

## Symbiosis versus Antisymbiosis: A Study of the Thiocyanate Bonding Mode in *trans*-Hydridothiocyanatotetrakis(piperidine)iridium(III) Thiocyanate and Tetraphenylborate\*

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Examples of symbiotic and antisymbiotic behavior involving ambidentate ligands such as the  $\text{NCS}^-$  ion have thus far been restricted to, respectively, octahedral complexes of class 'a' metals and square planar complexes of class 'b' metals. In the latter case, only the strong *trans*-influence of  $\pi$ -acid ligands has heretofore been observed to cause antisymbiosis. The title complex was chosen for study because it involves an octahedral complex of an ambidentate ligand and a class 'b' metal (re:  $[\text{Ir}(\text{SCN})_6]^{3-}$ ) wherein the former is subjected to the strong *trans*-influence of a ligand which can only function as a  $\sigma$ -base. In the solid state, antisymbiosis is demonstrated by the stability of the *N*-bound *trans*- $[\text{Ir}(\text{pip})_4\text{H}(\text{NCS})]\text{NCS}$ , and counteranion control by the synthesis and stability of the *S*-bound isomer as the  $\text{BPh}_4^-$  salt. When *trans*- $[\text{Ir}(\text{pip})_4(\text{NCS})(\text{H})]\text{NCS}$  or its  $\text{BPh}_4^-$  salt is put into solution, IR studies indicate that *N*-bonding initially prevails in solution, irrespective of solvent dielectric. The prolonged aging of methylene chloride solutions of either *trans*- $[\text{Ir}(\text{pip})_4(\text{NCS})(\text{H})]\text{NCS}$  or of *trans*- $[\text{Ir}(\text{pip})_4(\text{SCN})(\text{H})]\text{BPh}_4$  produces the soluble cation *trans*- $[\text{Ir}(\text{pip})_4(\text{SCN})_2]^+$ . The  $\nu\text{CN}$  frequency of the noncoordinated  $\text{NCS}^-$  is remarkably sensitive to the solvent dielectric, suggesting the existence of *H*-bonding to the amine proton of the piperidine ligands in the low dielectric solvents. NMR data support the existence of a mixture of six- and seven-coordinate species in all solvents for the  $\text{NCS}^-$  salt, as a consequence of the observation for each solution of a doublet hydride resonance. Solutions of the  $\text{BPh}_4^-$  salt, on the other hand, exhibit only a single hydride resonance, indicating the presence of only a six-coordinate moiety.

### Introduction

The advent of the Hard–Soft Acid–Base Principle<sup>1</sup> has stimulated much research and discussion in the

area of acid–base chemistry. One of the primary outgrowths of this activity has been the development of the principles of symbiosis and anti-symbiosis. Symbiosis, when used in the chemical sense, was defined by Jørgensen<sup>2</sup> as the phenomenon of like ligands flocking together, "like" referring to their relative hardness or softness. An example of this principle can be seen in the systems  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  vs.  $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ . When X is a halide ion, the order of complex stability for the pentaammine complex is  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ . However, the stability order for the pentacyano complex is  $\text{I}^- > \text{Br}^- > \text{Cl}^- \gg \text{F}^-$ . In the case of the pentaammine complex, the five hard nitrogens of the amines make the sixth site hard. Conversely, the five soft cyanides in the pentacyano complex make the sixth site soft. Other examples of symbiotic behavior include the system *trans*- $[\text{Co}(\text{dmg})_2\text{L}(\text{CNS})]$ , studied by Marzilli and co-workers<sup>3</sup>, where dmg is the monoanion of dimethylglyoxime, and L represents a series of substituted pyridines, phosphines, and phosphites. The symbol CNS is meant to imply the presence of the thiocyanate ion without specifying its bonding mode. As the  $\pi$ -acid character of the L ligand decreases, the S/N isomer ratio also decreases, i.e., the harder the L ligand becomes, the harder the sixth site (where the thiocyanate is located) becomes.

The principle of antisymbiosis and its relation to the *trans* effect was enunciated by Pearson<sup>4</sup>, i.e., "two soft ligands in mutual *trans* positions will have a destabilizing effect on each other when attached to a class 'b' metal atom". For example, *trans*- $[\text{M}(\text{PPh}_3)_2(\text{CO})\text{X}]$ , where X =  $\text{Cl}^-$  or  $\text{I}^-$  and M = Rh(I) or Ir(I), would be expected to be more stable when X =  $\text{I}^-$ , if the complex were behaving symbiotically. In reality, it is

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more stable when  $X = \text{Cl}^-$  because a good trans director (CO) is located *trans* to X.

Ambidentate ligands have been used to good advantage as test ligands for symbiotic or antisymbiotic behavior. The thiocyanate ion has been particularly useful in this regard<sup>5</sup>. Virtually all of the examples of antisymbiotic behavior for ambidentate ligands have involved square planar complexes with the *trans* ligand being a good  $\pi$ -acid. According to Pearson, the *trans* director need not be a good  $\pi$ -acid or, for that matter, a  $\pi$ -acid at all, to effect antisymbiotic behavior. It would, therefore, be advantageous to have an example of antisymbiosis involving a *trans* ligand with no  $\pi$ -acid character and one that was for a complex of different geometry, as well.

One complex which fits both of these requirements is *trans*-[Ir(pip)<sub>4</sub>(CNS)(H)][NCS] (pip = piperidine), which was first synthesized by Birnbaum<sup>6</sup>. The complex has octahedral geometry with a non- $\pi$ -acid, strongly *trans*-directing, ligand (hydride) *trans* to the thiocyanate. Since the corresponding thiocyanatopentammineiridium(III) complex was found<sup>7</sup> to be stable in the S-bound form, as in [Ir(SCN)<sub>6</sub>]<sup>3-</sup><sup>5</sup>, the fact that Birnbaum found<sup>6</sup> the title complex to be N-bound in the solid state suggests that it represents the example we sought. A study of the thiocyanate bonding mode as a function of solvent, temperature, and counter anion was compelling, since all of these factors can influence the bonding mode of ambidentate ligands<sup>5</sup>.

## Experimental

### Preparation of Complexes

The *trans*-hydridoisothiocyanatotetrakis(piperidine)iridium(III) thiocyanate complex was synthesized by the method of Birnbaum<sup>6</sup>.

### *Trans*-hydridothiocyanatotetrakis(piperidine)iridium(III) tetraphenylborate

To a solution of 0.352 g (0.54 mmol) of *trans*-[Ir(pip)<sub>4</sub>(NCS)(H)][NCS] in 20 ml of methylene chloride, was added 0.185 g (0.54 mmol) of Na(BPh<sub>4</sub>) in 20 ml of ethanol. The mixture was stirred for 15 min and evaporated to dryness under reduced pressure so as not to apply heat to the system. The residue was slurried in water, stirred for 0.5 hr, isolated by filtration, washed with distilled water, and dried *in vacuo*. Yield, 81%; melting pt., 189°C (dec). *Anal.* Calcd: C, 59.32; H, 7.19; N, 7.67. Found: C, 59.37; H, 6.95; N, 7.79. The complex was diamagnetic, and had the same pale yellow color as the starting complex. X-ray powder diffraction data, 10 most intense lines:  $d(A)$  ( $I/I_0$ ) 11.70 (.30); 10.16 (1.00); 8.22 (1.00); 6.48 (1.00); 5.40 (.50); 4.88 (.50); 4.50 (.40); 4.18 (.60); 3.93 (.60); 3.70 (.20).

### Physical Measurements

The magnetic susceptibility and X-ray diffraction instruments have been described elsewhere<sup>8</sup>. All infrared spectra were recorded on a Perkin-Elmer Model 180 grating spectrophotometer, using matched calcium fluoride cells for solution spectra and KBr disks with Nujol for the solid state mulls. A cold-pressed polyethylene disk was prepared by taking 4.2 mg of *trans*-[Ir(pip)<sub>4</sub>(SCN)(H)][BPh<sub>4</sub>] and 28.2 mg of powdered polyethylene, mixing well, and then pressing into a 1/2 inch disk at 500 pounds (25°C, 500 psi) for 20 seconds. The infrared spectrum of this disk was recorded on a Perkin-Elmer Model 457 Spectrophotometer. Integrated absorption intensities for the  $\nu\text{CN}$  bands in the infrared solution spectra were determined by Ramsey's method of direct integration<sup>9</sup>. Solid state  $\nu\text{CN}$  integrated absorption intensity ratios were determined by the method of Hassel and Burmeister<sup>10</sup>. Proton NMR measurements were made using a Bruker HFX-90 spectrometer in the time-average mode. All chemical shifts were assigned relative to TMS.

## Results

### *Trans*-[Ir(pip)<sub>4</sub>(NCS)(H)][NCS]

Table I summarizes the infrared and proton nmr data collected for the isothiocyanato thiocyanate complex. The solid state infrared spectrum (Nujol mull) exhibits a  $\nu\text{Ir-H}$  peak at 2215  $\text{cm}^{-1}$  and two peaks in the  $\nu\text{CN}$  stretching region corresponding to the N-bound thiocyanate (2087  $\text{cm}^{-1}$ ) and the ionic thiocyanate (2045  $\text{cm}^{-1}$ ). A KBr disk yielded the same spectrum and a solid state bound  $\nu\text{CN}$  integrated intensity ratio of 1.47, which supports Birnbaum's initial conclusion<sup>6</sup> that the coordinated thiocyanate is N-bound<sup>10</sup>. Upon heating a sample for 72 hr at 157°C, no change in the infrared spectrum was observed.

The infrared spectra of solutions of the complex in solvents of low dielectric constant exhibit two peaks in the  $\nu\text{CN}$  stretching region at 2087  $\text{cm}^{-1}$  and 2045  $\text{cm}^{-1}$ . As the dielectric constant of the solvent in which the complex is dissolved is increased, the latter peak diminishes in intensity, and a new peak appears at 2057  $\text{cm}^{-1}$ . When DMSO, which has the highest dielectric constant of the solvents employed, is used, the 2045  $\text{cm}^{-1}$  peak disappears entirely. The proton NMR spectrum of this complex in DMSO exhibits a doublet hydride resonance in accord with that reported by Birnbaum<sup>6</sup>. However, the very weak hydride resonance in Birnbaum's spectrum at -27.01 ppm ( $\delta$ ) is not observed. The proton NMR spectrum of the complex in every one of the other solvents investigated likewise has a doublet hydride resonance at *ca.* -25 ppm ( $\delta$ ), the actual position of the resonances being solvent-dependent; but in no case is there a resonance

TABLE I. Infrared and Proton NMR Data for *trans*-[Ir(pip)<sub>4</sub>(NCS)(H)][NCS].

Solvent	$\nu$ CN Stretch (cm <sup>-1</sup> )	$\nu$ CN Integrated Absorption Intensity, A ( $\times 10^{-4} M^{-1} \text{cm}^{-2}$ )	$-\delta$ (ppm) <sup>g</sup>
Nujol mull	2215 <sup>a</sup> , 2090 <sup>b</sup> , 2045 <sup>c</sup>	—	—
KBr disk	2215 <sup>a</sup> , 2087 <sup>b</sup> , 2045 <sup>c</sup>	1.47 <sup>f</sup>	—
1,1,2-Trichloroethane	2087 <sup>b</sup> , 2046 <sup>d</sup>	13.0 <sup>b</sup> , 11.4 <sup>d</sup>	25.19m, 25.40s
1,2-Dichloroethane	2087 <sup>b</sup> , 2043 <sup>d</sup>	13.1 <sup>b</sup> , 11.7 <sup>d</sup>	25.21m, 25.42s
Methylene chloride	2087 <sup>b</sup> , 2046 <sup>d</sup>	13.0 <sup>b</sup> , 12.5 <sup>d</sup>	25.17m, 25.37s
Acetone	2085 <sup>b</sup> , 2057 <sup>e</sup> , 2043 <sup>d</sup>	7.31 <sup>b</sup>	—
Acetonitrile	2086 <sup>b</sup> , 2058 <sup>e</sup> , 2050 <sup>d</sup> sh	7.48 <sup>b</sup>	25.47m, 25.59s
Nitromethane	2088 <sup>b</sup> , 2058 <sup>e</sup> , 2050 <sup>d</sup>	6.48 <sup>b</sup>	25.34w, 25.44m
Dimethylsulfoxide	2087 <sup>b</sup> , 2057 <sup>e</sup>	6.36 <sup>b</sup> , 4.01 <sup>e</sup>	25.73w, 25.82m

<sup>a</sup> Ir–H stretch. <sup>b</sup> N-bound  $\nu$ CN stretch. <sup>c</sup> Ionic  $\nu$ CN stretch (solid state). <sup>d</sup> Ionic  $\nu$ CN stretch (H-bound, see text).

<sup>e</sup> Ionic  $\nu$ CN stretch (free, see text). <sup>f</sup> Unitless ratio for  $\nu$ CN band of N-bound thiocyanate. <sup>g</sup> All  $\delta$  values are upfield, relative to TMS. Abbreviations: w = weak, m = medium, s = strong, sh = shoulder.

in the vicinity of  $-27$  ppm ( $\delta$ ). In view of the greater sensitivity of the NMR instrument employed in the present study, it seems reasonable to conclude that the original assignment of a hydride resonance at  $-27.01$  ppm ( $\delta$ ) is erroneous. One batch of the *trans*-[Ir(pip)<sub>4</sub>(NCS)(H)]NCS used in the current investigation produced a very small resonance in each spectrum just above the strong resonance (that is, at higher fields). Since this phenomenon did not appear in the proton NMR spectrum of a second batch of the complex, it is ascribed to a trace of an unknown impurity.

#### *Trans*-[Ir(pip)<sub>4</sub>(SCN)(H)][BPh<sub>4</sub>]

The thiocyanato tetraphenylborate complex, synthesized by a metathesis reaction between *trans*-[Ir(pip)<sub>4</sub>(NCS)(H)][NCS] and Na(BPh<sub>4</sub>), yields completely different results in its IR and NMR spectra than those of its precursor. Infrared and proton NMR data are summarized in Table II. The solid state infrared spectrum of the complex contains a hydride peak at 2215 cm<sup>-1</sup> and a  $\nu$ CN stretching band at 2104 cm<sup>-1</sup>. When the complex is pressed into a KBr disk, the  $\nu$ CN stretching frequency drops to 2087 cm<sup>-1</sup>. When the complex is heated for 3 days at 157 °C in the pure solid state, no change in its spectrum (Nujol mull) is observed. If the complex is pressed into a cold-pressed polyethylene disk, the  $\nu$ CN band remains at 2104 cm<sup>-1</sup>.

The initial solution infrared spectra of the complex exhibit two peaks in the  $\nu$ CN stretching region at 2104 cm<sup>-1</sup> (sh) and 2087 cm<sup>-1</sup> for solvents of low dielectric constant and only the 2087 cm<sup>-1</sup> peak for higher dielectric constant solvents. The proton NMR spectra exhibit only one hydride resonance, around  $-26$  ppm ( $\delta$ ), in all solvents examined. When an equimolar amount of thiocyanate anion was added to a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex, two resonances in

TABLE II. Infrared and NMR Data for *trans*-[Ir(pip)<sub>4</sub>(SCN)(H)][BPh<sub>4</sub>].

Solvent	$\nu$ CN Stretch (cm <sup>-1</sup> )	$-\delta$ (ppm)
Nujol mull	2215 <sup>a</sup> , 2104 <sup>b</sup>	—
KBr disk	2215 <sup>a</sup> , 2087 <sup>c</sup>	—
Cold-pressed polyethylene disk	2215 <sup>a</sup> , 2104 <sup>b</sup>	—
1,2-Dichloroethane	2104 <sup>b</sup> sh, 2077 <sup>s</sup> c	25.90
Methylene chloride	2104 <sup>b</sup> sh, 2087 <sup>s</sup> c	25.69 <sup>e</sup>
Acetone	2081 <sup>s</sup> , 2043 <sup>d</sup> w	—
Acetonitrile	2086 <sup>e</sup>	—
Nitromethane	2088 <sup>e</sup>	—
Dimethylsulfoxide	2087 <sup>e</sup>	26.07

<sup>a</sup> Ir–H stretch. <sup>b</sup> S-bound  $\nu$ CN stretch. <sup>c</sup> N-bound  $\nu$ CN stretch.

<sup>d</sup> Ionic  $\nu$ CN stretch (trace). <sup>e</sup> When an equimolar amount of thiocyanate anion was added to a CH<sub>2</sub>Cl<sub>2</sub> solution of this complex, two resonances in the hydride region appeared at  $-25.47$ s and  $-25.33$ w ppm.

TABLE III. Time Dependence of  $\nu$ CN (cm<sup>-1</sup>) for *trans*-[Ir(pip)<sub>4</sub>(CNS)H]X (X = NCS<sup>-</sup> and BPh<sub>4</sub><sup>-</sup>) Complexes.<sup>a</sup>

Time	X = NCS <sup>-</sup>	X = BPh <sub>4</sub> <sup>-</sup>
Initial	2087, 2046	2104, 2079
24 hr	2125, 2086, 2046	2125, 2083
65 d	2122, 2088, 2046	2125, 2089

<sup>a</sup> Solvent: methylene chloride.

the hydride region appeared at  $-25.47$ s and  $-25.33$ w ppm, as in the isothiocyanato thiocyanate spectrum.

#### Time Dependence of $\nu$ CN

The two complexes were dissolved in methylene chloride and their IR spectra monitored as a function

of time. The results are shown in Table III. After 246 hr, a new peak appears at *ca.* 2125  $\text{cm}^{-1}$  in both spectra, and continues to grow with time. In the case of the isothiocyanato thiocyanate, the intensities of both the Ir–H and ionic  $\nu\text{CN}$  bands diminish concurrently, as do the intensities of the Ir–H and N-bound  $\nu\text{CN}$  bands in the spectrum of the tetraphenylborate.

## Discussion

### Infrared Spectra

The solid state infrared spectra of both complexes provide an interesting study of the effects of internal and external controls on the bonding mode of the thiocyanate. The isothiocyanato thiocyanate complex exhibits the same infrared spectrum, irrespective of whether it is measured as a Nujol mull or a KBr disk, the  $\nu\text{CN}$  frequencies and intensities being characteristic<sup>11</sup> of one N-bound and one ionic thiocyanate. The spectrum of the thiocyanato tetraphenylborate complex, however, was found to be medium-dependent. The elimination of the thiocyanate counter anion results in a simpler infrared spectrum in the  $\nu\text{CN}$  region; however, the 2104  $\text{cm}^{-1}$   $\nu\text{CN}$  stretching frequency observed in its Nujol mull spectrum is suggestive<sup>11</sup> of S-bonding for the coordinated thiocyanate. A simple solid state  $\nu\text{CN}$  integrated absorption intensity study would have afforded confirmation of this. Unfortunately, upon pressing the complex into a KBr disk, the  $\nu\text{CN}$  frequency observed shifts to the N-bound 2087  $\text{cm}^{-1}$  value. Since heating the complex did not produce isomerization, the possibility of having observed either a pressure induced and/or a KBr assisted linkage isomerization became more and more attractive. A cold-pressed polyethylene disk was made, and the resulting observation of the 2104  $\text{cm}^{-1}$  peak provided convincing evidence that the presence of the KBr had caused the isomerization to occur. When the thiocyanato tetraphenylborate complex was dissolved in methylene chloride and the solvent evaporated off, the resulting solid complex was found to be N-bound. Upon heating, this complex reisolomerized to the S-bound form, proving that it is the more stable form in the solid state (in the absence of KBr). Thus, it represents a rare example of anion induced linkage isomerization<sup>5</sup>, the first example being the  $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}][\text{BPh}_4]$  complex, also discovered in one of our laboratories<sup>12</sup>. The rationale for the anion-induced linkage isomerism is probably the same as that described earlier<sup>12</sup> for the  $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}][\text{BPh}_4]$  system.

The proclivity of these complexes toward tautomerism has permeated this entire study. The solution infrared spectral behavior of the isothiocyanato thiocyanate complex is a good example of this. The coordinated thiocyanate is also N-bound in solution as reflected<sup>11</sup> by both the position and integrated absorption intensity

of the 2087  $\text{cm}^{-1}$  band in all solvents. It is, therefore, a valid example of antisymbiosis involving a non- $\pi$ -acid *trans* director in an octahedral complex. The ionic thiocyanate exhibits a unique behavior which is dependent on the dielectric or insulating ability of the solvent. In low dielectric solvents, the lower than normal frequency of the ionic  $\nu\text{CN}$  band is attributed to hydrogen bonding interactions with the proton on the nitrogen of the piperidine ring. As the dielectric constant of the solvent increases or as the insulating power of the solvent increases the hydrogen bonding interaction is inhibited and the "free" ionic band for the thiocyanate begins to appear, as in acetone and acetonitrile. When the dielectric constant becomes sufficiently large to overcome all H-bonding interactions, only the free ionic value is observed, as in DMSO. The presence of hydrogen bonding interactions in low dielectric solvents is further supported by the nature of the N–H stretching band at around 3200  $\text{cm}^{-1}$ . There is a very large enhancement of the intensity of the N–H stretching band in the solid state Nujol mull spectrum of the isothiocyanato thiocyanate complex relative to that of the thiocyanato tetraphenylborate complex. Similarly, the intensity of the N–H stretching band for complexes of the type *trans*- $[\text{Ir}(\text{pip})_4(\text{H})(\text{X})]\text{X}\cdot\text{H}_2\text{O}$ , where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , has also been found to be enhanced relative to that for complexes of the type *trans*- $[\text{Ir}(\text{pip})_4(\text{H})(\text{X})]\text{ClO}_4$ , where again  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ <sup>13</sup>. The integrated absorption intensity of the ionic  $\nu\text{CN}$  band is considerably enhanced, relative to the free ion value, when hydrogen bond, as previously observed by Pecile<sup>14</sup>. However, Pecile also observed an increase in the  $\nu\text{CN}$  frequency upon H-bonding as opposed to the frequency decrease observed in this study. The observation that the "free" ionic integrated absorption intensity value for the DMSO solution is rather high, relative to that of the N-bound group, can be rationalized by realizing that there is probably some dissociation of the coordinated thiocyanate in DMSO, which tends to promote ionization. This would contribute to a greater concentration of ionic thiocyanate than is calculated, and thus a greater integrated intensity value.

The solution infrared spectral behavior of the thiocyanato tetraphenylborate complex is less complicated than that of its isothiocyanato thiocyanate counterpart. The only unique feature is the initial presence of a weak band at 2104  $\text{cm}^{-1}$ , due to small amounts of the S-bound isomer in the low dielectric solvents. This is attributed to a kinetic effect of the solvents. The complex, being S-bound in the solid state, will isomerize more readily in those solvents which have greater ionicity. Complete isomerization occurs during the time of mixing in all solvents but 1,2-dichloroethane and methylene chloride. In these, the S-bound isomer eventually disappears entirely at longer times. In ad-

dition, upon long standing of either complex in  $\text{CH}_2\text{Cl}_2$ , the hydride peak as well as the ionic and N-bound  $\nu\text{CN}$  peaks slowly diminish, while simultaneously a new peak forms at  $2125\text{ cm}^{-1}$ . These observations most probably reflect a slow transfer of hydride to the solvent<sup>15</sup>; and, since the  $2125\text{ cm}^{-1}$  peak is very similar to the  $\nu\text{CN}$  frequency of the *trans*- $[\text{Pt}(\text{NH}_3)_4(\text{SCN})_2]^+$  cation ( $2122\text{ cm}^{-1}$ ), the formation in both cases of the *trans*-dithiocyanatotetrakis(piperidine)iridium(III) cation.

#### Proton NMR Spectra

The hydride resonances exhibited by the isothiocyanato thiocyanate complex represent the most enigmatic portion of this study. As reported earlier by Birnbaum<sup>6</sup>, both the corresponding isocyanato cyanate and the isoselenocyanato selenocyanate complexes exhibit (aside from a common, and now believed to be erroneous, very weak resonance at  $-27.01\text{ ppm}$  ( $\delta$ )) a single hydride resonance. Only the isothiocyanato thiocyanate complex exhibits multiple chemical shift values in the hydride resonance region. It was inferred<sup>6</sup> from this difference that the *trans*- $[\text{Ir}(\text{pip})_4(\text{NCS})(\text{H})]\text{NCS}$  existed in solution as a mixture of N-bonded and S-bonded linkage isomers. However, such an interpretation is not consistent with the infrared spectral results obtained during the present investigation. The hydride NMR spectrum of the isothiocyanato thiocyanate complex could, perhaps, be explained by considering the six-coordinate Ir(III) as being coordinatively unsaturated, *i.e.*, that seven-coordination is possible. Examples have previously been cited for seven-coordinate complexes of Ir(III)<sup>16-18</sup>. One of the hydride resonances would be attributed to the six-coordinate species while the other would be associated with the seven-coordinate species. The seven-coordinate species has the possibility of existing in two isomeric forms, one where the incoming thiocyanate is on the same side of the original octahedron as the hydride and the other where it is on the opposite side. Although these two possibilities might be expected to give slightly different resonances for the hydride, the difference does not seem to be within the resolving capability and/or sensitivity of the NMR instrument. When the anion is changed to tetraphenylborate, only one hydride resonance is observed at approximately  $-26\text{ ppm}$  ( $\delta$ ) in all solvents examined (see Table II). Although the solution infrared spectrum of the tetraphenylborate complex in methylene chloride initially indicates the presence of some S-bonding, the NMR spectrum exhibits only one hydride resonance, indicating that the NMR method cannot distinguish between linkage isomers of these complexes using the chemical shift of the hydride resonance as an indicator\*. Also, upon

addition of equimolar amounts of thiocyanate ion to a solution of the tetraphenylborate complex, one observed the growth of new peaks in the hydride resonance region (see Table II) whose position and intensity correspond to the position and intensity of the doublet in the spectrum of the isothiocyanato thiocyanate complex, allowing for small differences in chemical shifts caused by concentration differences and by the presence of the  $\text{BPh}_4^-$  ion. Clearly, the ionic thiocyanate is causing the doublet hydride resonance in the NMR spectrum and the seven-coordination rationale seems to best explain the observed data.

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\* The precision of the instrument is  $0.010\text{ ppm}$ .