tivation parameters for the aquation of the *cis*-aquachlorobis(ethylenediamine)chromium(III) cation, calculated by using the literature values (2.8×10^{-5} s^{-1} in 0.1 M $HClO_4$ at 25 °C,[1] 5.0×10^{-5} s^{-1} in 0.055 M $HClO_4$ at 30 °C,[3] and 9.23×10^{-5} s^{-1} in 0.1 M HNO_3 at 35 °C[2]), namely, $\Delta H^{\ddagger} = 88.5 \pm 1.1$ kJ mol^{-1} and $\Delta S^{\ddagger} = -35.2 \pm 3.7$ J K^{-1} mol^{-1}, are similar to those found in this work.

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Registry No. *cis*-$[CrCl(H_2O)(en)_2]^{2+}$, 14403-89-5; *cis*-$[CrBr(H_2O)(en)_2]^{2+}$, 60429-48-3.

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NMR Evidence for Thermodynamic Preference of Cis(N,olefin) over Trans(N,olefin) Isomers of Mixed Amino Acid–Olefin Complexes of Platinum(II)

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Though both trans(N,olefin) and cis(N,olefin) isomers of [Pt(amino acid)(olefin)Cl] have been reported, the relative stability of the isomers has not been previously determined. Synthetic routes have been used to obtain the separate isomers on the basis of relative trans effects of ethylene and Cl^-. Reactions of amino acid anions with Zeise's salt yield the trans(N,olefin) isomers exclusively,[1,2] while the cis isomers have been obtained by olefin displacement of chloride from [Pt(H-amino acid)Cl_3^-] in which the amino acid is N-coordinated and protonated.[3]

Our interest in the thermodynamic preference of these isomers originated in our earlier work on corresponding mixed amino acid–Me_2SO complexes, for which the cis(N,S) isomers are strongly preferred for simple amino acids like glycine, alanine, and α-aminoisobutyric acid (aba).[4,5] In view of the similar trans influence of Me_2SO and ethylene, it seemed likely that the cis isomer of the olefin complexes might also be preferred.[6,7]

After initial unsuccessful attempts to equilibrate trans isomers of ethylene complexes in H_2O and in some nonaqueous solvents, we turned our attention to the water-soluble olefins, allyl alcohol and allylsulfonate. Published equilibrium constants for the formation of Zeise's salt analogues of these ligands from $PtCl_4^{2-}$ ensure essentially complete conversion of $PtCl_4^{2-}$ to Pt(olefin)Cl_3^- for the equimolar mixtures of olefin and $PtCl_4^{2-}$ in aqueous solution.[8] On addition of weak base

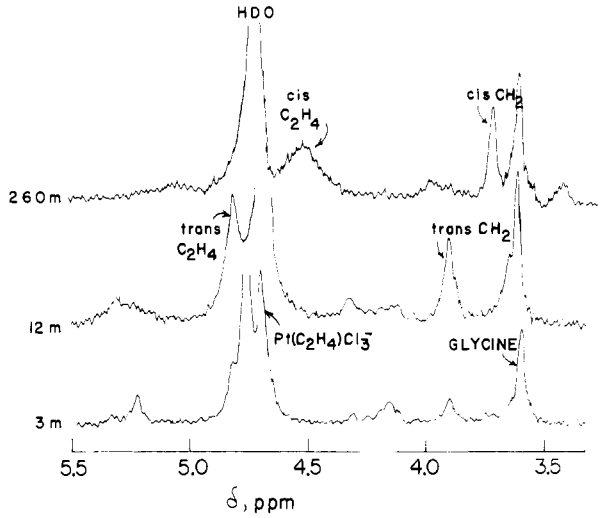

Figure 1. Proton NMR spectra as a function of time for 0.30 M $KPt(C_2H_4)Cl_3$, 0.30 M glycine, and 0.30 M sodium acetate showing rapid formation of *trans*(*N*,ethylene)-chloro(glycine)(ethylene)platinum and subsequent slow conversion to cis isomer.

(acetate) and the neutral zwitterionic amino acid to such solutions, the following equilibrium is rapidly established (where N∼O denotes the amino acid anion):

$$Pt(olefin)Cl_3^- + H\text{–}N\sim O^{\mp} + CH_3CO_2^- \rightleftarrows \textit{trans}\text{-}Pt(N\sim O)(olefin)Cl + CH_3CO_2H + 2Cl^- \quad (1)$$

Equilibration to the cis isomer, reaction 2, can then occur either

$$\textit{trans}\text{-}Pt(N\sim O)(olefin)Cl \rightleftarrows \textit{cis}\text{-}Pt(N\sim O)(olefin)Cl \quad (2)$$

via stepwise displacement and subsequent reverse addition of amino acid to Pt(olefin)Cl_3^- or by other pathways involving Cl^- displacement of olefin or Cl^- catalysis. The presence of the acetate ion ensures that the aqueous solutions are buffered in the pH 4–5 region when equilibrium is established. Thus hydrolysis of Cl^- or ring opening of the amino acid chelate by carboxyl protonation are not significant side reactions. Proton NMR spectroscopy has been used to follow the spectral changes associated with reactions 1 and 2. Though the technique was developed for the water-soluble olefins, equilibration of ethylene complexes was also successfully followed by the same approach.

Experimental Section

Reagents were all commercially available and were used without purification except for sodium allylsulfonate, which was synthesized by the reaction of sodium sulfite with allyl bromide.[9] Proton NMR spectra were recorded with a Perkin-Elmer R-12 NMR spectrometer.

Kinetic Runs. Stock solutions of Pt(olefin)Cl_3^- were prepared by adding the olefin and K_2PtCl_4 in a 1:1 mole ratio to D_2O. The formation of the 1:1 complex was monitored by NMR spectral changes and by color changes (red to yellow). A similar solution containing a 1:1 ratio of amino acid and acetate was also prepared. However, in order to avoid excess dilution of final solutions, a stochiometric quantity of this amino acid–acetate solution was rotary evaporated to dryness and the Pt(olefin)Cl_3^- solution was added to this dry solid to initiate reaction 1. For Pt(ethylene)Cl_3^- reactions, 0.30 mmol of Zeise's salt was dissolved in 1 mL of D_2O containing 0.30 M amino acid and 0.30 M sodium acetate. Spectral changes associated with subsequent equilibration of trans and cis isomers were monitored until no further changes were observed.

Analyses. Most of the complexes were quite soluble in water and were not actually isolated. However, *cis*-Pt(aba)(allyl alcohol)Cl precipitated from the reaction mixtures. The isomer assignment was based on NMR data. Anal. Calcd for $C_7H_{14}NO_3PtCl$: C, 21.63; H, 3.11; N, 3.60. Found: C, 21.32; H, 3.59; N, 3.82.

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Table I. Comparison of Chemical Shifts and Coupling Constants for Me_2SO and Ethylene Complexes[a]

complex	glycine		olefin or Me_2SO	
	δ (CH_2)	J_{Pt-H}	δ (CH_3 or CH_2)	J_{Pt-H}
$Pt(ethylene)Cl_3^-$			4.62	66
cis-Pt(ethylene)(gly)Cl	3.71	35	4.52	66
trans-Pt(ethylene)(gly)Cl	3.89	30	4.79	58
$Pt(Me_2SO)Cl_3^-$			3.53	24
cis-Pt(Me_2SO)(gly)Cl	3.68	42	3.56	25
trans-Pt(Me_2SO)(gly)Cl	3.66	30	3.44	19
$Pt(gly)Cl_2^-$	3.51	38		

[a] Chemical shifts in ppm relative to DSS; coupling constants in Hz.

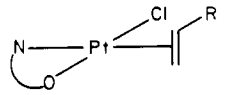
Results

Proton NMR spectral changes associated with the reaction of 0.30 M $Pt(ethylene)Cl_3^-$ and 0.30 M glycine/sodium acetate are shown in Figure 1. An initial relatively fast reaction with amino acid to form an equilibrium mixture of $Pt(ethylene)Cl_3^-$ and *trans*-Pt(ethylene)(glycine)Cl is revealed by a decrease in area of peaks due to Zeise's salt and free glycine CH_2 and an increase in the area of peaks assigned to the trans complex. This initial fast formation of the trans isomer typically reached a pseudoequilibrium in 10 min at magnet temperature for all of the combinations investigated. A downfield chemical shift of acetate CH_3 signal is also observed, indicating a drop in pH. The olefin peaks of both Zeise's salt and the complex show increased broadening with time, presumably due to the increased rate of exchange of coordinated olefin and a small amount of free olefin produced by displacement of Cl^-.[10] Such broadening of olefin peaks was observed for all combinations of olefins and amino acids included in this study, and the kinetics of these exchange reactions are currently being investigated further.

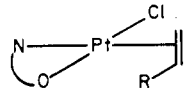
After relatively rapid formation of the trans isomer, the peaks assigned to it slowly decreased with time while new peaks in both the olefin and amino acid regions of the spectra appeared. The new peaks of both olefin and amino acid moieties are upfield from those of the trans isomer, in contrast to Me_2SO complexes for which the reverse is usually observed.

Comparative chemical shifts and coupling-constant data for Me_2SO and ethylene complexes of glycine are given in Table I. The more stable cis isomers of both Me_2SO and ethylene have larger coupling constants for amino acid and olefin protons, suggesting stronger bonding of these ligands in the cis isomer. For both Me_2SO and olefin complexes, the trans isomers are pale yellow while the cis isomers are nearly colorless.

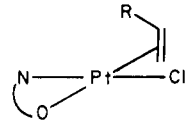
With the prochiral olefins allyl alcohol and allylsulfonate it is possible in principle to distinguish between trans rotamers **1** and **2** and between cis rotamers **3** and **4**. However, rates



1



2



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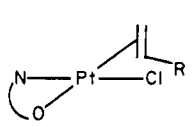

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of internal rotation are typically too fast to detect this difference, and we observed only one CH_3 peak each for the free amino acid and for the cis and trans isomers of aba complexes.[2,11] Similarly only one CH_2 peak was observed for each of the three species of glycine. With the chiral amino acid alanine, two distinguishable diastereomers are possible, even with rapid rotation about the Pt–olefin bond. However, the spectral changes in the methyl region closely parallel those observed for aba complexes. The chemical shift of alanine CH_3 protons at 60 MHz seems to be determined mainly by the coordination pattern around the central platinum and is less sensitive to the more subtle effects of olefin orientation.

Table II. Kinetic Data[a] for

$$trans\text{-}[Pt(amino\ acid)(olefin)Cl] \xrightarrow{k} cis\text{-}[Pt(amino\ acid)(olefin)Cl]$$

olefin	amino acid		
	glycine	alanine	α-amino-isobutyric acid
ethylene	3.9	1.3	0.23
allyl alcohol	6.2	4.1	2.6
allylsulfonate	16.5	9.1	4.1

[a] $k \times 10^5$, s^{-1}. $T = 36$ °C.

For all nine complexes examined the cis isomer is strongly favored at equilibrium. Attempts to determine reliable equilibrium constants for the trans → cis reaction were complicated by overlap of spectra of the two isomers, precipitation of one of the isomers, and thermal decomposition of the products with deposit of platinum. However the cis isomer was favored over the trans for most of the combinations by 10:1 or more. In no case was the equilibrium ratio less than 3.

The kinetics of the slow subsequent conversion of trans to cis isomers has been analyzed as a first-order process by plotting ln [trans] vs. time to obtain k as the slope. Comparative data for k are given in Table II. The trends in reaction rates are consistent among the amino acids (glycine > alanine > aba) and olefins (allylsulfonate > allyl alcohol > ethylene).

The solutions invariably decomposed on further standing, with deposit of platinum mirrors and release of amino acid. However, for Pt(aba)(allyl alcohol)Cl a white precipitate formed before decomposition became significant. Elemental analysis of this solid confirmed the assigned formula. Its infrared spectrum gave a band at 340 cm^{-1}, which Nakamoto has attributed to a Pt–Cl vibration of the cis isomer (vs. 360 cm^{-1} for the trans isomer).[3] The NMR spectrum of this white solid corresponds to that for the second product formed in the reaction.

This demonstration that the cis isomers of both Me_2SO and olefin complexes of Pt(amino acid)(L)Cl (where L = Me_2SO or olefin) are the thermodynamically favored isomers has enabled us to undertake a thorough study of the kinetics and mechanisms of the isomerization and exchange reactions of L and Cl^- and of the reactions of the ligands L with Pt(amino acid)Cl_2^-. The results of these investigations, which will be reported separately,[12] confirm the conclusions presented in this report and extend the systems that show the cis isomer preference to include sarcosine (*N*-methylglycine) and 2-methyl-3-buten-2-ol (γ,γ-dimethylallyl alcohol). The isomer preference decreases with methyl substitution on the amino acid nitrogen as we have noted earlier for Me_2SO complexes.[4]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical

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Society, for the support of this research.

Registry No. *cis*-Pt(ethylene)(gly)Cl, 80081-27-2; *cis*-Pt(allyl alcohol)(gly)Cl, 80041-73-2; *cis*-Pt(allylsulfonate)(gly)Cl, 80041-74-3; *trans*-Pt(ethylene)(gly)Cl, 31902-31-5; *trans*-Pt(allyl alcohol)(gly)Cl, 80081-28-3; *trans*-Pt(allylsulfonate)(gly)Cl, 80081-29-4; *cis*-Pt(ethylene)(ala)Cl, 32661-13-5; *cis*-Pt(allyl alcohol)(ala)Cl, 80041-75-4; *cis*-Pt(allylsulfonate)(ala)Cl, 80041-76-5; *trans*-Pt(ethylene)(ala)Cl, 32680-87-8; *trans*-Pt(allyl alcohol)(ala)Cl, 80081-30-7; *trans*-Pt(allylsulfonate)(ala)Cl, 80081-31-8; *cis*-Pt(ethylene)(aba)Cl, 80041-77-6; *cis*-Pt(allyl alcohol)(aba)Cl, 80041-78-7; *cis*-Pt(allylsulfonate)(aba)Cl, 80041-79-8; *trans*-Pt(ethylene)(aba)Cl, 80081-32-9; *trans*-Pt(allyl alcohol)(aba)Cl, 80081-33-0; *trans*-Pt(allylsulfonate)(aba)Cl, 80081-34-1; Pt(ethylene)Cl_3^-, 12275-00-2; Pt$(Me_2SO)Cl_3^-$, 60881-14-3; *cis*-Pt(Me_2SO)(gly)Cl, 60383-64-4; *trans*-Pt(Me_2SO)(gly)Cl, 60338-47-8; Pt(gly)Cl_2^-, 24653-14-3.

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Poly(pyrazolyl)borate Complexes of Zirconium(IV)

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The organometallic chemistry of complexes of the second- and third-row transition metals to the left of the periodic table has been one of the most exciting and fast developing areas of inorganic chemistry. Complexes showing new reactivity patterns with small molecules,[1] containing new types of interesting ligands,[2] and possessing great potential usefulness in organic synthesis[3] have all been developed. In a majority of this chemistry, cyclopentadienylmetal halides are the starting materials. It seemed to us that the development of alternative metal halide starting materials containing ligands other than cyclopentadienyl rings could lead to new and interesting chemical transformations. Specifically, it was decided to prepare a new family of poly(pyrazolyl)borate metal halide complexes of zirconium, niobium, and tantalum. Our initial goal is to synthesize and investigate the reactivity of complexes of the general formula $[R_mB(pz)_{4-m}]_nMX_{p-n}$ (pz = pyrazolyl ring; m = 1, 2; n = 1, 2; M = Zr, p = 4, M = Nb, Ta, p = 5). Also of interest are complexes containing substituted pyrazolyl rings and complexes containing two different poly(pyrazolyl)borate ligands.

Although poly(pyrazolyl)borate complexes have been extensively studied with other transition metals,[4] only two reports of their zirconium, niobium, and tantalum complexes have appeared. Wilkinson et al.[5] have reported the complex $[H_2B(pz)_2]_2TaMe_3$. In addition, a short paper reporting the complexes (characterized only by ^1H NMR and Zr and Cl analytical figures) $[B(pz)_4]_2ZrX_2$ (X = Cl, Br) and $[B(pz)_4]_4Zr$ has appeared.[6]

This paper reports our initial results in this area. We have prepared a number of $[RB(pz)_3]ZrCl_3$ complexes and a methoxide derivative of one of these complexes. Also reported is the first isolation of the known ligand $[n\text{-BuB}(pz)_3]^-$ and the new ligand $[i\text{-PrB}(pz)_3]^-$.

Results and Discussion

At the onset of the investigation it was anticipated that ligands of the type $[RB(pz)_3]^-$ where R = alkyl would be the most desirable for this study in order to avoid complications arising from possible reactions of a BH group and, more importantly, to insure good solubility characteristics of the new complexes. To this end, the $Na[n\text{-BuB}(pz)_3]$ ligand salt had been prepared (reaction 1) but it had been used only in aqueous solution and not isolated.[7] We have now prepared and isolated in good yield both this ligand salt and $Na[i\text{-PrB}(pz)_3]$ utilizing the methodology of reaction 1.

$$B(OMe)_3 \xrightarrow[2.\ H_2SO_4/H_2O]{1.\ n\text{-BuMgBr}} n\text{-BuB}(OH)_2 \xrightarrow[2.\ Hpz]{1.\ Na(pz)} Na[n\text{-BuB}(pz)_3] \quad (1)$$

The reaction of either of these ligands or $[HB(3,5\text{-}Me_2pz)_3]^-$ with 2 equiv of $ZrCl_4$ yields the respective $[ligand]ZrCl_3$ complex in good yield. Stoichiometric reactions yielded inseparable mixtures of products. In the case of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand, a series of reactions carried out between 1:1 and 1:2 molar ratios (ligand:metal) demonstrated that fully 2 equiv of $ZrCl_4$ are needed. Presumably, the extra equivalent of $ZrCl_4$ acts as a Lewis acid for the Cl^- being displaced. Note that in a very recent report it was stated that a 2:1 ratio of $ZrCl_4$ to TlCp was necessary in a new preparation of $CpZrCl_3$.[8]

The ^1H and ^{13}C NMR spectra of these new complexes show that the three pyrazolyl rings of the ligand are in equivalent environments (even at −80 °C for the $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ complex) as expected for these pseudooctahedral complexes. All three compounds are soluble in CH_2Cl_2 and partially soluble (ca. 0.1 g/100 mL) in toluene. The $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ complex is quite stable, decomposing in air only very slowly even in solution. It is also thermally stable as demonstrated by the fact that final purification (a step that presumably removes trace amounts of $ZrCl_4$) of this complex was effected by a 48-h Soxhlet extraction with benzene. The two $[RB(pz)_3]ZrCl_3$ complexes are much less stable, decomposing rapidly in air and also in refluxing benzene or pentane. Although less stable, these complexes are easily handled by standard Schlenk techniques. The higher stability of the $[HB(3,5\text{-}Me_2pz)_3]$ derivative is certainly not an unexpected result in view of the crystal structure data on $[HB(3,5\text{-}Me_2pz)_3]$ complexes, which show that the 3-Me substituents cause considerable steric crowding around the metal.[9]

In order to determine if this steric crowding would prevent possible reactivity, we prepared the methoxide derivative as shown in eq 2. This compound does not show fluxional be-

$$[HB(3,5\text{-}Me_2pz)_3]ZrCl_3 + NaOMe \xrightarrow{\text{toluene}} [HB(3,5\text{-}Me_2pz)_3]Zr(OMe)Cl_2 + NaCl \quad (2)$$

havior at 35 °C as has been observed in many poly(pyrazolyl)borate complexes.[10] Thus both ^1H and ^{13}C NMR spectra show a 2:1 ratio for each ring hydrogen and carbon atom, respectively, as expected for a static pseudooctahedral complex. These results also indicate that the ligand is indeed tridentate in this and, by extrapolation, in the three other new complexes reported above. The alternative explanation of a bidentate ligand could also possibly fit the NMR data but is unrea-

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