- < M\text{-}NCS < M\text{-}SCN$. These results indicate that, in general, no single nitrogen 2p orbital is occupied largely by a lone electron pair. For coordinated thiocyanate, the occupation of a single 2p orbital is greatest for the sulfur-bound complexes. These results support the resonance forms generally accepted, based on bond angle measurements from other techniques, e.g., X-ray crystal structures. Nitrogen-14 NQR via the ADLF–drlc experiment is the most unambiguous technique to date, short of a single-crystal X-ray crystal structure analysis, for the determination of the bonding mode of diamagnetic, hydrogen-containing complexes of thiocyanate in the solid state.

Introduction

Instrumental methods which depend upon nuclear properties have been employed with ever-increasing frequency in the determination of the bonding modes adopted by the ambidentate pseudohalide ions NCO^-, NCS^-, and $NCSe^-$ in coordination complexes.[3,4] Collectively, they offer significant advantages as more sensitive, unequivocal indicators of bond type. The NMR techniques utilized thus far have ranged from indirect probes, wherein nuclei external to the pseudohalides

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are examined, e.g., ^{1}H,[5,6] ^{1}H with lanthanide-induced shift,[7] ^{1}H{^{195}Pt} INDOR,[8] ^{31}P,[9–12] and ^{195}Pt,[13] to direct measurements of NMR-active nuclei in the pseudohalides themselves, e.g., ^{14}N,[14] ^{15}N,[13] ^{13}C,[15] and ^{77}Se.[16] In an earlier communication,[17] we demonstrated the efficacy of using ^{14}N nuclear quadrupole resonance (NQR) spectra, recorded by means of the recently developed technique of adiabatic demagnetization in the laboratory frame–double resonance level crossing (ADLF–drlc), as a solid-state probe of the thiocyanate's bonding mode. We now wish to present the results of this study in detail, including the first observation of thiocyanate ^{14}N NQR coupling constants for complexes containing *both* N- and S-bonded thiocyanates.

Experimental Section

Preparation of Compounds. All chemicals and solvents used were of reagent grade or better. The following complexes were prepared according to methods which have been, or will be, reported elsewhere: $K_2[Pd(SCN)_4]$,[18] *trans*-$[Pd(As(C_6H_5)_3)_2(SCN)_2]$,[19] *trans*-$[Pd(As(C_6H_5)_3)_2(NCS)_2]$,[20] $[Pd(2,2'\text{-bipyridine})(SCN)_2]$,[20] $[Pd(2,2'\text{-bipyridine})(NCS)_2]$,[20] *trans*-$[Pd(P(C_6H_5)_3)_2(NCS)_2]$,[19] $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}SCN]B(C_6H_5)_4$,[21] $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}NCS]B(C_6H_5)_4$,[21] $[Pd(4,4'\text{-dimethyl-}2,2'\text{-bipyridine})(SCN)(NCS)]$,[22] $[Pd(5\text{-nitro-}1,10\text{-phenanthroline})(SCN)_2]$,[23] and $[Pd(5\text{-nitro-}1,10\text{-phenanthroline})(NCS)_2]$.[23] The complex $[Ni(P(C_6H_5)_3)_2(NCS)_2]$ was kindly supplied by J. A. Kargol.

***trans*-Bis(thiocyanato)bis(triphenylstibine)palladium(II), $[Pd(Sb(C_6H_5)_3)_2(SCN)_2]$.** This complex was synthesized in a manner similar to that reported by Burmeister and Basolo;[19] however, the yield was improved from 49% to 91%. A solution of $K_2[Pd(SCN)_4]$ (1.3471 g, 3.231 mmol) dissolved in water/ethanol (35.0 mL, 2/5 by volume) was added, with stirring, to a solution of triphenylstibene (2.379 g, 6.739 mmol) dissolved in 50.0 mL of ethanol. The metal-containing solution was added to that containing the ligand in order to retard the formation of a presumably bridged species which forms a type of "tar ball". The mixture was stirred approximately 2 min, and then the solution was added to an approximately equal volume of water. There was an immediate formation of what appeared to be a gold-colored precipitate which slowly turned more orange over a period of 30 min. The now bright orange solid was isolated by filtration on a sintered glass filter and washed with 50% by volume ethanol. The infrared spectrum in the ν_{CN} region showed a single peak at 2113 cm^{-1} (s, sp), as compared to the 2119 (sh) and 2115 cm^{-1} (s, sp) peaks reported in the literature.[19] The melting point of this complex is 125–126 °C.

Bis(thiocyanato)[bis(diphenylphosphino)methane]palladium(II), $[Pd(dpm)(SCN)_2]$. This complex was prepared in a manner similar to the procedure reported by Palenik et al.[24] The synthesis involved the dissolving of $K_2[Pd(SCN)_4]$ (2.0616 g, 4.945 mmol) in 300 mL of ethanol, while bis(diphenylphosphino)methane (1.9002 g, 4.943 mmol) was dissolved in 20 mL of methylene chloride. The solution containing the ligand was added to the solution of the metal at room temperature. An immediate color change from deep red to yellow–orange occurred, simultaneously with formation of an apparently orange solid. The slurry was allowed to stir for approximately 15 h. The slurry changed from orange to yellow. The solid was recrystallized from methylene chloride by pouring the concentrated methylene chloride solution into ethanol and isolating the bright yellow solid. This compound gave only one ν_{CN} band at 2119 cm^{-1} (s, sp) and was obtained in 70% yield. A portion of this yellow solid was heated, and, at approximately 144 °C, it became more golden. At about 178 °C the complex turned gold-orange, and at 179 °C it became orange and appeared moist. The complex melted at 181 °C. No infrared information or other analytical data had been reported[24] for this complex.

(Isothiocyanato)(thiocyanato)[bis(diphenylphosphino)methane]palladium(II), $[Pd(dpm)(SCN)(NCS)]$. This previously unknown geminite[25] was prepared by dissolving 2.0652 g (4.9533 mmol) of $K_2[Pd(SCN)_4]$ in 200 mL of ethanol at room temperature. Bis(diphenylphosphino)methane (1.9005 g, 4.9441 mmol) was dissolved in approximately 25 mL of methylene chloride. The ligand solution was added slowly, with stirring, to the metal-containing solution. The solution gradually changed from deep red to bright yellow. The yellow solution was placed in an ice–salt bath. Within 10 min, the solution became cloudy. Precipitate formation continued, and after a total of 35 min the yellow-orange solid was isolated by filtration. The product was washed with small portions of methylene chloride, ethanol, and diethyl ether. The solid was recontacted with methylene chloride for about 18 h. A yellow-orange solid was recovered in approximately 70% yield. This complex gave two peaks in the ν_{CN} region of its infrared spectrum, one at 2126 cm^{-1} (m, sp), and the other at 2096 cm^{-1} (s, br).

(Isothiocyanato)(thiocyanato)[1,2-bis(diphenylphosphino)ethane]palladium(II), $[Pd(dpe)(SCN)(NCS)]$. The preparation of this geminite[25] has been described by Meek et al.[26] After repeated unsuccessful attempts to prepare the complex by this method, the following modification was made. The synthesis was carried out by dissolving $K_2[Pd(SCN)_4]$ (1.8141 g, 4.351 mmol) in 200 mL of ethanol and an excess of 1,2-bis(diphenylphosphino)ethane (1.8011 g, 4.521 mmol) in 20 mL of methylene chloride. The ligand solution was added to the metal-containing solution with stirring. An orange-red precipitate formed immediately. The slurry was stirred approximately 15 h, and the orange-red solid was isolated. This orange-red solid is believed to be the Magnus salt, $[Pd(dpe)_2][Pd(SCN)_4]$, which has been reported by Meek et al.[26] This compound was dissolved in methylene chloride, and ethanol was later added to induce precipitation. This yielded a very light yellow complex which exhibited ν_{CN} bands at 2118 (m, sp) and 2098 cm^{-1} (s, br). Similarly, if the orange-red compound was dissolved in methylene chloride and was then added to hexane, the very light yellow complex which formed exhibited ν_{CN} bands at 2123 (s, sp) and 2083 cm^{-1} (s, br). Both samples yielded satisfactory elemental analyses for the desired complex. A similar, but much smaller, difference was noted by Meek et al.[26] for different preparative techniques. The values reported were 2119 (m, sp) and 2095 cm^{-1} (s, br) and 2118 (m, sp) and 2093 cm^{-1} (s, br). These differences may be due to crystal-packing effects. The yield was 87%.

(Isothiocyanato)(thiocyanato)[1,3-bis(diphenylphosphino)propane]palladium(II), $[Pd(dpp)(SCN)(NCS)]$. This geminite[25] was prepared by dissolving $K_2[Pd(SCN)_4]$ (1.9698 g, 4.736 mmol) in 200 mL of ethanol at 55 °C and dissolving 1,3-bis(diphenylphosphino)propane (1.9485 g, 4.724 mmol) in 30 mL of methylene chloride at room temperature. The ligand solution was added to the warm metal-containing solution. An immediate color change from deep

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red to yellow occurred. This slowly faded over a period of 1.5 h. The resulting light yellow solid was isolated by filtration after 4 h and was washed with ethanol and ether. The solid gave ν_{CN} bands at 2118 (s, sp), 2093 (s, br), and 2051 cm^{-1} (vw). The last band is due to a very small amount of ionic thiocyanate which was undetectable by elemental analysis. The yield was at least 83%.

Bis(isothiocyanato)[1,3-bis(diphenylphosphino)propane]palladium(II), [Pd(dpp)(NCS)$_2$]. The synthesis for this complex has been described by Palenik et al.[24] After several unsuccessful attempts to prepare the complex by this method, the complex was prepared by dissolving the [Pd(dpp)(SCN)(NCS)] complex (2.3245 g, 3.660 mmol) described above in 25 mL of *N,N*-dimethylformamide at approximately 50 °C. A small amount of dpp was added and the mixture stirred for about 3 h. The solution was allowed to cool to room temperature and was then poured into approximately 25–30 times, by volume, as much ether. After 10 min of stirring, the light yellow solid was isolated by filtration and washed with small quantities of ethanol and diethyl ether. This was repeated until the ν_{CN} peak associated with the S-bound thiocyanate disappeared (from 2 to 4 times). The resulting complex gave a ν_{CN} band at 2091 cm^{-1} (s, br). No infrared or other characterizational information has been reported[24] for this complex. The yield was 76% based on $K_2[Pd(SCN)_4]$ or 96% based on [Pd(dpp)(SCN)(NCS)].

Bis(thiocyanato)(1,1,4,4-tetramethylethylenediamine)palladium(II), [Pd(Me$_4$en)(SCN)$_2$]. This complex was prepared by a procedure similar to that described by Hassel.[27] $K_2[Pd(SCN)_4]$ (1.8459 g, 4.423 mmol) was added neat to the metal-containing solution. After this solution was stirred for about 5 min, the precipitation of a yellow solid was noted. The yellow solid was isolated by filtration and washed with water, a small amount of ethanol, and diethyl ether. The infrared spectrum had a single ν_{CN} peak at 2121 cm^{-1} (s, br) which was identical with that reported by Hassel.[27] The yield was 91%.

Bis(thiocyanato)(1,4-diphenylethylenediamine)palladium(II), [Pd((C$_6$H$_5$)en(C$_6$H$_5$))(SCN)$_2$]. This complex was prepared in a manner similar to that of Hassel.[27] $K_2[Pd(SCN)_4]$ (0.9589 g, 2.289 mmol) was dissolved in a mixture of 100 mL of water and 60 mL of ethanol. $C_2H_4(NH(C_6H_5))_2$ (0.5370 g, 2.529 mmol) was dissolved in 40 mL of ethanol and added to the metal-containing solution dropwise at room temperature. The red solution immediately turned orange with the concurrent formation of an orange solid. The solid was isolated by filtration and washed successively with small portions of water, ethanol, and diethyl ether. The yield was approximately 93%.

Bis(isothiocyanato)(1,1,5,5-tetramethylpropylenediamine)palladium(II), [Pd(Me$_4$pn)(NCS)$_2$]. $K_2[Pd(SCN)_4]$ (2.3634 g, 5.6683 mmol) was dissolved in approximately 60 mL of acetone at room temperature. To this solution was added neat 8.24 g (63.3 mmol) of Me$_4$pn. The resulting red solution was stirred for about 2 min, whereupon the volume was reduced by aspiration. The reduction of volume was continued until precipitation began. A mixture of 100 mL of water and 150 mL of diethyl ether was then added, and the resulting slurry was stirred for approximately 15 min. The bilayered solution was filtered, and the isolated gold-colored solid was washed with small portions of water, followed by several small portions of diethyl ether. The solid was then dried under vacuum. The yield was approximately 78%.

***trans*-Bis(thiocyanato)bis(pyridine)palladium(II), [Pd(py)$_2$(SCN)$_2$].** The preparation of this complex has been reported by Burmeister and Basolo,[19] in 67% yield. A procedure which gives a 92% yield was developed. $K_2[Pd(SCN)_4]$ (3.8302 g, 9.187 mmol) was dissolved in 100 mL of water and excess pyridine (1.70 mL, 1.662 g, 21 mmol) was added dropwise, neat. The resulting slurry was stirred for approximately 30 min, and the yellow solid was then isolated by filtration. The solid was washed with water, a very small amount of ethanol, and diethyl ether and then dried under vacuum. The ν_{CN} region of the infrared spectrum had a single peak at 2116 cm^{-1} (s, sp). The reported values for this complex are 2115 (s, sp)[19] and 2112 cm^{-1} (s, sp).[22]

Tetrakis(pyridine)palladium(II) Tetraphenylborate, [Pd(py)$_4$][B(C$_6$H$_5$)$_4$]$_2$. This salt was prepared by dissolving [Pd(py)$_2$(SCN)$_2$] (0.3528 g, 0.927 mmol) in 40 mL of pyridine and adding slightly more than 2 equiv of $NaB(C_6H_5)_4$ (0.6538 g, 1.910 mmol). The mixture was stirred for 48 h and then added to 600 mL of water. A very fine precipitate resulted. This was allowed to coagulate by standing for 18 h. The white solid was isolated by filtration, washed with water, and dried under vacuum over Drierite. The infrared spectrum showed no peaks in the ν_{CN} region, while peaks corresponding to tetraphenylborate and pyridine were observed. The yield was 98%.

Physical Measurements. Full-scale, 4000–400 cm^{-1} infrared spectra were recorded for all complexes on a Pye Unicam SP1100 spectrometer. The ν_{CN} region, 2300–2000 cm^{-1}, was recorded on a Perkin-Elmer 180 spectrometer, both as a normal scan and with a 10-fold abscissa scale expansion. All spectra were determined as Nujol mulls between KBr or NaCl plates. Spectra taken on the Perkin-Elmer 180 were calibrated to polystyrene. Decomposition/melting point measurements were made by using a Thomas-Hoover melting point apparatus, and all values listed are uncorrected. Nitrogen-14 NQR measurements were carried out at the University of Illinois—Urbana, employing double-resonance techniques described elsewhere.[28-40] All spectra were obtained at 77 K. Elemental analyses were determined by the Microanalytical Laboratory of the Chemistry Department of the University of Illinois—Urbana. Satisfactory results were obtained in all cases.

Results and Discussion

Prior to this investigation, no extended studies had been made of ^{14}N NQR spectra of chalcogenocyanate ions in coordinating environments. Some limited ^{14}N quadrupole coupling constant information is available for ionic thiocyanates[41,42] and selenocyanate,[42] as well as for some organic thiocyanates,[43] isocyanic acid,[44,45] isothiocyanic acid,[44] and two thiocyanate complexes.[46]

The ^{14}N NQR signals in complexes containing chalcogenocyanates will appear at frequencies less than 4 MHz.[47] Thus, their detection by conventional NQR techniques is difficult.[48] The recent development of NQR double-resonance techniques has permitted the study of chalcogenocyanate complexes by ^{14}N NQR spectroscopy. The method is limited to diamagnetic complexes containing protons.

The ADLF–drlc technique has been used in this study to investigate a series of palladium(II) complexes containing coordinated thiocyanate. As can be seen from the data presented in Table I, this technique clearly establishes a basis for discernment of N-bonded vs. S-bonded thiocyanates. The ^{14}N NQR coupling constants for S-bound thiocyanates are greater than 2800 kHz but less than 3500 kHz. Organic thiocyanates have values greater than 3500 kHz. The ^{14}N NQR coupling constants for ionic thiocyanates are between 2400 kHz and 2600 kHz, while those for N-bound thiocyanates are generally much less than 1600 kHz.

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Table I. ^{14}N NQR Data for Compounds Containing Sulfur-Bound, Ionic, and Nitrogen-Bound Thiocyanates

compd[e]	ν_+[a]	ν_-[a]	ν_0[a]	e^2Qq/h[a]	η	ref
CH_3SCN				3515	0.473	43
C_2H_5SCN				3590	0.474	43
$NCSC_2H_4SCN$				3545	0.467	43
$(bpy)Pb(SCN)_2$				3407	0.207	49
$Pd(As(C_6H_5)_3)_2(SCN)_2$	2841	2279	562	3413	0.329	
$Pd(phen)(SCN)_2$	2770	(2208)[b]	562	3319	0.339	40
$Pd(dmp)(SCN)_2$	2570	(2150)[b]	420	3147	0.267	
	2683	(2263)[b]	420	3297	0.255	
$Pd(bpy)(SCN)_2$[c]	2787	2181	606	3312	0.366	
	2764	2226	538	3327	0.323	
$Pd(5\text{-}NO_2phen)(SCN)_2$	2692	(2144)[b]	548	3324	0.340	
$Pd(py)_2(SCN)_2$	2723	(2309)[b]	414	3355	0.247	
$Pd(Sb(C_6H_5)_3)_2(SCN)_2$	2693	(2285)[b]	408	3319	0.246	
$Pd(Me_4en)(SCN)_2$	2670	(2130)[b]	540	3200	0.338	
$K_2[Pt(SCN)_6]$	2715.0	2093.5	(621.5)[b]	3205.7	0.3878	46
$K_2[Hg(SCN)_4]$[c]	2304.6	2046.0	(248.6)[b]	2900.4	0.1783	46
	2382.9	2090.1	(292.8)[b]	2982.0	0.1964	
LiSCN				2607	0.016	41
KSCN	1840.6	1806.5	(34.1)[b]	2431	0.028	42
HNCS				1200[d] ± 50		44
$(C_6H_5)_2Sn(NCS)_2$				1538	0.566	49
$(C_6H_5)_3Sn(NCS)$				1335	0.325	49
$Pd(As(C_6H_5)_3)_2(NCS)_2$	301	238	(63)[b]	359	0.35	
$Pd(bpy)(NCS)_2$	463	445	(18)[b]	605	0.059	
$Pd(P(C_6H_5)_3)_2(NCS)_2$	298	247	(51)[b]	363	0.28	
$Pd(dpp)(NCS)_2$	776	731	(45)[b]	1005	0.090	
$Ni(P(C_6H_5)_3)_2(NCS)_2$	405	339	(66)[b]	496	0.266	
$Zn(py)_2(NCS)_2$[c]	760	660	100	947	0.211	28
	715	615	100	887	0.090	
Pd(dpe)(SCN)(NCS)	2680	(2290)[b]	390	3313	0.235	
	610	(610)[b]	(0)[b]	813	~0	
Pd(dpp)(SCN)(NCS)	2633	(2201)[b]	432	3223	0.268	
	738	(738)[b]	(0)[b]	984	~0	

[a] Frequencies in kHz. [b] Values in parentheses are calculated. [c] Two sets of values due to crystallographically nonequivalent molecules. [d] Based on gas-phase microwave spectral data. [e] Abbreviations: bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; dpm, bis(diphenylphosphino)methane; 5-NO_2phen, 5-nitro-1,10-phenanthroline; py, pyridine; Me_4en, 1,1,4,4-tetramethylethylenediamine; dpp, 1,3-bis(diphenylphosphino)propane; dpe, 1,2-bis(diphenylphosphino)ethane.

Table II. ^{14}N NQR Data for Nitrogens Other Than Thiocyanate Nitrogens in Complexes Studied

compd	ν_+[a]	ν_-[a]	ν_0[a]	e^2Qq/h[a]	η
$Pd(phen)(SCN)_2$[39]	1585	1585	(0)[b]	2113	0.0
$Pd(5\text{-}NO_2phen)(SCN)_2$	1620	1587	(33)[b]	2138	0.031
	838[c]	674[c]	(164)[b,c]	1008[c]	0.325[c]
$Pd(bpy)(SCN)_2$	1632	1511	(121)[b]	2095	0.116
$Pd(Me_4en)(SCN)_2$	1588	1490	(98)[b]	2052	0.096
$Pd(py)_2(SCN)_2$	1438	1301	(137)[b]	1826	0.150
$Pd(bpy)(NCS)_2$[d]	1241	1187	(54)[b]	1619	0.067
	1254	1200	(54)[b]	1636	0.066
$Pd(bpy)(SCN)_2$	1877	1800	(77)[b]	2451	0.063

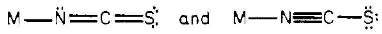
[a] Values in kHz. [b] Values in parentheses are calculated. [c] Nitrogen of the nitro group. [d] Two sets of values due to crystallographically inequivalent molecules.

The ^{14}N NQR resonances of the other nitrogen-containing ligands present in the complexes studied were also determined. These are listed in Table II.

The microwave spectrum of gaseous HNCS gives an interesting ^{14}N coupling constant value of 1200 ± 50 kHz. According to the trends observed in this work, it would appear that, in the gas phase, the hydrogen is bonded to the nitrogen, forming isothiocyanic acid.

Onyszchuk, Brown and Cheng[49] have observed ^{14}N NQR signals for several main-group thiocyanate compounds (see Table I). In their study, they observed the presence of an S-bound lead(II) complex which was previously believed to be bonded through the nitrogen. These values indicate that the N-bonded range may be even larger than observed in this study. These values, however, are still well below the value found for ionic thiocyanate, let alone the S-bonded complexes.

The field gradients at ^{14}N in the N-bonded complexes are substantially lower than those in the S-bonded compounds, with intermediate values for the ionic compounds. In view of the large M–N–C angles in N-bonded complexes,[3] it appears that there is no single 2p orbital that is occupied largely by a lone pair of electrons. Indeed, the distribution of electrons in the σ and π orbitals is apparently such that only a small net field gradient at nitrogen results. The large variation in relative value of coupling constant can be related to a corresponding variation in the relative importance of the two resonance structures



$$\mathrm{M-\ddot{N}=C=\underset{\cdot\cdot}{S}\!:} \quad \text{and} \quad \mathrm{M-N\equiv C-\underset{\cdot\cdot}{\ddot{S}}\!:}$$

This is the result of small differences in population of the orbitals in question, which are affected by changes in the degree of thiocyanate–metal interaction.

The ^{14}N coupling constants vary over a smaller range in the complexes containing S-bound thiocyanates. This would be expected, because the variation in field gradient at the nitrogen arises in these systems only through an inductive effect.

The asymmetry parameter does not vary in any discernible pattern with the bonding mode of the thiocyanate group. The value of the asymmetry parameter for ionic thiocyanate is quite small, as are its values in the case of several N-bound species.

Correlation of the field gradient parameters with more subtle aspects of metal–ligand bonding must await the acquisition of additional data, including the determination of some bond angles for the N-bound cases. For the present, it is clear that ^{14}N NQR is capable of unambiguously distinguishing the mode

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(49) Onyszchuk, M.; Brown, T. L.; Cheng, C. P., unpublished results.

Table III. Complexes of the Type $[Pd((C_6H_5)_2P(CH_2)_nP(C_6H_5)_2)(CNS)_2]$, Where *n* is 1-3

n	type of thiocyanate	ref
1	$(SCN)_2$	24
1	(SCN)(NCS)	this work
2	(SCN)(NCS)	24, 26
2	$(NCS)_2$	50
3	(SCN)(NCS)	this work
3	$(NCS)_2$	24

of coordination for thiocyanate in solid samples.

The complexes investigated in this study of the type $[Pd\{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\}(\text{thiocyanate})_2]$, are deserving of special mention. These complexes were reported to have S,S-bound thiocyanates for $n = 1$,[24,50] N,S-bound thiocyanates for $n = 2$,[24,26,50] and N,N-bound thiocyanates for $n = 3$.[24,50] Recently, McQuillan and Oxton[51] have reported the synthesis of many similar complexes of both palladium(II) and platinum(II). Among these complexes is listed a brown complex, with an infrared ν_{CN} frequency of 2077 cm^{-1} (s, br), which the authors attribute to $[Pd(dpe)(NCS)_2]$, where dpe is $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$. This complex is not pure however, inasmuch as three much weaker, higher wavenumber bands are also observed in the ν_{CN} region. No analytical data were reported. The authors concluded that, due to its ν_{CN} frequency and shape and brown colors at various times during the reaction, "the hitherto unreported thiocyanato-*N* complex $[Pd(Ph_2PC_2H_4PPh_2)(NCS)_2]$ must be formed at intermediate stages in the preparative reactions".[51] The previously reported[24,26,50] geminite [Pd(dpe)(SCN)(NCS)] gave ^{14}N e^2Qq/h values of 3313 and 813 kHz, within the S-bound and N-bound regions, respectively.

In attempting to synthesize the complexes previously reported, two heretofore unreported complexes were synthesized and characterized. The first of these is a bright yellow-orange complex of dpm, bis(diphenylphosphino)methane, which gave two peaks in the ν_{CN} region: one at 2126 cm^{-1} (m) and the other at 2096 cm^{-1} (s, br). This complex is believed to be the geminite[25] [Pd(dpm)(SCN)(NCS)]. The relative intensities of the two peaks did not change upon recrystallization. Unfortunately, the complex did not yield ^{14}N NQR data.

The other new complex, also a geminite,[25] is [Pd(dpp)(SCN)(NCS)], where dpp is 1,3-bis(diphenylphosphino)propane. This complex is an intermediate in the formation of the N,N-bound isomer. It exhibits two ν_{CN} bands at 2118 (s, sp) and 2093 cm^{-1} (s, br). The ^{14}N NQR coupling constants for this complex are 3223 and 984 kHz, within the S-bound and N-bound regions, respectively. The ν_{CN} frequency of the N,N-bound isomer was 2090 cm^{-1} (s, br), while a ^{14}N NQR coupling constant of 1005 kHz was obtained.

Table IV. Compounds for Which No ^{14}N NQR Resonances Were Observed[a]

$[Pd(5\text{-}NO_2phen)(NCS)_2]$
$[Pd(Et_4dien)(SCN)]B(C_6H_5)_4$
$[Pd(Et_4dien)(NCS)]B(C_6H_5)_4$
[Pd(dmp)(SCN)(NCS)]
[Pd(dmbp)(SCN)(NCS)]
$[Pd((C_6H_5)en(C_6H_5))(SCN)_2]$
$[Pd(Me_4pn)(NCS)_2]$
$[Pd(py)_4][B(C_6H_5)_4]_2$

[a] Abbreviations: Et_4dien, 1,1,7,7-tetraethyldiethylenetriamine; dmbp, 4,4′-dimethyl-2,2′-bipyridine; $(C_6H_5)_2$en, 1,4-diphenylethylenediamine; Me_4pn, 1,1,5,5-tetramethylpropylenediamine; also see Table I.

The preparation of these complexes, especially the dpp complex, poses difficulties for predictions based entirely upon steric effects.[24,50] The arguments embodying both steric and electronic effects[3] better fit all the cases now observed (see Table III).

The ^{14}N ADLF–drlc technique can only be used for crystalline, diamagnetic nitrogen-containing complexes that contain protons and that meet certain nuclear spin–lattice relaxation requirements. For the complexes listed in Table IV, an excessively short spin–lattice relaxation time of the protons prevented acquisition of the ^{14}N spectra. Unfortunately, it is not yet possible to predict what features of molecular structure will give rise to such short spin–lattice relaxation times.

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Registry No. $Pd(As(C_6H_5)_3)_2(SCN)_2$, 21239-62-3; $Pd(dpm)(SCN)_2$, 51320-63-9; $Pd(bpy)(SCN)_2$, 23672-08-4; $Pd(5\text{-}NO\text{-}phen)(SCN)_2$, 65060-51-7; $Pd(py)_2(SCN)_2$, 52152-22-4; $Pd(Sb(C_6H_5)_3)_2(SCN)_2$, 52152-23-5; $Pd(Me_4en)(SCN)_2$, 72692-67-2; $Pd(As(C_6H_5)_3)_2(NCS)_2$, 21239-61-2; $Pd(bpy)(NCS)_2$, 15613-05-5; $Pd(P(C_6H_5)_3)_2(NCS)_2$, 52194-15-7; $Pd(dpp)(NCS)_2$, 51886-81-8; $Ni(P(C_6H_5)_3)_2(NCS)_2$, 15709-62-3; Pd(dpe)(SCN)(NCS), 29893-44-5; Pd(dpp)(SCN)(NCS), 76793-82-3; Pd(dpm)(SCN)(NCS), 76793-83-4; $Pd((C_6H_5)en(C_6H_5))(SCN)_2$, 76793-84-5; $Pd(Me_4pn)(NCS)_2$, 76793-85-6; $[Pd(py)_4][B(C_6H_5)_4]_2$, 76793-86-7; $K_2[Pd(SCN)_4]$, 14516-47-3.

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