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A Kinetic Study of the Isomerism of *trans*-$HPt[P(C_2H_5)_3]_2N{\equiv}C{\cdot}BR_3$ to *trans*-$HPt[P(C_2H_5)_3]_2C{\equiv}N{\cdot}BR_3$

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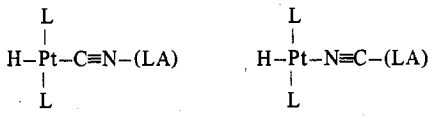
A series of organoboron adducts of the type *trans*-$HPtL_2NC{\cdot}BR_3$ (L = $P(C_2H_5)_3$) have been prepared. Rapid isomerization to the more thermodynamically stable isomer *trans*-$HPtL_2CN{\cdot}BR_3$ occurs. The reaction rates and activation energies for the isomerization process have been measured. The activation energy appears to be related to the strength of the Lewis acid and the isomerization reaction is catalyzed by triarylboron compounds. The Lewis acid in both the Pt–NC and Pt–CN isomers may be exchanged with other triarylborons. A possible mechanism for the catalyzed and uncatalyzed isomerizations is proposed.

Introduction

Metal cyanide complexes are known to coordinate to a variety of Lewis acids by donation of the pair of electrons on the nitrogen to the Lewis acid.[1] The cyanide is potentially capable of acting as an ambidentate ligand although the M—C≡N isomer is thermodynamically more stable than the M—N≡C isomer.[2] We have recently reported[3] the preparation of complexes of type **1** (where L = $P(C_2H_5)_3$ and LA



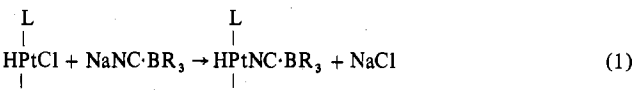
1 **2**

= Lewis acid). We were interested in the possibility of stabilizing the isocyano isomer **2** by coordination to a Lewis acid. In this paper we discuss the preparation of a series of compounds of type **2** where the Lewis acid is a trialkyl- or triarylboron compound. During the course of our investigation we discovered[4] that the isocyano isomers **2** are readily converted into the more stable cyano isomers **1**. We also report the reaction rates and activation energies for that isomerization process as determined by NMR spectroscopy.

Results and Discussion

(A) Preparation of *trans*-$HPtL_2N{\equiv}C{\cdot}BR_3$. The reaction between *trans*-$HPtL_2Cl$ and $Na^+NC{\cdot}B(C_6H_5)_3^-$ in methanol gives an immediate white precipitate of $HPtL_2NC{\cdot}B(C_6H_5)_3$ and NaCl. The platinum complex can be extracted from the sodium chloride with dichloromethane. Concentration of the dichloromethane by rotary evaporation followed by the addition of methanol gave $HPtL_2NC{\cdot}B(C_6H_5)_3$ as a white air-stable crystalline solid. The phosphine–ethyl resonances are typical of mutually trans phosphines and the hydride resonance appears at 18.15 ppm upfield from tetramethylsilane as a 1:2:1 triplet due to coupling with two equivalent ^{31}P nuclei. The resonance is flanked by ^{195}Pt satellites ($I = {}^1/_2$, 33.8% natural abundance) and the value of ^1J(Pt–H) is 1061 Hz. This coupling constant is very similar to that found in $HPtL_2(NCS)$[5] (1086 Hz) and indicates that the cyanide is N bonded to platinum.[6] The compound was dissolved in benzene, refluxed for 5 h, and cooled. The NMR spectrum showed only the presence of *trans*-$HPtL_2CN{\cdot}B(C_6H_5)_3$ which we had previously prepared[3] directly from $HPtL_2CN$ and triphenylboron. In view of the facile conversion of isomer **2** to **1** we decided to examine this reaction in more detail using a variety of organoboron compounds.

The only commercially available cyanide adduct of an organoboron compound is $NaNC{\cdot}B(C_6H_5)_3$ so other salts were needed. Sodium cyanide reacts very slowly with stoichiometric amounts of organoborons to give the salts, $Na^+NC{\cdot}BR_3^-$. In the case of the triarylborons the reaction mixture was stirred overnight and filtered, and the THF was removed by rotary evaporation to give colorless oils. With $B(CH_2C_6H_5)_3$ and $B(p\text{-}C_6H_4CH_3)_3$ stable crystalline sodium cyanide salts were isolated. The sodium salt with tricyclohexylboron was isolated as a solid but it was contaminated with unreacted $B(C_6H_{11})_3$. The sodium cyanide salts of $B(1\text{-}C_{10}H_7)_3$, $B(o\text{-}C_6H_4CH_3)_3$, and $B(C_2H_5)_3$ could not be induced to crystallize so they were used as oils. Rather surprisingly the sodium salts are quite soluble in dichloromethane and ether. The platinum derivatives were prepared directly as shown in (1) by mixing methanolic solutions of the hydridoplatinum chloride and



(1)

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sodium cyanotriorganoborate. The platinum complexes precipitated from solution and could be recrystallized from dichloromethane and pentane. The NMR spectra were recorded shortly after the compounds were isolated. With $NaNC{\cdot}B(C_2H_5)_3$ isomerization was rapid and the spectrum showed only the presence of the Pt–CN isomer. Similarly with $NaNC{\cdot}B(C_6H_{11})_3$ isomerization was facile. Initially both C- and N-bonded isomers were present; however, isomerization to the C-bonded isomers occurred as the spectrum was being recorded.

Table I. Kinetic Data for the Isomerization of $PtH(PEt_3)_2(NC{\cdot}BR_3)$ to $PtH(PEt_3)_2(CN{\cdot}BR_3)$

BR_3	Rate constant k, s^{-1} 41 °C	56 °C	77 °C	Activation energy, kcal/mol
$B(C_6H_5)_3$	6.7×10^{-5}	1.3×10^{-4}	1.2×10^{-3}	15 ± 2
$B(p\text{-tolyl})_3$	1.8×10^{-4}	4.7×10^{-4}		13 ± 5
$B(CH_2C_6H_5)_3$	2.5×10^{-4} 3.2×10^{-4}	1.7×10^{-3}		24 ± 5
$B(o\text{-tolyl})_3$	6.3×10^{-4}	3.7×10^{-3}		24 ± 2
$B(1\text{-naphthyl})_3$		1.8×10^{-4}	2.5×10^{-3}	31 ± 6

(B) Kinetic Measurements and Discussion. The rate of isomerism of *trans*-$PtHL_2NC{\cdot}BR_3$ to $PtHL_2CN{\cdot}BR_3$ has been measured by 220 MHz proton NMR in benzene and the reaction was found to follow first-order kinetics. The concentration of each isomer, at various times, was obtained from the integrated intensities of the hydride resonances at approximately δ 17 (*H*–Pt–NC) and δ 7 (*H*–Pt–CN). Typically, solutions of the Pt–NC complexes in C_6D_6/TMS were prepared in NMR tubes and heated in a constant temperature (±0.5 °C) oil bath for varying lengths of time. The rate constants in reciprocal seconds and Arrhenius activation energies for a variety of R groups are listed in Table I.

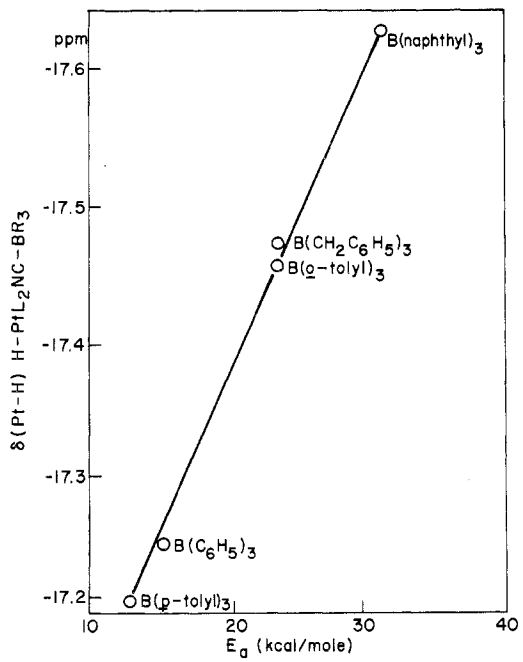
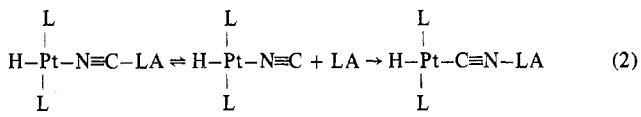


Figure 1. A comparison between the hydride chemical shift and the activation energy of isomerization.

A very good correlation exists between the activation energy and the chemical shift of the hydride in the Pt–NC isomer (Figure 1). The shielding constant (σ) for the hydride is comprised of a diamagnetic (σ_d) and a paramagnetic (σ_p) term such that $\sigma = \sigma_d + \sigma_p$. The main contribution to the high field shifts characteristic of transition metal hydrides has been shown to arise chiefly from σ_p and in particular R (the M–H bond distance).[7,8] As the M–H bond length increases σ_p decreases and the resonance shifts to low field. In the present system as the Lewis acidity decreases, the Pt–N bond strength increases. This would result in a lengthening of the M–H bond and a shift to low field. The good correlation shown in Figure 1 would imply that the activation energy for the isomerization is related to the Lewis acidity of the organoboron compound. Consistent with this is the fact that the complexes with weak Lewis acids, i.e., $B(C_2H_5)_3$, isomerized at room temperature. We believe the mechanism simply involves thermal dissociation of the Lewis acid to give an unstable "isocyano" derivative which then "flips" (possibly through a π-bonded CN) to give the cyanide (eq 2).



(C) Catalyzed Linkage Isomerization. The isomerization of $PtHL_2NC{\cdot}B(C_6H_5)_3$ does not occur to any extent within 24 h at room temperature and the addition of a stoichiometric amount of $NaNC{\cdot}B(C_6H_5)_3$ to the solution had no effect on the rate of isomerization. However, we have found that triarylboranes, but not trialkylboranes, accelerate the isomerization. For $B(C_6H_5)_3$ the catalyzed process appeared to be zero order in triarylborane in the range of $B(C_6H_5)_3/PtHL_2NC{\cdot}B(C_6H_5)_3$ 0.5–2.0. A number of NMR experiments were conducted to identify the species present in solution. The addition of $B(CH_2C_6H_5)_3$ to a solution of $PtHL_2NC{\cdot}B(C_6H_5)_3$ in an NMR tube gave a clear colorless solution whose NMR spectrum, after 8 h, at room temperature showed the presence of four hydride resonances corresponding to the four isomers $PtHL_2NC{\cdot}B(C_6H_5)_3$, $PtHL_2NC{\cdot}B(CH_2C_6H_5)_3$, $PtHL_2CN{\cdot}B(C_6H_5)_3$, and $PtHL_2CN{\cdot}B(CH_2C_6H_5)_3$. Also, after 3.5 h the NMR spectrum of a solution prepared from molar equivalents

Table II. Reactions of Free Lewis Acid (B) with $PtHL_2(NC\text{–}A)$ at Room Temperature

			Hydride resonances,[b] %			
A	B	Time, h[a]	Pt-NCA	Pt-NCB	Pt-CNA	Pt-CNB
$B(C_6H_5)_3$	$B(C_6H_5)_3$	6	75		25	
	$B(CH_2C_6H_5)_3$	8	8	11	16	65
	B(*o*-tolyl)$_3$	7.5	86		14	
	B(*p*-tolyl)$_3$	17	*c*	53	*c*	47
	B(1-naphthyl)$_3$	5.5	19		50	31
	$B(cy)_3$	4	100			
	BEt_3	6	100			
$B(CH_2C_6H_5)_3$	$B(C_6H_5)_3$	10	78	22		

[a] ±15 min. [b] Percentages are accurate to about ±5 %. [c] Resonances for $B(C_6H_5)_3$ and B(*p*-tolyl)$_3$ are in almost exactly the same region of the spectrum. The evidence for the exchange was provided by the coupling constants, but both compounds might be present.

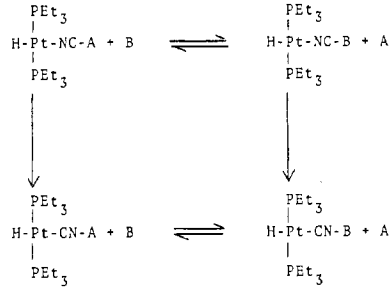
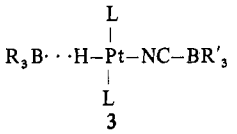


Figure 2. Scheme illustrating the various exchange processes observed with triarylborons.

of $PtHL_2CN{\cdot}B(C_6H_5)_3$ and $B(CH_2C_6H_5)_3$ showed the presence of 72% $PtHL_2CN{\cdot}B(C_6H_5)_3$ and 18% $PtHL_2CN{\cdot}B(CH_2C_6H_5)_3$. Therefore the exchange of free with coordinated borane to give the same linkage isomer is a reversible reaction but where exchange and linkage isomerism occurs the reaction is irreversible. The results of several NMR experiments using other boranes are given in Table II and the exchange reactions are summarized in Figure 2. Due to the complexity of these exchange processes we are not able, at this time, to determine the mechanism of the Lewis acid catalyzed isomerization. A possible mechanism can be envisioned as involving weak coordination of the triarylboron with the platinum hydride as shown in **3**. Electron density would then be pulled toward



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the hydride, weakening the C–BR'_3 bond and catalyzing the dissociation. Once the C–BR'_3 bond is broken, the complex can then isomerize. In the absence of free Lewis acid, heat is necessary to break the bond and cause the isomerization.

Experimental Section

trans-$HPtL_2Cl$ was prepared as previously described.[9] The trialkyl- and triarylboron compounds were purchased from Orgmet. Chemical Co. All reactions involving free boron compounds were performed in a Vacuum Atmospheres drybox under an atmosphere of dry nitrogen.

NMR spectra were recorded on a Varian Associates HR-220 spectrometer. Chemical shifts are reported in parts per million (positive) downfield from TMS. Coupling constants are given in hertz.

All solvents were dried by passing them through molecular sieves (Linde 4A) and were sparged with nitrogen prior to use.

Preparation of *trans*-$HPtL_2NC{\cdot}B(C_6H_5)_3$. To a solution of *trans*-$PtHClL_2$ (0.92 g, 1.97 mmol) dissolved in methanol was added

a solution of sodium cyanotriphenylboron (0.572 g) in methanol. A white crystalline solid precipitated immediately from solution. It was filtered off and washed with methanol. Yield, 1.2 g. The solid was dissolved in methylene chloride, the solution was filtered to remove sodium chloride, and the methylene chloride was reduced in volume. Methanol was then added to precipitate white crystals. After cooling the flask at 0 °C for 1 h the solution was filtered and the crystals were washed with methanol. Yield, 0.86 g after recrystallization; mp 106–107 °C. Anal. Calcd for $PtBNP_2C_{31}H_{46}$: C, 53.15; H, 6.62; N, 2.00. Found: C, 53.84; H, 6.96; N, 2.14. NMR in C_6D_6 at 220 MHz: $\delta(PCH_3)$ 0.78, $\delta(PCH_2)$ 1.32, δ(PtH) −18.15 (J(PtH) = 1061 Hz, J(PH) = 13 Hz).

Preparation of $NaNC{\cdot}B(CH_2C_6H_5)_3$. To a solution of tribenzylboron (1.42 g, 5.0 mmol) in THF was added, as a solid, sodium cyanide (0.245 g, 5.0 mmol). The mixture was stirred overnight at room temperature. The sodium cyanide dissolved and the resultant solution was clear and colorless. The THF was removed by rotary evaporation to give a clear colorless oil. The oil was dissolved in ether, the solution was filtered, and pentane was added causing white crystals to precipitate from solution. The crystals were filtered, washed with pentane, and air dried. Yield, 1.62 g (97%); IR ν(NC) 2200 cm^{-1}.

The other salts were prepared similarly.

Preparation of *trans*-$PtHL_2NC{\cdot}B(CH_2C_6H_5)_3$. To a solution of *trans*-$PtHClL_2$ (0.233 g, 0.5 mmol) in methanol was added a solution of sodium cyanotribenzylboron (0.167 g, 0.5 mmol) in methanol. A white solid immediately precipitated from solution. It was filtered, washed with methanol, and air dried. It was then dissolved in a small amount of methylene chloride and filtered to remove the sodium chloride. The methylene chloride was concentrated, methanol was added, and the white crystals were filtered, washed with methanol, and air dried. Yield, 0.209 g (56%); mp 81–82 °C. NMR in C_6D_6 (220 MHz): δ(PtH) −17.48 (J(PtH) = 1111 Hz, J(PH) = 14.0 Hz). Anal. Calcd for $PtBP_2NC_{34}H_{52}$: C, 54.99; H, 7.01; N, 1.89. Found: C, 55.00, 55.11; H, 6.90, 6.65; N, 2.16, 1.80. IR: ν(PtH) 2230 cm^{-1}; ν(NC) 2270 cm^{-1}.

Preparation of *trans*-$PtHL_2NC{\cdot}B(1\text{-}C_{10}H_7)_3$. To a solution of *trans*-$PtHL_2Cl$ (0.935 g, 2.0 mmol) in methanol was added a methanol solution of sodium cyanotri-β-naphthylboron (0.886 g, 2.0 mmol). A white solid which formed immediately was filtered and washed with methanol and air dried. It was then dissolved in a small amount of methylene chloride, the solution was filtered, and methanol was added to precipitate large white crystals. They were filtered off, washed with methanol, and air dried. Yield, 0.78 g (46%); mp 165–166 °C. Anal. Calcd for $PtP_2BC_{43}H_{52}N$: C, 60.71; H, 6.11; N, 1.65. Found: C, 60.96; H, 6.17; N, 1.89. NMR in C_6D_6 at 220 MHz: δ(PtH) −17.62 (J(PtH) = 1126 Hz, J(PH) = 14.5 Hz). IR: ν(PtH) 2200 cm^{-1}, ν(NC) 2250 cm^{-1}.

Preparation of *trans*-$PtHL_2NC{\cdot}B(p\text{-}C_6H_4CH_3)_3$. To a solution of *trans*-$PtHL_2Cl$ (0.47 g, 1 mmol) in methanol was added a methanol solution of sodium cyanotri-*p*-tolylboron (0.3 g, 1 mmol). The white solid which formed immediately was filtered, washed with methanol, and air dried. It was dissolved in a minimum amount of methylene chloride, the solution was filtered, and pentane was added to give white crystals. The white crystals were filtered off, washed with pentane, and air dried. Yield, 0.2 g; mp 138–140 °C. Anal. Calcd for $PtP_2BC_{34}H_{52}N$: C, 54.99; H, 7.01; N, 1.89. Found: C, 54.79; H, 7.19; N, 1.70. NMR in C_6D_6 at 220 MHz: δ(PtH) −17.21 (J(PH) = 14.0 Hz, J(PtH) = 1122 Hz).

The sample was kept in a dry ice–acetone bath until just before the spectrum was measured since isomerization to the PtCN bonded isomer occurs slowly at room temperature.

Preparation of *trans*-$PtHL_2NC{\cdot}B(o\text{-}C_6H_4CH_3)_3$. To a methanol solution of $PtHClL_2$ (0.33 g, 1.0 mmol) was added a methanol solution of sodium cyanotolylboron (0.467 g, 1.0 mmol). A white solid slowly formed. After stirring for 0.5 h the solution was cooled then filtered and washed with cold methanol. The solid was dissolved in a minimum amount of methylene chloride, the solution was filtered, and the volume was reduced. Methanol was then added to give white crystals which were filtered off and washed with pentane. Yield, 0.34 g (45%); mp 101–102 °C. Anal. Calcd for $PtP_2BC_{34}H_{52}N$: C, 54.99; H, 7.01; N, 1.89. Found: C, 54.83; H, 7.09; N, 1.83. IR: ν(PtH) 2200 cm^{-1}; ν(NC) 2280 cm^{-1}. NMR in C_6D_6 at 220 MHz: δ(PtH) −17.46 (J(PtH) = 1122 Hz, J(PH) = 14.8 Hz).

Some isomerization had occurred at room temperature during the preparation.

Attempted Preparation of *trans*-$PtHL_2NC{\cdot}B(C_2H_5)_3$. A solution of *trans*-$PtHClL_2$ (2.51 g, 10 mmol) in THF was added to a solution of sodium cyanotriethylboron in THF. Sodium chloride precipitated and was removed by filtration. The THF was then removed by rotary evaporation. Some crystals formed as the solution cooled during the removal of the solvent but melted as the flask warmed to room temperature. The solvent was pumped off and the NMR of the liquid was recorded at room temperature. NMR spectrum in C_6D_6 at 220 MHz: δ(PtH) −7.8 (^1J(PtH) = 840 Hz).

There is no detectable J(PH) presumably due to rapid exchange of the phosphorus ligands. The NMR data were consistent with formation of the Pt–CN isomer. Presumably isomerization had occurred at room temperature during the workup.

Preparation of *trans*-$PtHL_2NC{\cdot}B(C_6H_{11})_3$. To a solution of *trans*-$PtHL_2Cl$ (0.46 g, 20 mmol) in methanol was added a methanol solution of sodium cyanotricyclohexylboron. White crystals slowly formed, were filtered off, and were washed with methanol and air-dried. They were dissolved in a small amount of methylene chloride, the solution was filtered, and the methylene chloride was removed by rotary evaporation to give an oil. The oil was dissolved in methylene chloride and the spectrum was recorded at 220 MHz. Two sets of hydride resonances were present: one which corresponded to the PtNC isomer and the other to the PtCN bonded isomer. The predominant isomer was the Pt–CN bonded complex and isomerization was continuing to take place in the NMR cavity. No further characterization was attempted.

Acknowledgment. We are particularly grateful to Dr. W. C. Seidel for many very helpful discussions.

Registry No. *trans*-$HPtL_2NC{\cdot}B(C_6H_5)_3$, 55157-04-5; *trans*-$PtHL_2NC{\cdot}B(CH_2C_6H_5)_3$, 61885-98-1; *trans*-$PtHL_2NC{\cdot}B(1\text{-}C_{10}H_7)_3$, 61885-99-2; *trans*-$PtHL_2NC{\cdot}B(p\text{-}C_6H_4CH_3)_3$, 61886-00-8; *trans*-$PtHL_2NC{\cdot}B(o\text{-}C_6H_4CH_3)_3$, 61885-94-7; *trans*-$PtHL_2NC{\cdot}B(C_6H_{11})_3$, 61885-95-8; *trans*-$PtHL_2CN{\cdot}B(C_6H_5)_3$, 55157-03-4; *trans*-$PtHL_2CN{\cdot}B(p\text{-tolyl})_3$, 56237-29-7; *trans*-$PtHL_2CN{\cdot}B(CH_2C_6H_5)_3$, 56237-28-6; *trans*-$PtHL_2CN{\cdot}B(o\text{-tolyl})_3$, 56237-30-0; *trans*-$PtHL_2CN{\cdot}B(1\text{-naphthyl})_3$, 61885-96-9; *trans*-$PtHClL_2$, 16842-17-4; $NaNC{\cdot}B(CH_2C_6H_5)_3$, 61885-97-0; tribenzylboron, 1694-84-4; sodium cyanide, 143-33-9; BEt_3, 97-94-9.

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