Olefin−Amino Acid Complexes of Platinum(II). 2. NMR Study of the Effect of Olefin Structure on the Stability and on the Stereoselectivity of Binding for η^2-Coordinated Prochiral Olefins

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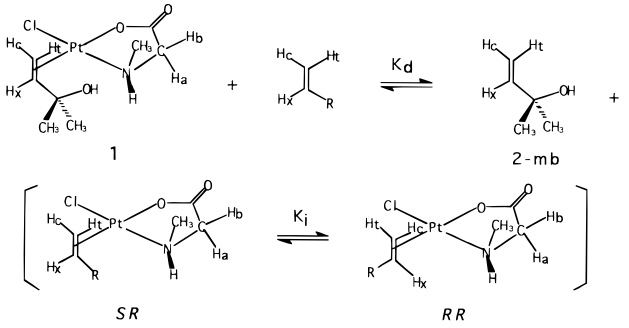
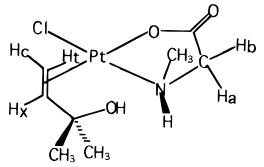
The exceptional stereoselectivity of coordination (*RS* isomer favored) of the prochiral olefinic alcohol 2-methyl-3-buten-2-ol in *cis*(*N*,*olefin*)-chloro(2-methyl-3-buten-2-ol)(sarcosinato)platinum(II), **1**, prompted this investigation of the effect of olefin structure on the equilibrium constant for platinum binding (K_d) and on the stereoselectivity of coordination, as measured by $K_i = [RR]/[RS]$, for 32 other monosubstituted ethylenes with the same chiral template. The only other olefins which show significant preference for the *RS* diastereomer ($K_i < 0.5$) contain hydrogen-bond acceptor atoms in close proximity to the N−H proton of the coordinated olefin which is *cis* to that nitrogen. Increasing the distance between the N−H proton and the proton acceptor atom by one C−C link has a dramatic effect on K_i. Almost no correlation was found between K_d and K_i, but a significant correlation between the formation constant, K_f, for formation of $PtCl_3(olefin)^-$ species of 14 of the olefins and the ^{195}Pt chemical shift suggested a way to separate electronic effects from steric and hydrogen-bonding effects on the relative stabilities of the mixed olefin−amino acid complexes. Deviations from a simple correlation between log K_d and log K_f are discussed in terms of this model, but a clean separation of electronic effects from other effects cannot be claimed.

Introduction

A better understanding of the factors that influence stereoselectivity, both in reactions and in equilibrium isomer ratios, is important to the systematic development of transition metal-based catalysts for chiral syntheses.[1−4] In reporting the exceptional stereoselectivity of coordination of 2-methyl-3-buten-2-ol, 2-mb, in mixed olefin−amino acid complexes of general formula *cis*(*N*,*olefin*)-Pt(olefin)(amino acid)Cl for the amino acids sarcosine and proline, which contain a chiral nitrogen adjacent to the coordinated chiral olefin, we suggested that the source of the additional stability of the highly favored diastereomer, **1**, might be the energy stabilization provided by an intramolecular hydrogen bond between the N−H proton of the coordinated amino acid and the oxygen of the olefin moiety.[5] Precedent for such stabilization had been reported for *cis*-dichloro((*S*)-α-methylbenzylamine)(olefin)platinum(II) isomers.[6] The convenient availability of **1** and of a wide range of other monosubstituted olefins, CH_2═CHR, has now enabled us to confirm this interpretation and to establish more clearly the structural features that lead to exceptional stereoselectivity of coordination for other olefin analogs of **1**.

Scheme 1





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This report examines the effect of changes in the structure of a competing olefin on the equilibrium constant for displacement of 2-mb from the single diastereomer of the mixed sarcosine−2-mb complex and on the diastereomer ratio of the products obtained in that reaction (Scheme 1). The feasibility of such experiments depends on relatively fast olefin exchange between species, which ensures equilibration of species in a matter of minutes or less[7] and on the consistent proton NMR spectral changes, which permit convenient quantitative deter-

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.

(1) The stereochemistry of several olefin complexes of Re, in which the asymmetric Re center serves as the chiral template for stereoselective coordination of prochiral olefins (analgous to the platinum complexes reported here), serves as a useful parallel for the work reported here. See: Kowalczyk, J. J.; Arif, A. M.; Glaydz, J. A. *Chem. Ber*. **1991**, *124*, 729. Pu, J.; Peng, T.-S.; Mayne, C. L.; Arif, A. M.; Gladyz, J. A. *Organometallics* **1993**, *12*, 2686. Pu, J.; Peng, T.-S.; Mayne, A. M.; Gladyz, J. A. *Organometallics* **1994**, *13*, 929.

(2) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.

(3) Morrison, J. D., Ed., *Asymmetric Synthesis*, Vol. 1−5; Academic Press: New York, 1983−1985.

(4) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; Chapter 12.

(5) Erickson, L. E.; Jones, G. S.; Blanchard, J. L.; Ahmed, K. J. *Inorg. Chem.* **1991**, *30*, 3147−3155.

(6) Uccello-Barretta, G.; Lazzaroni, R.; Bertucci, C.; Salvadori, P. *Organometallics* **1987**, *6*, 550; *J. Organomet. Chem*. **1985**, *297*, 117; *J. Organomet. Chem*. **1984**, *275*, 145.

(7) Erickson, L. E.; Bemis, J. Fourth International Conference on Bioinorganic Chemistry, MIT, Boston, July 1989. (Abstract in *J. Inorg. Biochem*. **1989**, *36*, 256.)

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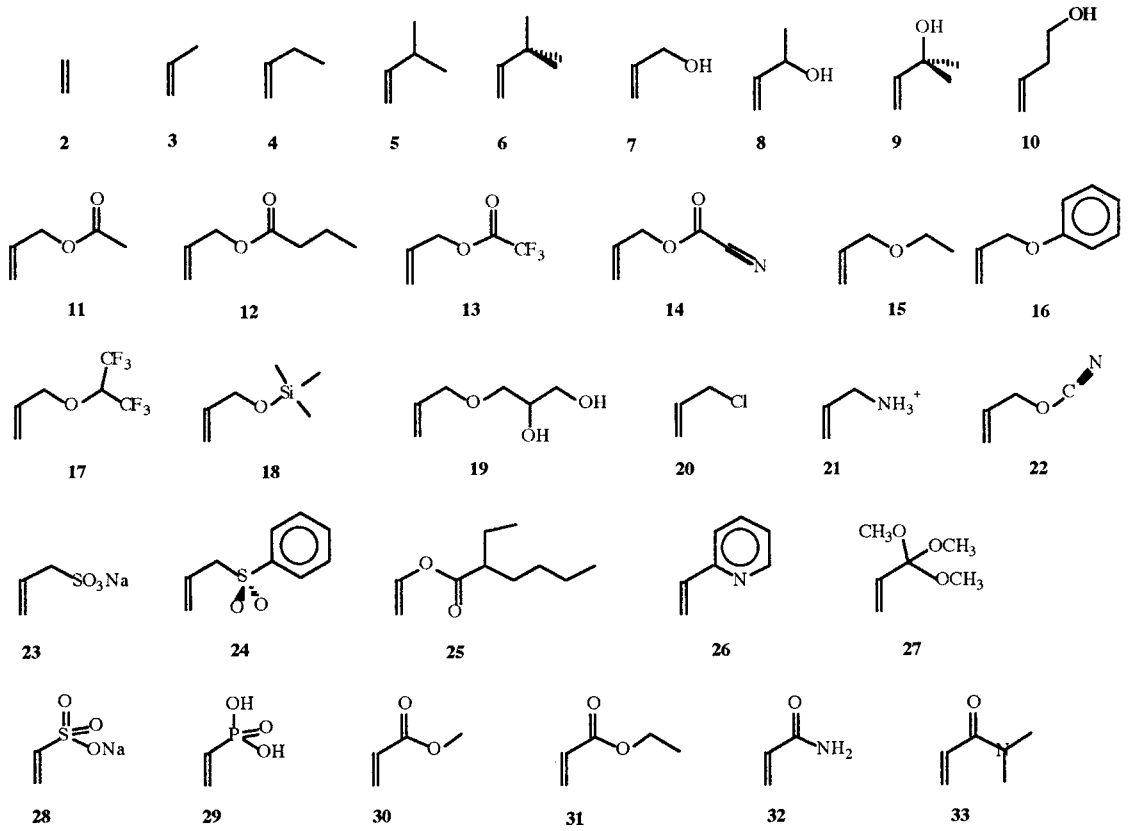
Chart 1



mination of relative concentrations of diastereomers. The range of olefins examined (**2**−**33**, Chart 1) was sufficient to establish empirically some structural features required to achieve high stereoselectivity of coordination in these mixed olefin−sarcosine species.

The equilibrium reactions of Scheme 1 can be rewritten in condensed form as eq 1,

$$(RS)\text{-Pt(2-mb)(sar)Cl} + \underset{\mathbf{1}}{} \text{CH}_2{=}\text{CHR} \overset{K_d}{\rightleftharpoons} \text{2-mb} + [(RS)\text{-Pt}(\text{CH}_2{=}\text{CHR})(\text{sar})\text{Cl} \overset{K_i}{\rightleftharpoons} (RR)\text{-Pt}(\text{CH}_2{=}\text{CHR})(\text{sar})\text{Cl}] \quad (1)$$

with corresponding equilibrium constants $K_d = [\text{Pt}(\text{CH}_2{=}\text{CHR}\text{-}(\text{sar})\text{Cl}][\text{2-mb}]/[(SR)\text{-Pt(2-mb)(sar)Cl}][\text{CH}_2{=}\text{CHR}]$ for the displacement and $K_i = [(RR)\text{-Pt}(\text{CH}_2{=}\text{CHR})(\text{sar})\text{Cl}]/[(SR)\text{-Pt}\text{-}(\text{CH}_2{=}\text{CHR})(\text{sar})\text{Cl}]$ for the isomerization. The equilibrium constant, K_d, for the displacement reaction reflects the relative coordinating ability of 2-mb and the second olefin, $\text{CH}_2{=}\text{CHR}$, while the equilibrium constant, K_i, for the isomerization reaction indicates the degree of stereoselectivity of $\text{CH}_2{=}\text{CHR}$ in its mixed $(\text{CH}_2{=}\text{CHR})$−sarcosine complex. Consistent with this definition, $\text{Pt}(\text{CH}_2{=}\text{CHR})(\text{sar})\text{Cl}$ in the definition of K_d denotes the total concentration of both diastereomers of $\text{Pt}(\text{CH}_2{=}\text{CHR})\text{-}(\text{sar})\text{Cl}$. Our principal concern has been with the degree of stereoselectivity, as measured by K_i, but specification of K_d also provides a quantitative index of total platinum binding affinity for each of the olefins examined.

An alternative probe of the relative stability of olefin complexes of NMR-active metals has been recently reviewed and extended by Ohrstrom.[8] Both empirical data and theoretical models suggest a strong correlation between the metal atom chemical shift and log K_f, where K_f is the formation constant of the metal complex. Relatively low solubilities of the mixed sarcosine−olefin complexes discouraged us from completing such a study on the sarcosine−olefin complexes, but we were able to determine both the ^{195}Pt chemical shift and the relative formation constant for a series of Zeise's salt analogs with several of the olefins included in this investigation. The importance of the amino acid to the extent and the selectivity of olefin binding was emphasized by comparing equilibrium constants for displacement of 2-mb, by the same series of olefins, from **1** and from the corresponding Zeise's salt analog, $[\text{PtCl}_3(\text{2-mb})]^-$. For these comparisons, the relative formation constant, K_f, is defined as the equilibrium constant for the reaction as depicted in eq 2, the displacement of coordinated 2-mb by another olefin, $\text{CH}_2{=}\text{CHR}$.

$$\text{PtCl}_3(\text{2-mb})^- + \text{CH}_2{=}\text{CHR} \rightarrow \text{PtCl}_3(\text{CH}_2{=}\text{CHR})^- + \text{2-mb} \quad (2)$$

An accompanying report details subsequent NMR experiments, both low-temperature NMR measurements and room temperature NOE enhancement experiments, which provide further direct experimental evidence for the importance of intramolecular hydrogen bonding in stabilizing one rotamer of a coordinated olefin to strongly affect equilibrium species distributions.[9] The final part of this multipart investigation is an NMR study of the rates and energy barriers for internal rotation for some selected coordinated olefins in the series.[10]

Experimental Section

***cis*(*N*,*2-mb*)-Pt(2-mb)(sar)Cl, 1**, was synthesized from K_2PtCl_4, 2-mb, and sarcosine as reported earlier.[5] The compound was obtained in about 25% yield as a racemic mixture of optical isomers (denoted

(8) Ohrstrom, L. *Comments Inorg. Chem.* **1996**, *18*, 305.

(9) Morris, K. F.; Erickson, L. E.; Ding, F.; Jiang, D.; Panajotova, B. *Inorg. Chem.*, in press.

(10) Erickson, L. E.; Ding, F.; Gross, J.; Morris, K. F.; Panajotova, B., to be submitted for publication.

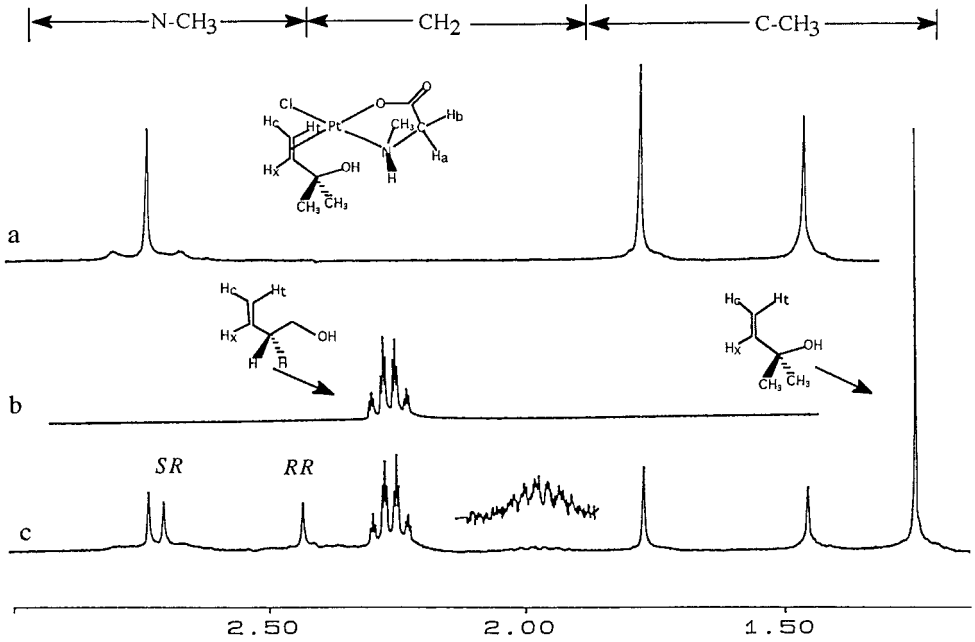


Figure 1. Proton NMR spectra of CD_3-OD solutions (a) of **1**, (b) of the olefin 3-butene-1-ol (**10**), and (c) of an equilibrium mixture of **1** and **10**, used to determine both K_i and K_d. Note lack of stereoselectivity indicated by equal intensities of peaks of *SR* and *RR* isomers of the displacement product.

SR and *RS*) of the single diastereomer whose structure had been established by X-ray crystallography.[5]

Other Olefins. Most of the other olefins employed in the competition experiments were obtained from Aldrich Chemical Co. They were used without further purification only after their purity was confirmed by NMR spectroscopy. Volatile hydrocarbon olefins (ethene, propene, etc.) were obtained as compressed gases from Matheson Gas.

NMR Solvents. The deuterated solvents, D_2O and methanol-d_4, were obtained from Aldrich. For most experiments, 0.5 or 1.0 mL ampoules were employed in order to permit as much as possible the efficient use of pure solvents in the preparation of solutions.

NMR Spectra. Proton, carbon-13, and platinum-195 NMR spectra were obtained with a Bruker AF-300 NMR spectrometer equipped with a proton/carbon probe, a broad-band probe for low-frequency nuclei, including ^{195}Pt, and a temperature control unit. The FID of samples were collected at the console, but were then transferred to a PC workstation which employed PC NMR to work up the data.[11] Proton chemical shift values were based on the methyl resonance of the residual protons in the CD_3OD solvent = 3.30 ppm (TMS = 0). Platinum-195 shifts were based on an external standard of 0.2 M K_2PtCl_4 = −1630 ppm (H_2PtCl_6 = 0).

Olefin Equilibration Experiments. Equilibration experiments were carried out on an NMR-tube scale as follows: About 0.010 M **1** (1 mL) in CD_3OD, obtained from a 10 mL stock solution or freshly prepared by dissolving 0.01 mmol of **1** (4 mg) in 1.0 mL of solvent, was transferred to a 5-mm NMR tube. The proton NMR spectrum of this sample was usually recorded to establish the purity and approximate concentration of the sample before a second olefin was added. A syringe or pipet was then employed to add the second olefin (either directly or as a 0.10 M solution in CD_3OD) to the solution of **1** in the NMR tube. For the volatile olefins, a stock solution of the olefin in CD_3OD was prepared by bubbling the gas into a chilled sample of the solvent, and a small amount of **1** was dissolved in this solution to initiate the equilibration reaction. Alternatively, a small amount of volatile olefin was bubbled into a 0.01 M solution of **1** in CD_3OD.

After each solution was prepared, a proton spectrum was recorded within minutes. A second proton spectrum was recorded at least 10 min later. If it differed significantly from the first spectrum, additional spectra were recorded to ensure equilibration of olefins among the platinum species. For every olefin examined, equilibrium was established by the time the second spectrum was recorded (less than 30 min from solution preparation). After several hours some samples showed additional spectral changes associated with other reactions or slow decomposition.

Olefin Competition in Zeise's Salt Analogs. A 0.10 M stock solution of $PtCl_3$(2-mb)$^-$ (10 mL) in D_2O was prepared by adding 1.0 mmol of 2-mb to 1.0 mmol of K_2PtCl_4 dissolved in 10 mL of 0.01 M DCl/D_2O in a 10-mL volumetric flask. After 2 days at room temperature, displacement of Cl^- by 2-mb to form $PtCl_3$(2-mb)$^-$ had reached equilibrium with only a trace of free 2-mb still evident. After the composition of the stock solution was confirmed by proton NMR spectroscopy, 0.01−1.0 mmol of a second olefin was added with a 10-μL syringe to 1.0 mL of the stock solution in an NMR tube and the solutions were allowed to equilibrate at room temperature, 22 °C, for at least 1 h. Both proton and platinum-195 NMR spectra of the equilibrated reaction mixtures were then recorded and used to calculate the relative formation constant, K_f = [$PtCl_3(CH_2{=}CHR)^-$][2-mb]/[$PtCl_3$-(2-mb)$^-$][$CH_2{=}CHR$] from the relative concentration of the two platinum species (based on the area ratio of correponding peaks in the ^{195}Pt spectrum) and the relative concentration of free olefins (based on the area ratio of corresponding peaks in the proton NMR spectrum).

Results

***K_d* and *K_i* for Sarcosine Complexes.** The results of a typical equilibration experiment are shown in Figure 1 for the reaction of **1** with 3-buten-1-ol. The proton spectrum of **1** consists of sharp methyl singlets from coordinated 2-mb at 1.47 and 1.78 ppm, the *N*-methyl singlet of coordinated sarcosine (with well-defined ^{195}Pt satellites; $^3J_{Pt-H}$, 40 Hz) at 2.73 ppm, a pair of AB doublets for the sarcosine methylene protons at 3.24 and 3.93 ppm, and three well-separated patterns for the three olefinic protons, denoted H_t, H_c, and H_x, at 4.04 (d, J = 13.5 Hz), 4.15-(d, J = 8.6 Hz), and 5.35 (dd, J = 13.5, 8.6 Hz) ppm; respectively. The spectral changes which most clearly indicate simple olefin exchange are (a) the appearance of a sharp singlet at 1.26 ppm for the methyl protons and of smaller multiplets for olefinic protons of liberated 2-mb, (b) a decrease in the intensity of the *N*-methyl peak of **1** and its replacement by two detectable *N*-methyl peaks from the two diastereomers of the product of olefin substitution, and (c) replacement of the AB pattern of the sarcosine methylene protons of **1** by two AB patterns of the corresponding olefin substitution product(s).

(11) Available through T. Farrar, Department of Chemistry, University of Wisconsin, Madison, WI.

Table 1. Equilibrium Constant Data for Olefin Displacement (K_d) from **1** and for Isomerization (K_i) of the Product Complex

olefin	K_d	K_i
hydrocarbons (compd no.)		
ethene (**2**)	6.4	
propene (**3**)	0.49	1.2
1-butene (**4**)	0.6	1.15
3-methyl-1-butene (**5**)	0.29	1.2
3,3-dimethyl-1-butene (**6**)	0.09	1
alcohols		
allyl alcohol (**7**)	1.57	0.134
3-buten-2-ol (**8**)	0.46	0.16
2-methyl-3-buten-2-ol (**9**)	1.00 (reference)	0.01
3-buten-1-ol (**10**)	0.48	0.95
allyl esters		
allyl acetate (**11**)	0.08	1.0
allyl butyrate (**12**)	0.05	1.0
allyl trifluoroacetate (**13**)	0.19	1.0
allyl cyanoacetate (**14**)	0.08	1.0
allyl ethers		
allyl ethyl ether (**15**)	0.39	0.43
allyl phenyl ether (**16**)	0.05	0.62
allyl hexafluoropropyl ether (**17**)	0.034	1.0
(allyloxy)trimethylsilane (**18**)	0.49	0.16
3-(allyloxy)-1,2-propanediol (**19**)	0.76	0.12
allyl-X		
allyl chloride (**20**)	0.17	1.0
allylammonium ion (**21**)	0.43	1.0
allyl isocyanate (**22**)	0.34	1.0
2-propenesulfonate (**23**)	0.5	1.27
allyl phenyl sulfone (**24**)	0.044	1.1
vinyl compounds		
vinyl 2-ethylhexanoate (**25**)	0.31	0.4
2-vinylpyridine (**26**)	0.047	0.16
vinyltrimethoxysilane (**27**)	0.041	0.16
ethenesulfonate (**28**)	0.17	0.013
vinylphosphonic acid (**29**)	0.16	0.013
acrylates/amides		
methyl acrylate (**30**)	0.006	0.5
ethyl acrylate (**31**)	0.003	0.56
acrylamide (**32**)	0.022	0.21
N,*N*-dimethylacrylamide (**33**)	0.034	0.36

The relative concentrations of all the species involved in the equilibria described by Scheme 1 were determined from the proton spectrum of equilibrium mixtures. The relative concentration of free and coordinated 2-mb can be determined most easily from the relative areas of the corresponding methyl singlets. The relative concentrations of the two diastereomers of the displacing olefin can be determined from the relative areas of the corresponding *N*-methyl peaks. For every compound for which two products are obtained, the *N*-methyl peak of one isomer is typically very close to the *N*-methyl peak of **1**, while the *N*-methyl peak of the other is about 0.3 ppm more shielded. The former is therefore identified with the *S*,*R* (and *R*,*S*) diastereomer, and the latter with the *R*,*R* (and *S*,*S*) diastereomer. Finally, the relative concentrations of free and coordinated forms of the displacing olefin can be obtained in several ways, most simply from the relative area of peaks of corresponding protons of free and coordinated species, when separate peaks can be identified. For the spectra shown in Figure 1, the ratios of the two olefin complexes and of the two free olefins were determined from the spectra in Figure 1 as [Pt(CH_2═CHR)]/[Pt-2-mb] = 1.75, [R,R]/[S,R] = 1.0, and [2-mb]/[CH_2═CHR] = 0.30. These values lead to $K_d = (0.1.75)(0.30) = 0.53$ and $K_i = 1.0$. Thus, 3-buten-1-ol is somewhat less tightly bound to platinum than 2-mb and shows essentially no stereoselectivity of olefin coordination in its sarcosine−olefin complex.

Equilibrium data for 32 olefins (ethene and 31 prochiral olefins), arranged by substituent group, are included in Table 1. Since none of the *K* values would be expected to depend on the extent of dilution of the solution, the actual concentrations of all species were not determined precisely, and initial concentrations of CH_2═CHR were varied as required to ensure displacement of enough 2-mb to be able to identify products of substitution at equilibrium for solutions that were approximately 0.01 M in total platinum concentration. All data are for samples at ambient magnet temperture, 292 K. Equilibrium constants are estimated to be reliable to ±20%.

Table 2. Equilibrium Constant and ^{195}Pt Chemical Shift Data for Comparison between 1:1 Complexes and Corresponding Mixed Olefin−Amino Acid Complexes

olefin	K_f	K_d	K_i	Pt shifts/ppm[a]
ethene (**2**)	30	6.4	1	−2810
allyl alcohol (**7**)	3.4	1.6	0.13	−2766
2-methyl-3-buten-2-ol (**9**)	1	1	0.01	−2714
3-buten-2-ol (*RR* or *RS*) (**8**)	16	0.46	0.16	−2777
3-buten-2-ol (*RS* or *RR*) (**8**)	18	0.46	0.16	−2736
3-buten-1-ol (**10**)	61	0.48	0.95	−2769
4-penten-1-ol	62			−2765
allyl ethyl ether (**15**)	6.6	0.39	0.43	−2759
2-propenesulfonate (**23**)	0.67	0.16	1.3	−2740
acrylamide (**32**)	0.18	0.5	0.21	−2663
N,*N*-dimethylacrylamide (**33**)	0.7	0.034	0.36	−2685
vinylphosphonic acid (**29**)	0.087	0.022	0.013	−2686
ethenesulfonate (**28**)	0.004	0.17	0.013	−2645
3,3-dimethyl-1-butene (**6**)	0.19	0.09	1.0	−2635

[a] Relative to 0.25 M K_2PtCl_4/D_2O = −1630 ppm.

Platinum-195 Chemical Shifts and the Stability of $PtCl_3$(olefin)$^-$ Species. Chemical shift and formation constant data for the 15 olefins examined are summarized in Table 2. In most cases, the ^{195}Pt peaks of the two species were well separated so that relative areas could be determined by integration of the peaks. Relative concentrations of the two platinum species determined in this way agreed with relative concentrations estimated from peak areas of coordinated olefins when those were well resolved. Relative concentrations of free olefins were determined by integration of corresponding peaks in the proton NMR spectrum of equilibrium mixtures. Like the data for the sarcosine complexes, all values correspond to a magnet temperature of 292 K. Equilibrium constants are estimated to be reliable to ±20%.

Discussion

Both the extent of binding (K_d) and the stereoselectivity of binding (K_i) vary widely for the olefins in the series. Of the large number of olefins examined, only ethene has a K_d substantially greater than that of **1** (6.4). All of the others have a substituent on one of the olefinic carbons, and this substituent reduces the platinum binding tendency, relative to the unsubstituted ethene. Allyl alcohol, **7**, ($K_d = 1.6$) is a somewhat better ligand than 2-mb, **9**. Spectrophotometric study of similar olefin displacement reactions of Cl^- from $PtCl_4^{2-}$ in aqueous solutions also indicate that allyl alcohol is more strongly bound than more substituted olefins.[12] Of the other hydrocarbons examined, propene (**3**), 1-butene (**4**), and 3-methyl-1-butene (**5**), all have K_d values between 0.3 and 0.6, and they show a slight preference for the *RR* diastereomer ($K_i = 1.1-1.2$). Addition of another methyl group, 3,3-dimethyl-1-butene (**6**), lowers the K_d to 0.1, and the product shows no stereoselectivity. The only olefins that show significant selectivity of olefin binding appear to be those containing a good hydrogen-bond acceptor in a site that allows ready access to the N−H proton of coordinated sarcosine *cis* to the olefin.

Clear evidence for the hydrogen-bond stabilization argument for stereoselectivity of **1** is provided by comparison of equi-

(12) Hartley, F. R.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 330.

librium data for 3,3-dimethyl-1-butene (**6**), 3-methyl-1-butene (**5**), and 2-methyl-3-buten-2-ol (2-mb) (**9**), which differ only by one of the substituents on the first carbon of the R group (CH_3, H, or OH, respectively). Although each of the hydrocarbons competes reasonably well with 2-mb for the coordination site ($K_d = 0.1-0.5$), neither shows significant stereoselectivity. Similarly, small allyl substituents like Cl (**20**), NH_3^+ (**21**), and isocyanate (**22**) force no significant stereoselectivity, although these allylic olefins also compete reasonably well with 2-mb for the Pt coordination site ($K_1 = 0.2-0.4$). So the oxygen attached to the allylic carbon of 2-mb apparently plays a key role in the stereoselectivity of coordination of 2-mb. On the other hand, the fact that 2-mb (**9**) is more stereoselective than either allyl alcohol (**7**) or 3-buten-2-ol (**8**) by about a factor of 10^5 indicates that the steric effects of the other substituents also contribute importantly to the overall equilibrium distribution of species.

Location of the H-Bond Acceptor. A comparison of correponding vinyl and allyl species and of olefinic alcohols that differ only in location of the OH along the carbon chain shows most clearly the critical importance of the location of the hydrogen-bond acceptor on the coordinated olefin. Ethenesulfonate (**28**) and vinyl phosphonate (**29**) show stereoselectivity of coordination comparable to that of 2-mb, but 2-propenesulfonate (**23**), with only an intervening CH_2 group, shows essentially no selectivity. Similarly, 3-buten-1-ol (**10**), in spite of having a potential hydrogen-bond acceptor oxygen atom only one bond further away from the nearest olefinic carbon than 2-mb (**9**) or allyl alcohol (**7**), also shows essentially no selectivity. For ethenesulfonate (**28**), the hydrogen-bonding propensity is very likely enhanced by the negative charge of sulfonate oxygens.

The presence of a potential hydrogen-bond acceptor atom, like oxygen, connected to the first carbon of the side chain of the olefin appears to be essential for significant stereoselectivity ($K_i < 0.3$), but the nature of the acceptor atom and the structure of the rest of the molecule are also important. The four allyl esters examined (**11**−**14**) show weak binding and essentially no stereoselectivity, so the O-R oxygen is apparently not effective. However, four of the five allyl ethers (**15**−**19**) show some stereoselectivity, and (allyloxy)trimethylsilane (**18**) is both relatively strongly bound ($K_d = 0.5$) and as stereoselective as allyl alcohol ($K_i = 0.16$). The more highly substituted 3-(allyloxy)-1,2-propanediol (**19**) is similarly highly stereoselective. So, as noted earlier for 2-vinyltetrahydropyran *cis* to a coordinated amine,[6] ether oxygen atoms in the critical site can provide the extra stabilization that is required for stereoselectivity.

Other vinyl compounds in the series follow a similar pattern. 2-Vinylpyridine (**26**), with a nitrogen acceptor, and vinyltrimethoxysilane (**27**), with three ether oxygens to ensure a favorable orientation of one of the oxygens whatever the rotational conformation of the $Si(OCH_3)_3$ moiety, are both as stereoselective as allyl alcohol ($K_i = 0.16$), even though neither is particularly strongly bound ($K_d = 0.04-0.05$). On the other hand, the ester vinyl 2-ethylhexanoate (**25**) is quite strongly bound ($K_d = 0.31$) and shows significant selectivity ($K_i = 0.4$). Though the carbonyl oxygen of the ester could be serving as the hydrogen-bond acceptor, the other ester oxygen, which allows formation of a five-membered ring hydrogen-bonded species, is more likely the source of the stabilization. Further evidence about selective carbonyl oxygen stabilization of one diastereomer is provided by the data for acrylic acid esters and amides. The data for four compounds in that series (**30**−**33**) are included in Table 1. Though none competes well with 2-mb for the Pt-coordination site ($K_d < 0.05$), all show modest stereoselectivity ($K_i = 0.2-0.5$).

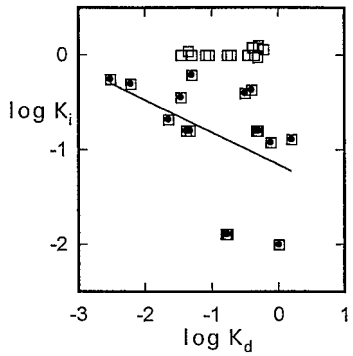


Figure 2. Plot of log K_i vs log K_d for 31 olefin analogs of **1**. Legend: open square, fifteen olefins which show essentially no stereoselectivity; dotted square, sixteen olefins for which $K_i < 0.6$. Linear regression line (log $K_i = -0.34 \log K_d - 1.16$) for the latter 16 points.

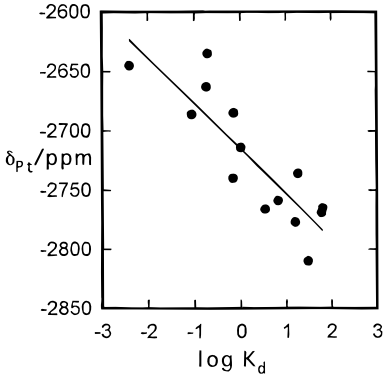


Figure 3. Plot of ^{195}Pt chemical shift of $PtCl_3(olefin)^-$ vs log K_f for D_2O solutions of 14 Zeise's salt analogs. Linear regression line (^{195}Pt shift $= -38 \log K_f - 2715$ ppm) for the 14 points.

Correlation between K_d and K_i. With the expectation that the isomer preference of *RS* isomers over *RR* isomers reflects an extra stabilization of *RS* isomers, one might expect that such stabilization should also be reflected in the competition between olefins for platinum binding sites. Thus, it would not be unreasonable to anticipate some correlation between the K_i and K_d values listed in Table 1. An attempt to establish such a correlation is shown in Figure 2, a plot of log K_i vs log K_d. To a first approximation there appears to be no significant correlation between K_i and K_d. On the other hand, the three most strongly selective olefins ($K_i = 0.01$) have larger average K_d values than the next seven most selective olefins ($K_i = 0.10-0.20$), and these seven are somewhat more stable on average than next six most selective olefins ($K_i = 0.20-0.62$). The linear least-squares regression fit of the data for these 16 olefins is included in Figure 1. Of course, this analysis excludes a nearly equal number of olefins that show no significant stereoselectivity ($K_i = 0.95-1.2$), but which span almost as big a range of K_d values as the 16 olefins that show some selectivity.

^{195}Pt Chemical Shift vs Stability of $PtCl_3(olefin)^-$. A plot of the ^{195}Pt chemical shift vs log K_f for the series of Zeise's salt analogs is shown in Figure 3. The range of chemical shifts is not large, <200 ppm for the series, but there is a clear trend toward greater shielding with increased stability of the complex. The linear regression line is included in the plot. The slope, −38 ppm/log K_f, is less than the slopes obtained for a series of halogen species[8,13] whose shifts vary over several thousand parts per million (−110 ppm/log K_f) or of amine complexes[8,14] which spanned a narrower shift range (−70 ppm/log K_f). Although the trend in the data is clear, the wide scatter in the points

indicates that the ^{195}Pt chemical shift is also sensitive to small stereochemical distinctions. For example, the chemical shifts of the two diastereomers of the 3-buten-2-ol complex, with adjacent chiral carbons, differ by 40 ppm, even though they have essentially identical formation constants, K_f, as reflected in the nearly equal concentrations of the two 1:1 species in equilibrium mixtures of Pt(2-mb)Cl_3^- and free 3-buten-2-ol. On the basis of the slope of the line in Figure 3 for the whole series, one would expect an order of magnitude difference in the K_f values between the two isomers, so relative ^{195}Pt chemical shift values are not reliable indicators of relative stabilities of closely similar stereoisomers.

Hydrogen-Bonding Considerations and Internal Rotation. The free energy differences between isomers reported here cannot be attributed simply to one isomer allowing hydrogen bonding between the sarcosine N−H proton and an acceptor atom of the olefin while the other does not. The total range in K_i values is only 2 orders of magnitude, from 0.01 to 1, essentially. This corresponds to a free energy difference between isomers of 0−11.4 kJ/mol. If it were simply a matter of hydrogen-bond formation or nothing, the free energy difference should be considerably greater, 30−50 kJ/mol.[15] Of course, in the methanol solvent, the N−H proton and the R group acceptor oxygen atom would be expected to be involved in hydrogen bonding to methanol molecules, even when they are not part of an intramolecular hydrogen bond. So a complete analysis should examine the difference between intramolecular hydrogen bonding to the N−H proton and intermolecular hydrogen bonding involving the solvent molecules, as well as the effect of these solute−solvent interactions on the hydrogen bonding between solvent molecules. We have not attempted to estimate contributions from each of these separate interactions, but it is certainly plausible that the 0−11 kJ/mol stabilization implied by the equilibrium ratio can be accounted for in this way. The effects of solvent change (from methanol to water) and of substitution of the Cl atom *cis* to the olefin by H_2O or OH^- on the olefin rotamer distribution, as determined from NOE and low-temperature NMR experiments, add convincing evidence for the interpretation offered here.[9] Substantial evidence for hydrogen-bonding interactions involving protons of metal-coordinated amines or amino acids has been identified. The solid state structure and the geometric isomer preference for *cis*(*N*,*S*)- over *trans*(*N*,*S*)-Pt(sarcosine)(Me_2SO)Cl[5,16] suggest a similar intramolecular N−H···O stabilization for the favored *cis* geometric isomer. The earlier work of Salvadori and coworkers on the preferred conformations of the diastereomers of *cis*(*N*,*olefin*)benzylamineolefinic ether complexes of Pt was accounted for by invoking a similar hydrogen-bond stabilization.[6] A clear example of the strong influence of multiple M−N−H···O and M−N−H···N interactions of a metal-coordinated amine is provided by the stabilization of the *Z* conformation of polynucleotides by small amounts of $Co(NH_3)_6^{3+}$.[17] These examples all involve the N−H proton bound to a suitable Lewis base. We have even noted evidence for a quite unusual deprotonation involving the basic lone pair of a coordinated N of Pt(1,3,5-triaminocyclohexane-H)(bpy)-$(OH)^{2+}$ acting as a base to catalyze the exchange of the proton from C_6 of coordinated 2,2-bipyridine *cis* to the nitrogen.[18]

What is clear from the variation in stereoselectivities for this series of olefins is that the geometric constraints on the formation of a stable intramolecular hydrogen-bond between the N−H proton and donor atoms on the olefin moiety are severe. Only those olefins that have a good hydrogen-bond acceptor atom two bonds removed from the nearest olefinic carbon show significant selectivity. In the crystal structure of **1**, the N−H···O bond distance is 2.70 A, quite within the range that would be considered an acceptable hydrogen-bond distance. Our attempts to model the olefin rotamer stabilization by molecular mechanics calculations have met with limited success, although olefinic allyl alcohols do yield a minimum energy for rotamers in which the alcohol oxygen is oriented toward the N−H proton of the sarcosine.[19] Similar difficulties were reported by Gellman and Dado in their attempts to use molecular mechanics to model the intramolecular hydrogen-bond stabilization of di- and triamides.[20]

We have not included a full tabulation of thermodynamic data for the reactions in this report, though we made some attempts to determine ΔH and ΔS for some of the isomerization reactions from the temperature dependence of K_i. Gellman and co-workers' extensive studies of the hydrogen-bonding patterns in di- and triamides in which alternative hydrogen-bonding patterns are possible provide an appropriate parallel.[21] Hydrogen-bonding patterns and equilibrium constants for the intramolecular dimerization process were determined as a function of temperature on the basis of IR and NMR data for CH_2Cl_2 solutions of the amides to permit an assessment of ΔH and ΔS for the process. The fraction of hydrogen-bonded species they find in their amides is comparable to the ratio of isomers we observe in these olefin complexes. Ring size is important, but far from decisive, in determining which pattern is more stable, and measureable differences in ΔH and ΔS for different amides are reported. The observed effects of temperature on K_i for the systems we examined was not large enough to separate reliably the contributions of ΔH and ΔS to the Gibbs free energy change for the isomerization reactions, $\Delta G° = -RT \ln K_i$.

Correlation between K_d and K_f Values. We had initially hoped that the trend in K_f values shown in Figure 3 would enable us to quantify the effects of substituents on the electronic contribution to K_d. Then the complexes which show strong selectivity might be expected to be more stable (larger K_d) than expected on the basis of electronic effects alone. One way to test this model is to examine a plot of log K_d vs log K_f, Figure 4. A weak correlation between log K_d and log K_f is evident in the data, and a linear least-squares fit of the data is included in the graph. A second straight line with slope = 1 is drawn through the point for the 2-mb reference complexes. The fact that almost all points lie below this line can be taken as evidence

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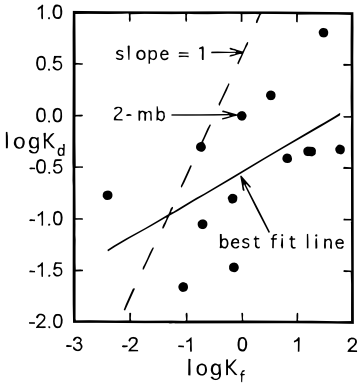

Figure 4. Plot of log K_d for reaction 1 vs log K_f for reaction 3: (—) best fit line, $\log K_d = 0.317 \log K_f - 0.54$; (– – –) line drawn through the point for the 2-mb complexes (0,0) with slope = 1.0.

that few of the other sarcosine−olefin complexes are as stabilized (by hydrogen bonding) as is the 2-mb complex, so their K_d values are less than would be expected on the basis of their K_f values in $PtCl_3(olefin)^-$ complexes where this stabilization would be lacking. However, some of the least stereoselective olefins lie closer to the line than some olefins that are among the most stereoselective, so this attempt to separate cleanly the electronic and steric effects on olefin bonding on the basis of a comparison of K_d and K_f values has somewhat limited utility.

Principal Conclusions. The principal conclusions to be drawn about the effect of olefin structure (R in CH_2═CHR) on the strength and stereoselectivity of binding to the chiral background provided by the $NH(CH_3)$ of chelated sarcosine in *cis*(*N*,*olefin*)-Pt(CH_2═CHR)(sar)Cl and on the strength of binding to Pt in $PtCl_3(CH_2$═$CHR)^-$ species can be summarized as follows:

(a) The almost complete stereoselectivity of coordination found for 2-mb in **1** is the exception rather than the rule. Only ethenesulfonate and vinyl phosphonate show comparable selectivity.

(b) When significant stereoselectivity is found, the *SR* isomer, the only significant isomer of **1**, is the one that is favored.

(c) Significant stereoselectivity requires a good hydrogen-bond acceptor atom on the olefin, apparently to allow facile formation of an intramolecular hydrogen bond with the N−H proton of coordinated sarcosine located *cis* to the olefin.

(d) Exceptional selectivity is observed only when the hydrogen-bond acceptor atom on the olefin is two bonds (or in one case, **25**, one bond) removed from the closest olefin carbon, which permits formation of a five- or six-membered ring hydrogen-bonded structure.

(e) Though some of the most stereoselective olefins are also among the most strongly bound, exceptions to this pattern are frequent and of both kinds: some strongly bound olefins show no selectivity and some weakly bound olefins are among the most selective. This poor correlation is most evident in Figure 2, a plot of log K_i vs log K_d.

(f) Zeise's salt analogs show a strong correlation between ^{195}Pt chemical shifts and relative formation constants (Figure 3) with the more stable complexes showing the greatest shielding, but the correlation is not strong enough to permit one to determine the relative equilibrium stability of closely similar isomers on the basis of ^{195}Pt chemical shift data alone.

(g) Both electronic and steric/hydrogen-bonding effects contribute to the observed variation in stabilities of sarcosine−olefin complexes, and the ^{195}Pt chemical shifts and K_f values for Zeise's salt analogs (Figure 4) provide a rough index of the electronic contribution to relative stabilities.

Potential Applications to Catalytic Processes. Any chiral template that binds a prochiral olefin stereoselectively might serve as a key component in the catalytic conversion of the olefin to another compound in a stereoselective manner. For example, if either *cis* or *trans* addition of HX to the double bond of the initially coordinated olefin is strongly favored, a specific stereoisomer will be produced in the reaction. Of course, the sarcosine complexes reported here would not be appropriate for such applications, since the chirality at the nitrogen site is not controlled. Compound **1**, which is shown in Scheme 1 as the *RS* diastereomer, actually exists as a racemic mixture of *RS* and SR species. Facile exchange of the olefin moiety and lone-pair inversion at the coordinated nitrogen (in its deprotonated form) insures equilibration of the two species. Under the conditions of our experiments (no excess base and in methanol solvent), nitrogen inversion is relatively slow,[22] but making other mixed olefin−sarcosine complexes from **1** by olefin exchange yields both *RS* and *SR* isomers of the product, so no selectivity is possible in the subsequent reaction with HX, for example. Fortunately, the chemistry and stereoselectivity of parallel proline−olefin complexes of Pt(II) are sufficiently similar to make them an attractive alternative.[5,9] The chirality at the nitrogen atom of metal-coordinated *S* (at α-C) proline is constrained by the simultaneous formation of both the five-membered chelate ring and the five-membered pyrrolidine ring of coordinated (*S*)-proline. This insures that the proline counterpart of **1** is a single optical isomer, so the (*S*)-proline−prochiral olefin complexes which show strong stereoselectivity of coordination might be expected to provide a convenient pathway to specific stereoisomers of the products of subsequent reactions. We are currently investigating reactions that might exploit these properties of the stereochemically well-defined proline−olefin complexes. The sarcosine complexes described in this report are proving to be convenient and effective guides to these explorations.

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