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The Effects of Interligand Steric Hindrance *versus* Counterion Interactions on the Bonding Modes of the Thiocyanate and Nitrite Ions in Nickel(II), Palladium(II) and Platinum(II) Complexes[1]

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The competing effects of interligand steric hindrance versus counterion interactions on the bonding modes adopted by the thiocyanate and nitrite ions have been studied in the complexes $[MLX][B\Phi_4]$ *(M = Pd*^{II} *and Pt*^{II}*, L = 1,1,7,7-tetraethyldiethylenetriamine (Et*$_4$*dien) and 4-methyl-1,1,7,7-tetraethyldiethylenetriamine (MeEt*$_4$*dien), X = thiocyanate),* $[Pd(tripy)NCS][B\Phi_4]$ *(tripy = 2,2′,2″-tripyridine) and* $[M(Et_4dien)NO_2][B\Phi_4]$ *(M = Pd*^{II}*, Ni*^{II}*). Whereas the* $[PdL(NCS)][B\Phi_4]$ *complexes undergo S → N bonded linkage isomerizations in solution and N → S-bonded reisomerizations in the solid state, the* $[PtL(SCN)][B\Phi_4]$ *complexes were found to be stable S-bonded species, both in the solid state and in solution. The* $[Pd(tripy)NCS][B\Phi_4]$ *and* $[M(Et_4dien)NO_2][B\Phi_4]$ *(M = Pd*^{II}*, Ni*^{II}*) complexes were all isolated as stable N-bonded species. Bonding assignments were based on infrared or electronic spectral data. The bonding trends observed are discussed in terms of the several factors involved including, in addition to the two mentioned above, the nature of the metal ion.*

Introduction

Following the initial discovery[2] that steric factors alone were sufficient to alter the normal bonding pattern of the thiocyanate ion, e.g., [Pd(diethylenetriamine)SCN]$^+$ *versus* [Pd(1,1,7,7-tetraethyldiethylenetriamine)NCS]$^+$, examples have come to light which involve an interplay between electronic and steric factors which has become ever more subtle. Among the more fascinating examples are the series of palladium(II) thiocyanate complexes with bidentate ligands having different Group VA donor atoms which have been synthesized by Meek and his co-workers.[3,4] Some of these complexes have been the subject of single crystal X-ray diffraction studies by Palenik and his co-workers.[5,6] The following series will serve to illustrate the point: $[Pd(\Phi_2As(CH_2)_2As\Phi_2)(SCN)_2]$,[4] $[Pd(\Phi_2PCH_2P\Phi_2(SCN)_2]$,[7] $[Pd(\Phi_2P(CH_2)_2P\Phi_2)(SCN)(NCS)]$,[4,5] $[Pd(\Phi_2P(CH_2)_3P\Phi_2)(NCS)_2]$,[7] $[Pd(\Phi_2P(CH_2)_3N(CH_3)_2)(SCN)(NCS)]$.[4,6]

The bonding mode of the thiocyanate ion in the [Pd(Et$_4$dien)NCS]$^+$ complex[8] has also been found to be subject to counterion control in the solid state, i.e., [Pd(Et$_4$dien)NCS]X (X$^-$ = SCN$^-$, PF$_6^-$)[2,9] *versus* $[Pd(Et_4dien)SCN][B\Phi_4]$.[10,11,12] Complexes of the type [Pd(Et$_4$dien)X]$^+$ have provided substrates which have been shown to be subject to an intriguing variety of mechanistic controls in substitution reactions, including the nature of the incoming group,[13,14] the solvent,[15] and the outgoing group.[16,17]

As part of a continuing study[18] of the relative effects of interligand steric hindrance and counterion interactions on the bonding modes adopted by ambidentate ligands in cationic coordination complexes, this paper describes the results we have obtained by changing the metal ion [to platinum(II)], the tridentate ligand (to 4-methyl-1,1,7,7-tetraethyldiethylenetriamine[19] and 2,2′,2″-tripyridine[19]), and the ambidentate ligand (to NO$_2^-$).

Experimental

Preparation of Complexes

$[Pd(MeEt_4dien)SCN][B\Phi_4]$

Sodium thiocyanate (4.08 mmol) was added to a suspension of 1.01 mmol of palladium(II) chloride in 100 ml of acetone. A clear, blood red solution formed, with stirring, over a period of two hr, accompanied by the precipitation of sodium chloride. The mixture was filtered and the filtrate cooled to –10° in an ice–salt bath. As the filtrate was being stirred rapidly, 0.7 ml of 4-methyl-1,1,7,7-tetraethyldiethylenetriamine was added dropwise. The color of the solution changed to straw yellow within a few minutes, coincident with the appearance of a light precipitate, presumably sodium thiocyanate. The solution was filtered after being stirred for an additional 0.5 hr, and to the filtrate was added a solution of 1.05 mmol of sodium tetraphenylborate in acetone at –10°, resulting only in the further precipitation of sodium thiocyanate. After another 0.5 hr stirring period, the mixture was filtered into 400 ml of ice water, yielding a light yellow precipitate. It was isolated by filtration, washed with water and anhydrous ethyl ether, and dried *in vacuo* over P_4O_{10}, yield 91%. Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2N(CH_3)(CH_2)_2N(C_2H_5)_2\}SCN][B(C_6H_5)_4]$: C, 64.13; H, 7.17; N, 7.87. Found: C, 64.28; H, 7.37; N, 7.84.

[Pd(MeEt$_4$dien)NCS][BΦ_4]

A $10^{-3}M$ solution of [Pd(MeEt$_4$dien)SCN][BΦ_4] in N,N-dimethylformamide was stirred for 3 hr at 25°. It was then filtered into approximately forty times its volume of ice water, yielding a cream colored precipitate. After the mixture was stirred for several minutes, to coagulate the precipitate, the precipitate was isolated by filtration, washed with water and anhydrous ether and dried *in vacuo* over P_4O_{10}, yield 70%. Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2N(CH_3)(CH_2)_2N(C_2H_5)_2\}NCS][B(C_6H_5)_4]$: C, 64.13; H, 7.17. Found: C, 64.11; H, 7.46.

[Pt(Et$_4$dien)SCN][BΦ_4]

Aqueous solutions of potassium tetrathiocyanatoplatinate(II) (1.0 mmol) and sodium tetraphenylborate (2.1 mmol) were mixed. The creamy precipitate of potassium tetraphenylborate which formed immediately was removed by filtration and the filtrate evaporated to near dryness on a Rotovac. The moist solid thus obtained, which was sodium tetrathiocyanatoplatinate(II), was then dissolved in 100 ml of acetone. As this solution was stirred rapidly at room temperature, 0.6 ml of 1,1,7,7-tetraethyldiethylenetriamine was added dropwise. No color change occurred and, hence, the solution was refluxed for *ca.* 220 hr. During the reflux, the solution turned straw yellow in color, and a light precipitate, presumably sodium thiocyanate, formed. The solution was filtered, and to the filtrate was added a solution of 1.05 mmol of sodium tetraphenylborate in acetone. After 0.5 hr further stirring, the mixture was filtered into 400 ml of ice water, yielding a straw yellow precipitate. It was isolated by filtration, washed with water and anhydrous ethyl ether, and dried *in vacuo* over P_4O_{10}. It was recrystallized from DMF/water, yield 90%. Anal. Calcd. for $[Pt\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}SCN][B(C_6H_5)_4]$: C, 56.41; H, 6.27; N, 7.11. Found: C, 56.27; H, 6.44; N, 7.25.

[Pt(MeEt$_4$dien)SCN][BΦ_4]

The procedure used was completely analogous to that used for [Pt(Et$_4$dien)SCN][BΦ_4]. Anal. Calcd. for $[Pt\{(C_2H_5)_2N(CH_2)_2N(CH_3)(CH_2)_2N(C_2H_5)_2\}SCN][B(C_6H_5)_4]$: C, 56.92; H, 6.41; N, 6.99. Found: C, 56.74; H, 6.27; N, 7.15.

[Pd(tripy)NCS][BΦ_4]

After 0.283 g (0.61 mmol) of chloro-(2,2′,2″-tripyridine)palladium(II) chloride trihydrate, prepared according to the method of Morgan and Burstall,[20] was dissolved in 25 ml of water, the solution was treated with 0.207 g (1.22 mmol) of silver nitrate dissolved in 10 ml of water. Warming helped to coagulate the precipitated silver chloride, which was removed as the solution was passed through a fine fritted filter. When a 10 ml aqueous solution of 0.208 g (0.61 mmol) of sodium tetraphenylborate was introduced to the filtrate, the precipitate which formed immediately was redissolved by adding 30 ml of water, heating, and bringing the volume to 200 ml with acetone. While the solution was still warm, 0.049 g (0.61 mmol) of sodium thiocyanate in 5 ml of water was added. Sheet-like yellow crystals precipitated as the solution cooled. Yield, 32%; mp, 185–187° (dec); Λ_m, 137 ohm^{-1} cm^2 mol^{-1} ($10^{-3}M$ nitromethane solution at 25°). Anal. Calcd. for $[Pd(C_{15}H_{11}N_3)NCS][B(C_6H_5)_4]$: C, 67.01; H, 4.36; N, 7.81. Found: C, 67.19; H, 4.44; N, 7.68.

[Pd(tripy)Br][BΦ_4]

After 0.283 g (0.61 mmol) of chloro-(2,2′,2″-tripyridine)palladium(II) chloride trihydrate was dissolved in 25 ml of water, the solution was treated with 0.207 g (1.22 mmol) of silver nitrate dissolved in 10 ml of water. The solution was warmed, and the precipitated silver chloride was removed by filtration. A solution of 0.063 g (0.63 mmol) of sodium bromide in 10 ml of water was added, and the solution was warmed. Precipitation of the product occurred immediately after the addition of 0.208 g (0.61 mmol) of sodium tetraphenylborate dissolved in 10 ml of water. The precipitate was washed with extra portions of water and then dried *in vacuo.*

[Pd(Et$_4$dien)NO$_2$][BΦ_4]

Sodium nitrite (1.17 mmol) was added to 50 ml of N,N-dimethylformamide containing 0.50 mmol of [Pd(Et$_4$dien)SeCN][B(C$_6$H$_5$)$_4$][11] and the resulting solution stirred for 12 hr at room temperature. The original golden solution became pale yellow in color as the reaction proceeded. The solution was filtered into 800 ml of ice water, with vigorous stirring. A very light cream-colored precipitate formed instantaneously. The mixture was stirred for 1 hr at room temperature, filtered, and the solid thereby obtained was washed with two 25 ml portions of water, followed by two 25 ml portions of anhydrous ethyl ether. It was air-dried on a filter paper for 15 min, followed by drying *in vacuo* over P_4O_{10} for 2 hr. Yield, 70%; mp, 172° (dec). Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}NO_2][B(C_6H_5)_4]$: C, 62.97; H, 7.48; N, 8.16. Found: C, 63.03; H, 7.54; N, 7.98.

[Pd(Et$_4$dien)Br]Br

To 10 ml of an aqueous solution containing 1.0 mmol of [Pd(Et$_4$dien)Cl]Cl[13] was added 2.05 mmol of sodium bromide, resulting in the formation of a yellow precipitate. The total volume of the reaction mixture was reduced to *ca.* 5 ml, and the solid was isolated by filtration. It was dissolved in a minimum volume of water–ethanol (1:1, by volume) with heating on a steam bath. Upon cooling the solution in an ice bath, bright yellow crystals formed which were isolated by filtration, washed with two 10 ml portions of ice water and two 10 ml portions of anhydrous ethyl ether, air dried for 10 min, and dried *in vacuo* over P_4O_{10} for 2 hr. Yield, 88%; mp 238° (darkens at 120°). Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}Br]Br$: C, 29.29; H, 6.08; N, 8.74. Found: C, 29.89; H, 6.18; N, 8.47.

[Pd(Et$_4$dien)Br][$B\Phi_4$]

To 5 ml of an aqueous solution containing 0.50 mmol of [Pd(Et$_4$dien)Br]Br was added, with stirring, a solution of 0.51 mmol of sodium tetraphenylborate dissolved in 5 ml of acetone. Dropwise addition of water produced a slight turbidity. The mixture was then cooled in an ice bath for 30 min, yielding bright yellow needle-like crystals, which were isolated by filtration. The filtrate was evaporated under vacuum, resulting in further crystallization. The combined crystals were dissolved in about 5 ml of acetone to which water was again added dropwise until the first sign of turbidity was observed. The mixture was cooled in an ice bath for 30 min, yielding large, needle-like crystals, which were isolated by filtration, and washed and dried as in the preceding preparation. Yield, 96%; mp, 172° (dec.). Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}Br][B(C_6H_5)_4]$: C, 59.99; H, 6.85; N, 5.83. Found: C, 60.00; H, 6.80; N, 5.74.

[Pd(Et$_4$dien)I]I

A solution of sodium iodide (3.35 mmol) in 5 ml of water was added to 10 ml of an aqueous solution of [Pd(Et$_4$dien)Cl]Cl[13] (1.30 mmol), yielding an immediate precipitate which was isolated by filtration after the mixture had been stirred for 2 hr. The crystals were dissolved in a minimum volume of ethanol–water (1/1) with heating on a steam bath. Bright orange, needle-like crystals formed upon cooling the solution. They were isolated by filtration, washed with two 5 ml portions of anhydrous ethyl ether, air-dried on a filter paper for 15 min and dried *in vacuo* over P_4O_{10} for 1 hr. Yield, 74%; mp, 174°. Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}I]I$: C, 25.09; H, 5.08; N, 7.30. Found: C, 24.89; H, 5.18; N, 7.09.

[Pd(Et$_4$dien)I][$B\Phi_4$]

To the first filtrate resulting from the isolation of the solid [Pd(Et$_4$dien)I]I in the preceding preparation (0.34 mmol calculated to remain in the solution) was added, with stirring, 0.35 mmol of sodium tetraphenylborate in 20 ml of acetone. The resulting orange solution was mixed with a liter of water, yielding an immediate precipitate. The mixture was stirred for 30 min, whereupon orange yellow crystals were separated by filtration. The crystals were dissolved in a minimum volume of acetone and crystallization induced by the dropwise addition of water. The recrystallized solid was separated by filtration, and washed and dried in the same manner as the corresponding bromide complex. Yield, 92%; mp, 178°. Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}I][B(C_6H_5)_4]$: C, 56.23; H, 6.42; N, 5.47. Found: C, 56.51; H, 6.67; N, 5.36.

[Pd(Et$_4$dien)N_3][$B\Phi_4$]

Seven hundredths of a mmol of solid sodium azide was added to 50 ml of an N,N-dimethylformamide solution containing 0.52 mmol of [Pd(Et$_4$dien)SeCN] $[B(C_6H_5)_4]$.[11] The golden color of the [Pd(Et$_4$dien)SeCN]$^+$ solution changed to an intense yellow as the solid sodium azide dissolved. The solution was stirred for 3 hr, after which it was filtered into 800 ml of cold water, with vigorous stirring, resulting in the immediate formation of a light yellow precipitate. The mixture was stirred for 30 min at room temperature, filtered, and the yellow solid thus obtained was washed and dried in the same manner as the corresponding bromide complex. Yield, 90%; mp, 152°; strong, broad $\nu N{\equiv}N$ band at 2047 cm^{-1}. Anal. Calcd. for $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}N_3][B(C_6H_5)_4]$: C, 63.24; H, 7.22; N, 12.32. Found: C, 63.17; H, 7.48; N, 12.06.

[Ni(Et$_4$dien)NO_2][$B\Phi_4$]·CH_3OH

Solid nickel(II) nitrate hexahydrate (2.91 g, 0.01 mol) was dissolved in 30 ml of a methanolic solution that contained 1.38 g (0.02 mol) of sodium nitrite. The precipitation of sodium nitrate was increased by cooling the solution to –78° in a Dry Ice–acetone bath. Filtration at a low temperature produced a clear solution, to which 2.8 ml of Et$_4$dien was added. After bringing the volume to 80 ml with additional methanol, the solution was warmed and added to 30 ml of warm methanol containing 3.42 g (0.01 mol) of sodium tetraphenylborate. The orange crystals of the product appeared as the solution cooled. Yield, 68%; mp, 160° (dec.). Anal. Calcd. for $[Ni\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}NO_2][B(C_6H_5)_4]\cdot CH_3OH$: C, 66.19; H, 7.96; N, 8.35. Found: C, 66.60; H, 8.15; N, 8.44.

Physical Measurements

High resolution infrared spectra were measured with Perkin–Elmer Model 421 and Model 180 spectrophotometers. The complexes were held in Nujol suspension between potassium bromide plates. Visible–

ultraviolet spectra were measured with a Cary 14 spectrophotometer, using matched 1 cm quartz cells. Melting points were determined with a Fisher–Johns melting point apparatus, and are uncorrected. Carbon, hydrogen, and nitrogen microanalyses were carried out by the following laboratories: Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany; Micro-Analysis, Inc., Wilmington, Delaware, 19808; M–H–W Laboratories, Garden City, Michigan, 48135.

Results

The thiocyanate νCN frequencies for the complexes whose preparations were described in the preceding section are shown in Table I. By comparing the infrared spectrum of $[\mathrm{Pd(Et_4dien)NO_2}][\mathrm{B\Phi_4}]$ with those of the other $[\mathrm{Pd(Et_4dien)X}]\mathrm{B\Phi_4}$ ($\mathrm{X^-} = \mathrm{Br^-}, \mathrm{I^-}, \mathrm{N_3^-}$) complexes, $\nu_{as}(\mathrm{NO_2})$ and $\nu_s(\mathrm{NO_2})$ bands were assigned in the former spectrum at, respectively, 1370 and 1329 cm^{-1}. The complex also exhibits a weak $\mathrm{NO_2}$ wagging band at 580 cm^{-1}.

Electronic spectral data for $[\mathrm{Pd(Et_4dien)NO_2}][\mathrm{B\Phi_4}]$, $[\mathrm{Ni(Et_4dien)NO_2}][\mathrm{B\Phi_4}]\cdot\mathrm{CH_3OH}$, and related complexes are presented in Table II.

TABLE I. Solid State (Nujol mull) Thiocyanate νCN Frequencies.

Complex	νCN, cm^{-1}
$[\mathrm{Pd(Et_4dien)SCN}][\mathrm{B\Phi_4}]$[a]	2113 s, sp
$[\mathrm{Pd(Et_4dien)NCS}][\mathrm{B\Phi_4}]$[a]	2088 s, br
$[\mathrm{Pd(MeEt_4dien)SCN}][\mathrm{B\Phi_4}]$	2110 s, sp
$[\mathrm{Pd(MeEt_4dien)NCS}][\mathrm{B\Phi_4}]$	2087 s, br
$[\mathrm{Pt(Et_4dien)SCN}][\mathrm{B\Phi_4}]$	2120 s, sp
$[\mathrm{Pt(MeEt_4dien)SCN}][\mathrm{B\Phi_4}]$	2122 s, sp
$[\mathrm{Pd(tripy)(NCS)_2}]$[b,c]	2088 s, br
$[\mathrm{Pd(tripy)NCS}][\mathrm{B\Phi_4}]$[d]	2115 vw, sp[e]
	2068 s, br
$[\mathrm{Pt(tripy)NCS}]\mathrm{NCS}$[b,f]	2089 s, br
	2040 s, br[g]

[a] Data taken from ref. 11. [b] Data taken from ref. 22. [c] Both thiocyanates N-bonded; tripy either functions as a bidentate ligand, or complex is five coordinate; νCS band at 848 cm^{-1}. [d] νCS band at 848 cm^{-1}, δNCS band at 454 cm^{-1}; band assignments made by comparing spectrum with that of $[\mathrm{Pd(Et_4dien)Br}][\mathrm{B\Phi_4}]$. [e] Due to trace of S-bonded isomer. [f] νCS band at 863 cm^{-1}. [g] Due to non-coordinated thiocyanate.

TABLE II. Ligand Field Bands for $[\mathrm{M(Et_4dien)X}][\mathrm{B\Phi_4}]$ Complexes.

M	X	ν_{max}, kK	M	X	ν_{max}, kK
Pd	$-\mathrm{NO_2}$[a]	34.5[b]	Ni	$-\mathrm{NO_2}$[e]	20.9
Pd	–NCS[a,c]	30.7	Ni	–NCSe[f,g]	20.4
Pd	–NCO[a,d]	30.0	Ni	–NCS[f,g]	20.2
Pd	Br[a]	27.4	Ni	–NCO[f,g]	19.9
Pd	I[a]	24.9	Ni	Cl[f,g]	18.7

[a] DMF solution, $\mu = 0.1$ ($\mathrm{NaClO_4}$). [b] Charge-transfer band, masks actual position of ligand field band. [c] Prepared as described in ref. 11. [d] Data taken from ref. 18(b). [e] Nitromethane solution. [f] Acetonitrile solution. [g] Data taken from ref. 18(c).

Discussion

The following considerations are important in explaining the behavior of the $[\mathrm{M(Et_4dien)(SCN/NCS)}]\mathrm{X}$ complexes [M = Pd$^{\mathrm{II}}$, Pt$^{\mathrm{II}}$]:

(a) Neglecting the electronic and steric effects of the other ligands in a given palladium(II) or platinum(II) complex, S-bonding prevails as a consequence of the more favorable Pd–SCN and Pt–SCN soft–soft interactions, as in $[\mathrm{Pd(SCN)_4}]^{2-}$ and $[\mathrm{Pt(SCN)_4}]^{2-}$.

(b) There is less steric interference between the ethyl groups of the Et$_4$dien ligand and the linear M–NCS linkage than with the bent M–SCN linkage. Hewkin and Poë[21] have calculated that $[\mathrm{Pd(Et_4dien)NCS}]^+$, in the absence of a counter ion, is 6 kcal/mole more stable than the S-bonded isomer. Accordingly, the $[\mathrm{Pd(Et_4dien)SCN}]^+ \rightarrow [\mathrm{Pd(Et_4dien)NCS}]^+$ isomerization goes to completion in solution.[9] The unhindered complex $[\mathrm{Pd(dien)SCN}]^+$ is a stable S-bonded species.[2]

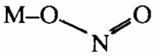
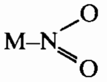
(c) With the bulky tetraphenylborate ion as the counter ion, crystal packing considerations result in an almost complete $[\mathrm{Pd(Et_4dien)NCS}][\mathrm{B\Phi_4}] \rightarrow [\mathrm{Pd(Et_4dien)SCN}][\mathrm{B\Phi_4}]$ reisomerization in the solid state.[11] The N-bonded isomer remains the more stable isomer in the solid state with the smaller $\mathrm{SCN^-}$ or $\mathrm{PF_6^-}$ ions as the counter ion.[9] This appears to result from the more spherical nature of the $[\mathrm{Pd(Et_4dien)SCN}]^+$ cation due to the bent Pd–SCN linkage, which renders it more compatible with the large spherical $[\mathrm{B\Phi_4}]^-$ ion. The $[\mathrm{Pd(Et_4dien)NCSe}][\mathrm{B\Phi_4}]$ complex has also been found[11] to undergo an Se → N-bonded reisomerization in the solid state.

The thiocyanate–MeEt$_4$dien complexes of palladium(II) prepared in this study were found to behave in a completely analogous manner:

$$[\mathrm{Pd(MeEt_4dien)SCN}][\mathrm{B\Phi_4}] \underset{\text{solid state}}{\overset{\text{solution}}{\rightleftharpoons}} [\mathrm{Pd(MeEt_4dien)NCS}][\mathrm{B\Phi_4}] \quad (1)$$

However, the corresponding $[\mathrm{Pt(Et_4dien)SCN}][\mathrm{B\Phi_4}]$ and $[\mathrm{Pt(MeEt_4dien)SCN}][\mathrm{B\Phi_4}]$ complexes exhibited surprising stability in solution. Even after extended reflux in strongly ionizing solvents, e.g., DMF, DMSO, no isomerization to the N-bonded isomer occurred in either case. This implies that, in going from palladium(II) to platinum(II), factor (a) has increased in importance, due to the softer character of the latter. Factor (b) would not be expected to change markedly, due to the comparable size of the metal ions. Factor (c) would only tend to reinforce the tendency toward S-bonding in the solid state.

The $[Pd(tripy)NCS][B\Phi_4]$ complex exhibited completely opposite behavior. Although a trace of the S-bonded isomer was formed during its preparation, the complex failed to undergo any noticeable Pd–NCS → Pd–SCN isomerization when heated at 40° in the solid state (only gradual decomposition took place). Thus, the driving force toward N-bonding provided by the 2,2′,2″-tripyridine ligand, which must be primarily electronic in nature, is the dominant factor in this complex, as well as in its [Pt(tripy)NCS]NCS analog.[22] In this connection, the complex is similar to $[Pd(2,2'\text{-bipyridine})(NCS)_2]$[22] and $[Pd(5\text{-nitro-}1,10\text{-phenanthroline})(NCS)_2]$.[23] Why these three ligands promote N-bonded thiocyanates, 4,4′-dimethyl-2,2′-bipyridine yields a mixed bonding mode complex ([Pd (4,4′-dimethylbipy)(SCN)(NCS)]),[24] and 1,10-phenanthroline and pyridine do not affect the normal Pd–SCN bonding mode ($[Pd(1,10\text{-phen})(SCN)_2]$[22] and *trans*-$[Pd(py)_2(SCN)_2]$[23]) is not understood. It should be noted, however, that the tendency toward N-bonding increases as the basicity of these neutral ligands decreases.[25] The bonding mode assignments made for the tripy, Et_4dien, and $MeEt_4$dien complexes are based[26] on the infrared data shown in Table I.

As far as the nitrite complexes are concerned, Pd–NO_2 bonding is strongly favored in an unhindered complex, such as $[Pd(NO_2)_4]^{2-}$ [25], whereas, with nickel(II) the unhindered Ni–NO_2 and Ni–ONO bonds are much more comparable in strength, e.g., an $[Ni(NO_2)_4(ONO)_2]^{4-}$ complex has been prepared by Goodgame and Hitchman.[27] The steric hindrance created by the Et_4dien ligand would most likely favor  $M{-}O{-}N{=}O$ bonding, as opposed to the  $M{-}NO_2$ isomer, whereas the reverse should be true as far as the influence of the $[B\Phi_4]^-$ ion is concerned.

As indicated by the increased $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ frequencies exhibited by the $[Pd(Et_4dien)NO_2][B\Phi_4]$ complex (relative to the free ion values of 1328 and 1261 cm^{-1}, respectively) and the presence of an NO_2 wagging band in its infrared spectrum, the complex was isolated as a stable, N-bonded species. The $[Ni(Et_4dien)NO_2][B\Phi_4]\cdot CH_3OH$ complex also contains a stable, N-bonded nitrite group, as evidenced by its high energy ligand field band (see Table II). Although the former result might have been anticipated, the latter is quite remarkable in view of the series of octahedral nickel(II) complexes of the type $[Ni(D)_2(ONO)_2]$, containing sterically promoted O-bonded nitrite groups, which have been reported.[28–31] (D represents either an alkyl substituted ethylenediamine,[28–30] or bidentate alkyl substituted 2-aminomethylpyridine or -piperidine derivatives[31]). The N-bonding observed in the present case may be due to the greater ligand field stabilization created by the square planar array of ligands, which would be further enhanced by the greater ligand field strength of the N-bonded (versus O-bonded) nitrite group.

Although an additional example of anion-induced linkage isomerization was not produced in this study, additional evidence for the stabilizing influence of the counterion was uncovered. Thus, under the conditions of preparation for $[Pd(Et_4dien)SeCN][B\Phi_4]$[11], with ammonium hexafluophosphate substituted for sodium tetraphenylborate, a hexafluophosphate salt will not precipitate. When a complex was forced out of solution by the addition of diethylether, the solid gradually turned into a tar, indicating that the hexafluophosphate ion was unable to stabilize the cation. The stabilization of bulky ions by large counterions having a charge equal in magnitude but opposite in sign has been discussed in detail by Basolo.[32] The hexafluophosphate ion can be used to precipitate the $[Pd(Et_4dien)NCS]^+$ ion, but no N → S-bonded reisomerization was found to occur, even after ten days of heating at 78°.

Finally, Chatt, *et al.*[33] have described a solid state interaction between counteranions and complexes of the type $[Ru(NH_3)_5X{\equiv}Y]^{2+}$, where $X{\equiv}Y$ represents N_2, CO, or an organic nitrile. The $X{\equiv}Y$ stretching frequency was found to be higher for anions of larger radius. The effect was attributed to polarization of the ammine hydrogens; the smaller the polarizing anion, the greater the electron density released to the π antibonding orbitals of the $X{\equiv}Y$ moiety.

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