$$Fe(CO)_4 \xrightarrow{\text{wall}} Fe + 4CO$$

$$Fe(CO)_4 + B_5H_9 \rightarrow \text{ferraboranes}$$

As demonstrated with the hot–cold reactor, the initial ferraborane produced in the pyrolysis is $B_5H_9Fe(CO)_3$. Thus, we also write

$$Fe(CO)_4 + B_5H_9 \rightarrow B_5H_9Fe(CO)_3 + CO$$

Finally, the other ferraboranes that have been observed in this system may well be produced by the subsequent decomposition of $B_5H_9Fe(CO)_3$. For example, since $Fe(CO)_3B_5H_9$ is known to produce $Fe(CO)_3B_4H_8$ on heating (see above) and since nido heteroboranes are known to disproportionate,[15] the following reaction may take place:

$$2Fe(CO)_3B_5H_9 \rightarrow Fe(CO)_3B_4H_8 + Fe(CO)_3B_6H_{10}$$

The latter product, which is an analogue of B_7H_{11} (a very unstable borane),[16] may well decompose and, thus, contribute to the substantial amount of intractable material formed in the system.

These results allow one to explain the fact that the reported preparations of both $Fe(CO)_3B_4H_8$[3] and $Fe(CO)_3B_5H_9$[2] use essentially the same type of hot–cold pyrolytic reactor. Clearly, the ferraborane observed as product will depend on the net effectiveness of trapping at the cold surface. This in turn depends on the distance between hot and cold surfaces *and* the mean free path, i.e., the pressure. Reactor geometry is important, but, in addition, in this particular reaction as considerable quantities of CO are produced, the pressure in the reactor rises with time thereby decreasing the mean free path and effectiveness of trapping. Thus, removal of the CO enhances formation of $Fe(CO)_3B_5H_9$ while letting the pressure build up results in formation of the more stable $Fe(CO)_3B_4H_8$.

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Registry No. $B_5H_9Fe(CO)_3$, 61403-41-6; $Fe(CO)_5$, 13463-40-6; B_5H_9, 19624-22-7.

References and Notes

(1) T. P. Fehlner, J. Ragaini, M. Mangion, and S. G. Shore, *J. Am. Chem. Soc.*, **98**, 7085 (1976).

(2) J. A. Ulman and T. P. Fehlner, *J. Chem. Soc., Chem. Commun.*, 632 (1976).

(3) N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 718 (1974).

(4) Other analogues of B_6H_{10} are known: $(\eta^5\text{-}C_5H_5)FeB_5H_{10}$ isomers, R. Weiss and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 8087 (1977); $Mn(CO)_3B_5H_{10}$, M. B. Fischer, D. F. Gaines, and J. D. Kessler, Abstracts, 174th National Meeting of the American Chemical Society, Chicago, IL, Sept 1977, No. INOR 167.

(5) Other analogues of B_5H_9 are isomeric species of composition $(\eta^5\text{-}C_5H_5)CoB_4H_8$: V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973); L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 118 (1976); V. R. Miller, R. Weiss, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 5646 (1977); R. Weiss, J. B. Bowser, and R. N. Grimes, *Inorg. Chem.*, **17**, 1522 (1978).

(6) Among the other ferraboranes reported are the following: $\mu\text{-}Fe(CO)_4B_2H_5^-$, G. Medford and S. G. Shore, *J. Am. Chem. Soc.*, **100**, 3953 (1978); $\mu\text{-}Fe(CO)_4B_6H_{10}$, A. Davison, D. D. Traficante, and S. S. Wreford, *ibid.*, **96**, 2802 (1974); $\mu\text{-}Fe(CO)_4B_7H_{12}^-$, O. Hollander, W. R. Clayton, and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 605 (1974), and M. Mangion, W. R. Clayton, O. Hollander, and S. G. Shore, *Inorg. Chem.*, **16**, 2110 (1977); two $Fe\text{-}Be_3H_8$ compounds, D. F. Gaines and S. Hildebrandt, *ibid.*, **17**, 794 (1978); $Fe_2(CO)_6B_2H_6$, E. L. Andersen and T. P. Fehlner, *J. Am. Chem. Soc.*, **100**, 4606 (1978).

(7) J. A. Ulman, E. L. Andersen, and T. P. Fehlner, *J. Am. Chem. Soc.*, **100**, 456 (1978).

(8) M. Mangion, J. D. Ragaini, T. Schmitkons, and S. G. Shore, *J. Am. Chem. Soc.*, in press.

(9) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, 1969.

(10) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Am. Chem. Soc.*, **95**, 6629 (1973).

(11) G. L. Geoffroy and J. R. Lehman, *Adv. Inorg. Chem. Radiochem.*, **19**, 198 (1977).

(12) H. Beal and C. H. Bushweller, *Chem. Rev.*, **73**, 465 (1973).

(13) J. I. Kaplan and G. Fraenkel, *J. Am. Chem. Soc.*, **94**, 2907 (1972), and references cited therein.

(14) F. A. Cotton, A. K. Fischer, and G. Wilkinson, *J. Am. Chem. Soc.*, **81**, 800 (1959).

(15) T. Onak, "Boron Hydrides", E. L. Muetterties, Ed., Academic Press, New York, 1975, Chapter 10.

(16) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, 1963.

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^1H, ^{13}C, and ^{195}Pt Nuclear Magnetic Resonance Studies on Diastereomeric Platinum(II) Complexes of Prochiral Olefins Containing a Chiral Amino Acid Ligand

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The nature of diastereomeric discrimination in the series of platinum(II) complexes *trans*(*N*,olefin)-chloro(*N*-methyl-(*S*)-prolinato)(olefin)platinum (olefin = propene, *trans*-2-butene, *tert*-butylethylene, styrene, *p*-chlorostyrene, or *p*-methoxystyrene) has been investigated by using ^1H, ^{13}C, and ^{195}Pt nuclear magnetic resonance. The observed trend of diastereomeric difference in the NMR properties (especially $^1J_{PtC}$ for coordinated carbons and δ_{Pt}) indicated that the abundant diastereomers had a stronger platinum–olefin bonding, and thus enhanced thermodynamic stability. Contrasting NMR features found for the styrene and *tert*-butylethylene diastereomers are interpreted in terms of a different mode of distortion of coordinated olefins upon complex formation.

Introduction

Enantioface differentiation[1] in the η^2 coordination of prochiral olefins to chiral metallic species often forms a key step for asymmetric syntheses with olefinic compounds used as sources.[2] Because of quite high stability, platinum(II)–olefin complexes have been utilized as a suitable model for studying the stereoselectivity in this step in the presence of an optically active ligand.[3]

Since NMR spectroscopy is useful for the analysis of molecular structures in solutions or the elucidation of bonding characteristics of molecules, detailed examination of various NMR properties should afford a precise description of the nature of diastereomeric molecules. As far as coordination compounds are concerned, platinum is one of the most favorable metals for this purpose, because extra information on nuclear spin coupling is obtainable by virtue of the presence of a ^{195}Pt nucleus ($I = {}^1/_2$, natural abundance 33.8%).

In the present paper, ^1H, ^{13}C, and ^{195}Pt NMR data have been collected for a number of diastereomeric platinum(II)–olefin complexes and combined to study (i) their solution

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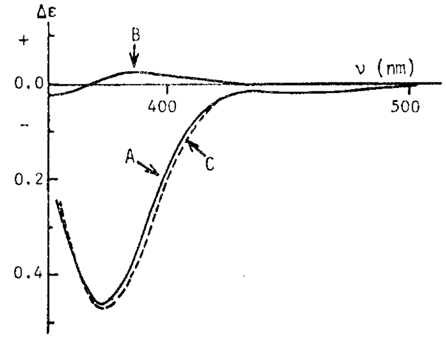


Figure 1. Circular dichroism spectra of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(olefin)] complexes (olefin: A, styrene; B, ethylene). The curve C corresponds to A − B.

structures, (ii) the diastereomeric discrimination of the platinum–olefin bonding characteristics, and (iii) the interaction between the substituents on chiral centers. The choice of appropriate olefins permitted the diastereomeric compositions to be directly determined by ^{1}H NMR spectroscopy in the equilibrated state. *N*-Methyl-(*S*)-proline was chosen as the chelate amino acid ligand to provide sufficient solubility of the complexes for NMR measurements.[4]

Experimental Section

N-Methyl-(*S*)-proline (*N*-Me-*S*-Pro) was obtained by the formic acid–formaldehyde methylation[5] of (*S*)-proline virtually without racemization, $[\alpha]^{25}_{D}$ −79.9° (*c* 1.76, H_2O; lit.[6] −80.2°). Ethanol–acetone was found to be an excellent solvent for the recrystallization of this compound. Complexes of the type *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(olefin)] (olefin = propene, *trans*-2-butene, *tert*-butylethylene, styrene, *p*-chlorostyrene, or *p*-methoxystyrene) were prepared by olefin exchange[3] with the corresponding ethylene complex.[7] All gave satisfactory elemental analyses. The chemicals used were obtained from standard commercial sources and were of GR grade.

The circular dichroism (CD) measurement was carried out on a JASCO J-20 spectrometer in a chloroform solution at 25 °C. ^{1}H NMR spectra were recorded on Hitachi R-20B (60 MHz) and JEOL PS-100 (100 MHz) spectrometers. ^{13}C and ^{195}Pt NMR spectra were obtained in a deuteriochloroform solution (0.5 M) with noise-modulated proton decoupling on Fourier transform pulsed NMR spectrometers, operating at 25.03 MHz (JEOL PFT-100) and 21.35 MHz (JEOL FX-100), respectively. Field-frequency control (lock) was effected by means of a solvent deuterium resonance. In each case 16 384 data points were acquired, yielding 8192 output points in the phase-corrected real spectrum. The ^{13}C chemical shifts were measured relative to the internal solvent resonance and are reported in ppm downfield from Me_4Si using the conversion $\delta_{Me_4Si} = \delta_{CDCl_3} - 76.98$ ppm. All the data are the results of at least two independent runs with a precision of ±0.05 ppm or better. The accuracy of the relative magnitude of $^1J_{PtC}$ values was 0.6 Hz (5000 Hz/8192 output points) for the individual spectrum of the diastereomeric mixtures. The ^{195}Pt chemical shifts are reported by use of the standard frequency 21.4 MHz[8] that is related to the proton resonance of (internal) Me_4Si at a frequency of 100 MHz exactly (high frequencies being taken as positive).

In determining the diastereomeric ratio, ^{1}H NMR measurements were repeated on an expanded scale of the standard sweep width, selecting both radio-frequency power and sweep rate so as to avoid saturation of signal intensities. Values were obtained within an error of 5% (standard deviation).

Results

Table I. Circular Dichroism and Preponderant Absolute Configuration of Coordinated Olefins for the *trans*-(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(olefin)] Complexes

olefin[c]	Δε,[a] M^{-1} cm^{-1}	ν_{max}, nm	diastereomeric ratio[b]
propene	−0.07	373	1.04
trans-2-butene	−0.08	378	1.12
tert-butylethylene	−0.18	375	1.24
p-chlorostyrene	−0.50	375	1.43
styrene	−0.47	375	1.83
p-methoxystyrene	−1.07	375	1.63

[a] Corrected for the contribution of the *N*-Me-*S*-Pro moiety by use of the CD of the corresponding ethylene complex. [b] In $CDCl_3$ solution (0.5 M) at 35 °C. [c] The absolute configuration is *R* in all cases.

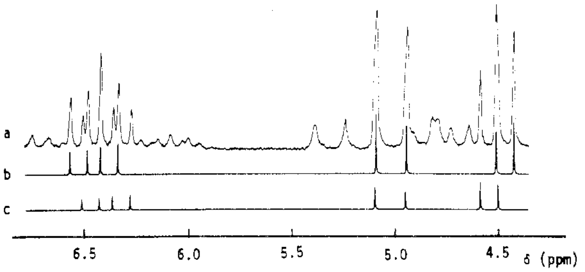


Figure 2. ^{1}H NMR spectrum (vinyl region) of the diastereomeric mixture of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(styrene)] complex at 25 °C and 100 MHz in $CDCl_3$ solution: (a) experimental spectrum (taken after equilibrium); (b) and (c) simulated spectra (without ^{195}Pt coupling) of the abundant and less abundant diastereomers, respectively.

Circular Dichroism Spectra. The CD spectrum of the diastereomeric complexes of styrene has been measured in the equilibrated state and is reproduced in Figure 1. The absorption band at 375 nm is negative in sign. It was corrected for the small contribution of the amino acid moiety by use of the CD spectrum of the corresponding ethylene complex.[9] A quadrant rule has been proposed for the relationship between the absolute configuration of the coordinated olefin and the circular dichroism associated with the lowest energy d–d transition of the platinum chromophore in square-planar platinum(II) complexes.[10] According to this rule, the result would indicate the preponderance of the *R* absolute configuration of the coordinated styrene.

It is noteworthy that all the complexes studied here exhibited a negative CD absorption near 375 nm (Table I), showing a uniform orientation of asymmetric induction (*R*) in the presence of the common chiral ligand. This contrasts with the case of *cis*-[dichloro((*S*)-*p*-tolyl methyl sulfoxide)(olefin)platinum] diastereomers, since a different preference of induction was observed among seemingly analogous olefins for this type of complex.[11]

Diastereomeric Proportions and ^{1}H NMR Spectra. Diastereomeric proportions of each of the complexes were determined quantitatively in the equilibrated state (0.5 M, $CDCl_3$ solution) by means of ^{1}H NMR spectroscopy, which showed a sufficient amount of chemical shift difference for the analyses between the diastereomers. The diastereomers were equilibrated rapidly and spontaneously at 25 °C for styrene and its derivatives.[12,13] For the diastereomers of aliphatic olefins, second-order asymmetric transformation[14] occurred during the crystallization procedure, and the rates of equilibration were very slow (even in the presence of a comparable amount of free olefins);[11] the ^{1}H NMR spectra of the freshly dissolved solution of the isolated complexes gradually changed reaching equilibrium in about a day, while the sign and the intensity of the CD absorption (diluted to ca. 10^{-3} M just before measurement) altered synchronously to conform to the change in the diastereomeric composition of the nondiluted solutions. This behavior ensured that the NMR gave the quantitative diastereomeric ratio. The results are tabulated in Table I.

Figures 2 and 3 show the ^{1}H NMR spectra (vinyl region) of the diastereomeric mixture of styrene and *tert*-butylethylene, respectively, together with simulated patterns[15] used to give unambiguous peak assignments for each of the diastereomers.

Table II. ^{1}H NMR Spectral Parameters (Vinyl Protons) of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(RCH=CH$_2$)] Complexes[a,d]

		complex					free ligand					
R	confign[c]	$\delta_{H(g)}$	$\delta_{H(t)}$	$\delta_{H(c)}$	$J_{H(g)H(t)}$	$J_{H(g)H(c)}$	$\delta_{H(g)}$	$\delta_{H(t)}$	$\delta_{H(c)}$	$J_{H(g)H(t)}$	$J_{H(g)H(c)}$	$J_{H(t)H(c)}$
t-C_4H_9[b]	*R*	5.75	4.63	4.60	8.26	14.85	5.86	4.82	4.91	10.9	16.8	1.3
	S	5.76	4.62	4.56	8.51	14.62						
p-ClC_6H_4	*R*	6.39	4.54	5.00	8.5	14.9	6.66	5.23	5.67	10.7	17.6	1.0
	S	6.34	4.59	5.00	8.5	14.9						
C_6H_5	*R*	6.45	4.47	5.02	8.5	14.9	6.72	5.21	5.71	10.5	17.6	1.1
	S	6.39	4.55	5.02	8.5	14.9						
p-$CH_3OC_6H_4$	*R*	6.46	4.39	4.90	8.5	14.9	6.68	5.10	5.58	11.1	17.9	1.1
	S	6.42	4.46	4.90	8.5	14.9						

[a] δ's in ppm from internal Me$_4$Si reference; *J*'s in Hz. [b] Determined with the aid of spectral simulations. [c] Absolute configuration of coordinated olefin. [d] Spin coupling between H(t) and H(c) was not clearly observed for the coordinated state except the *tert*-butylethylene complexes (1.28 Hz; cf. Figures 2 and 3).

Table III. ^{195}Pt Coupling Constants for Olefinic Protons of *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(RCH=CH$_2$)] Complexes[a]

	J_{PtH},[b] Hz		
R	H(g)	H(t)	H(c)
t-C_4H_9	63.5	64.4	59.6
p-ClC_6H_4	66.5	60.4	58.8
C_6H_5	65.7	60.4	59.0
p-$CH_3OC_6H_4$	65.4	61.7	59.7

[a] Distinctive difference was not observed between the diastereomers. [b] Within the accuracy of 0.5 Hz.

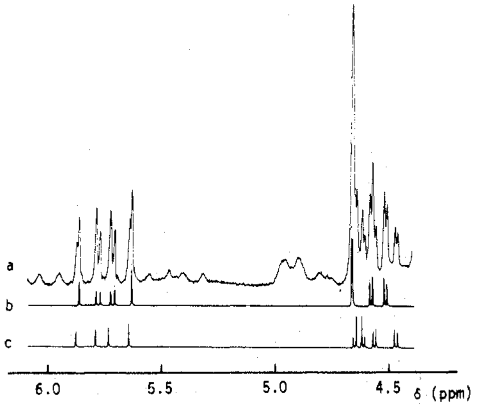
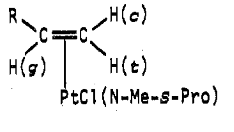


Figure 3. ^{1}H NMR spectrum (vinyl region) of the diastereomeric mixture of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(*tert*-butylethylene)] complex at 25 °C and 100 MHz in CDCl$_3$ solution: (a) experimental spectrum (taken before equilibrium with a greater abundance of the stable diastereomer); (b) and (c) simulated spectra (without ^{195}Pt coupling) of the abundant and less abundant diastereomers, respectively.

The simple spectral pattern of the styrene diastereomers permitted a first-order interpretation (AMX approximation[16]) for the set of three olefinic protons (designated as in I) and



I: R = CH$_3$, *tert*-C$_4$H$_9$, *p*-ClC$_6$H$_4$
C$_6$H$_5$, *p*-CH$_3$OC$_6$H$_4$

similarly for other styrene systems. For the *tert*-butylethylene diastereomers, repeated simulations were required to analyze the two ABC spin systems;[16] the assignment was confirmed by comparing the simulated pattern at 60 MHz with an experimental spectrum also at 60 MHz. The ^{1}H NMR data are collected in Tables II and III.

For the styrene complexes, considerable line broadening was observed upon the addition of excess olefin, although the effect was scarcely detected for other olefins. Variation of temperature showed, that the line broadening was much more pronounced for the less abundant diastereomer than for the abundant one (Figure 4) for all the styrenes. This shows that the rate of the olefin exchange reaction is faster for the less abundant diastereomer in the temperature range studied. For solutions of the styrene complexes, obtained after the rigorous removal of free olefin by evacuation, the diastereomer ratios were essentially unchanged in the equilibrated state between 0 and 60 °C, and there was no detectable line broadening.

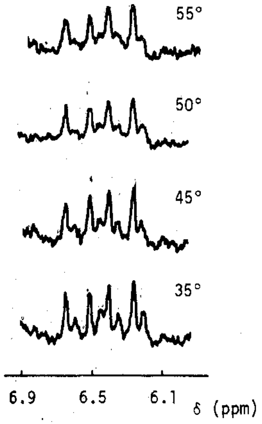


Figure 4. Temperature-variation profile of the ^{1}H NMR signals (H(g), 60 MHz) of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(styrene)] diastereomers in the presence of free styrene (mole ratio of 0.088 to the complex).

^{13}C and ^{195}Pt NMR Spectra. The ^{13}C NMR spectra of each of the diastereomeric complexes (measured in the equilibrated state) showed significant chemical-shift differences for nearly all the carbons, reflecting the subtle difference in chemical (magnetic) environment between the diastereomers. Most importantly, the coordinated olefinic carbons showed not only different chemical shifts but also different values for the platinum–carbon one-bond coupling constant ($^1J_{PtC}$) between the diastereomers (Figure 5), although the propene and *trans*-2-butene complexes with a diastereomeric ratio near to unity gave essentially the same $^1J_{PtC}$ values. The ^{13}C and ^{195}Pt NMR properties are summarized in Tables IV and V.

^{13}C NMR data for a series of para-substituted styrene–platinum(II) π complexes[17] show the following trends. Electron donor groups in the para position increased markedly both the shielding of C(1) (methylene carbon) and $^1J_{PtC(1)}$ while the shielding of C(2) (methine carbon) and $^1J_{PtC(2)}$ were decreased. This trend is seen in Table IV for the averaged values of the styrene diastereomers (para substituent: Cl, H, CH$_3$O). The more abundant diastereomer has a more favorable interaction with the metal. It is of interest that a relationship similar to the substituent effect holds for both δ_C and $^1J_{PtC}$ values for each diastereomeric pair of styrenes; the abundant diastereomer acting as though it possessed a more electron-donating substituent.

Table IV. ^{13}C (Vinyl Carbons) and ^{195}Pt NMR Spectral Parameters of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(olefin)] Complexes[a]

olefin	confign[b]	$^{1}J_{PtC}$ =CH$_2$	$^{1}J_{PtC}$ =CHR	δ_C(complex) =CH$_2$	δ_C(complex) =CHR	δ_C(free ligand) =CH$_2$	δ_C(free ligand) =CHR	δ_{Pt}
propene	*R*	165.4	154.4	71.30	98.19	115.9[c]	136.2[c]	2001
	S	165.4	154.4	71.42	98.05			2001
trans-2-butene	*R*		158.7		91.81		126.0[c]	2010
	S		158.7		91.81			2010
tert-butylethylene	*R*	158.1	154.4	65.68	115.17	108.85	149.79	2038
	S	155.6	154.4	65.20	115.90			2043
p-chlorostyrene	*R*	175.8	137.9	62.08	96.73	114.38	135.59	2142
	S	174.6	140.4	62.62	96.44			2131
styrene	*R*	176.2	135.0	61.22	98.50	113.73	136.84	2152
	S	174.0	136.6	61.98	98.07			2138
p-methoxystyrene	*R*	183.1	125.7	58.52	100.71	111.46	136.14	2168
	S	175.8	126.9	59.23	100.51			2162

[a] δ's in ppm; *J*'s in Hz. [b] Absolute configuration of coordinated olefin. [c] Data are from Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* 1971, *36*, 2757 (converted using $\delta_{Me_4Si} = \delta_{CS_2} - 193.7$ ppm).

Table V. ^{13}C NMR Chemical Shifts (*N*-Me-*S*-Pro Carbons) of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(olefin)] Complexes[a]

olefin	confign[c]	C(α)[b]	C(β)	C(γ)	C(δ)	NCH$_3$	C=O
propene	*R*	73.57	29.31	22.92	61.01	48.04	183.25
	S	73.57	29.31	22.92	60.84	48.40	183.25
trans-2-butene	*R*	73.13	28.97	22.50	60.30	47.89	182.69
	S	73.22	28.97	22.50	60.30	47.89	182.69
tert-butylethylene	*R*	73.22	29.19	23.16	61.28	48.25	183.59
	S	73.74	29.45	23.00	60.74	48.25	183.40
p-chlorostyrene	*R*	74.49	29.19	23.16	61.50	48.30	182.69
	S	74.40	29.75	23.24	61.50	49.13	183.13
styrene	*R*	74.21	28.79	22.85	61.07	47.84	182.44
	S	74.05	29.52	23.03	61.07	48.75	182.99
p-methoxystyrene	*R*	74.35	28.94	22.97	61.15	47.94	182.69
	S	74.14	29.62	23.11	61.15	48.91	183.22

[a] In ppm; α, β, etc. designate the pyrrolidine ring carbons. [b] About 18 Hz of spin–spin coupling with ^{195}Pt. [c] Absolute configuration of coordinated olefin.

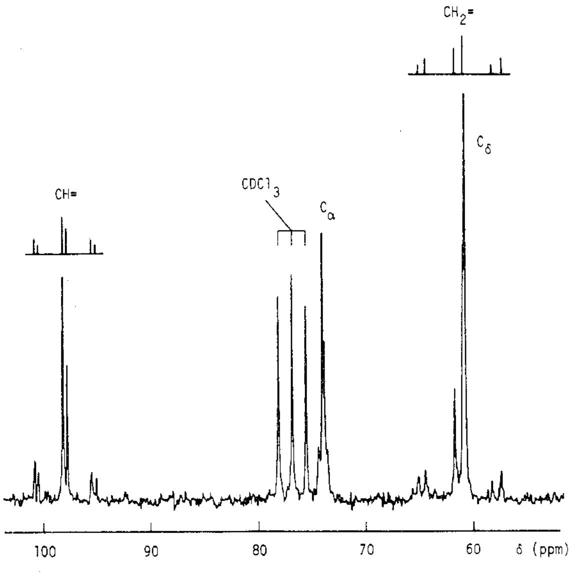


Figure 5. ^{13}C NMR spectrum (vinyl region) of the diastereomeric mixture (equilibrated) of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)-(styrene)] complex at 25 °C and 25.03 MHz in CDCl$_3$ solution.

The diastereomeric discrimination in the NMR chemical shift of the central metal atom in the complex (Figure 6) is scarcely reported.[18] A trend is shown in Table IV that the more electron-donating the para substituent of styrene, the more deshielded is the ^{195}Pt resonance. It should be noticed that the abundant diastereomer exhibited a more deshielded ^{195}Pt resonance than the less abundant one for all the styrenes.

Discussion

Coordination Structure in Solutions. For square-planar platinum(II) π complexes of monosubstituted olefins with different neighboring cis ligands, two isomers are possible which differ by a 180° rotation about the metal–olefin bond axis (the vinylic substituent points to either of the cis ligands); the isomers usually interchange freely at room temperature.[19]

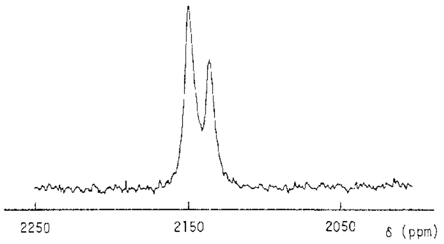


Figure 6. ^{195}Pt NMR spectrum of the diastereomeric mixture (equilibrated) of the *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(styrene)] complex at 25 °C and 21.35 MHz in CDCl$_3$ solution.

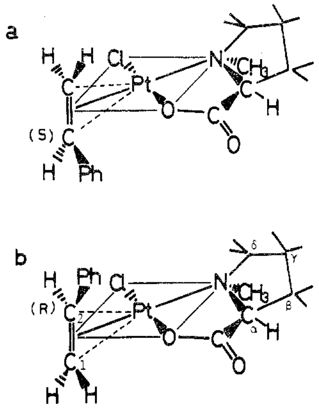


Figure 7. The pair of diastereomeric complexes of *trans*(*N*,olefin)-[PtCl(*N*-Me-*S*-Pro)(styrene)]; the rotamers with a phenyl group pointing to the smaller cis-ligand atom (O) are shown.

According to the observations of Lewis et al.,[20] the van der Waals radius of the cis-ligand atom is a measure of the relative stability of the corresponding rotamers. Judged by this criterion (O < Cl), the favorable rotamers with the vinylic substituent pointing to the cis O ligand are shown in Figure 7, where the position of the coordinated olefin is depicted conceptually as perpendicular to the coordination plane.

Since even propene showed an isomer ratio as large as 1:3 in chloro(acetylacetonato)(propene)platinum which also contained cis O and Cl ligands and since this value was rather insensitive to temperature change,[20] we presume that the orientation of the vinylic substituent is primarily determined by this kind of steric requirement for both of the diastereomers and that the rotamers with the vinylic substituent pointing to the cis O ligand populate predominantly in the solutions. It was suggested that the rotation of a chiral sulfoxide ligand in the cis position might cause a different preference of induction among seemingly analogous olefins.[11] In the present case, however, the chelated nature of the chiral ligand and the simplified situation of olefin rotamers may lead to the uniform orientation (*R*) of asymmetric induction.

The nonbonded interaction between the vinylic substituent and the cis ligands seems to exert a different kind of steric effect. Since we found larger values of both $J_{\mathrm{PtH(g)}}$ and $J_{\mathrm{PtH(t)}}$ compared to that of $J_{\mathrm{PtH(c)}}$ for the α-olefin complexes (Table III), the vinylic substituents would be twisted away from the platinum atom around the carbon–carbon bond axis.[21]

With regard to the platinum(II) complexes of styrenes, the distortion of sliding was reported for para-substituted styryl(pyridyl)platinum(II) complexes, *trans*-[$PtCl_2(NC_5H_4X)(p\text{-}YC_6H_4CH{=}CH_2)$] ($Y = NO_2$, X = Cl; Y = H, X = Me; $Y = NMe_2$, X = Me).[22] On going from $Y = NO_2$ to Y = H to $Y = NMe_2$, the Pt–C(1) distance becomes shorter, and the Pt–C(2) distance becomes longer, while the position at which the $PtCl_2N$ coordination plane bisects the styrene C=C bond is displaced from the midpoint toward C(1) by 0.085 Å ($Y = NO_2$), 0.117 Å (Y = H), and 0.221 Å ($Y = NMe_2$). This type of distortion is not so important for aliphatic olefins; twisting and tilting were noticed for them.[23,24]

Diastereomeric Difference in the Coordination of Styrenes. The introduction of para substituents in the platinum(II)–styrene complexes causes systematic changes in various kinds of molecular characteristics, i.e., the infrared spectroscopic properties (ν(PtC_2–ring), etc.),[17] equilibrium constants,[17,25] and so on. All of them were interpreted to indicate an increase in the platinum–styrene bond strength with the increasing electron-donating ability of the para-substituent and were claimed to be consistent with the view of the predominance of donation from the olefin π orbital to the platinum σ orbital in the olefin–metal bond.[17] As far as ^{13}C NMR properties are concerned, the presence of an electron-donating group in the para position increases the shielding of C(1) and $^1J_{\mathrm{PtC(1)}}$ and decreases the shielding of C(2) and $^1J_{\mathrm{PtC(2)}}$. The platinum resonance is also deshielded with increasing electron-donating ability of the para substituent. Therefore, the diastereomeric difference observed for the corresponding ^{13}C and ^{195}Pt NMR properties that *the abundant diastereomers act as though they possessed more electron-donating substituents* leads us to the conclusion that the stable diastereomers have a stronger platinum–olefin bonding, because electrons are more efficiently donated from the olefin π orbital to the platinum σ orbital. The viewpoint of the strength of coordination bonding should be emphasized in understanding asymmetric catalysis, since a net increase in the metal–olefin bond strength will enhance the thermodynamic stability of the abundant diastereomers.

Taking into account the direction of the distortion of C(1)–Pt–C(2) triangle with the change of para substituent, the platinum atom in the stable diastereomers would be positioned closer to the C(1) carbon atom. The ^1H NMR data showing that the abundant diastereomers have more-shielded methylene proton resonances ($\delta_{\mathrm{H(t)}}$) and less-shielded methine proton resonances ($\delta_{\mathrm{H(g)}}$) (Table II) seem to support this effect of sliding.

Diastereomeric Difference in the Coordination of *tert*-Butylethylene. It is of interest that the *tert*-butylethylene diastereomers exhibited quite different NMR properties relative to those of styrenes: (i) the abundant diastereomer has less-shielded methylene proton resonances and a more-shielded methine proton resonance (Table II), (ii) the geminal spin coupling $J_{\mathrm{H(t)H(c)}}$ is essentially retained for both of the diastereomers (Table II), which seems rather rare in the case of platinum(II)–olefin complexes,[26] (iii) the difference between the values of $^2J_{\mathrm{PtH(t)}}$ and $^2J_{\mathrm{PtH(c)}}$ is very large (Table III), (iv) the order of the high-field coordination shift of the olefinic carbons[27] is abundant diastereomer < less abundant diastereomer for C(1) and abundant diastereomer > less abundant diastereomer for C(2) (Table IV), and (v) the order of platinum shift is abundant diastereomer < less abundant diastereomer (Table IV).

The data in items (ii) and (iii) suggest that twisting is an important distortion occurring in the coordination of this olefin. Taking into consideration that $^1J_{\mathrm{PtC(2)}}$ is virtually the same for both diastereomers (Table IV) and the data in items (i) and (iv), the effect of sliding may not be important for the diastereomeric differentiation of this complex. Twisting and/or tilting, both of which occur for platinum(II)–isopropylethylene[23] and –1-butene[24] complexes, are conceivably significant. Since the larger $^1J_{\mathrm{PtC}}$ value ($^1J_{\mathrm{PtC(1)}}$) is an indication of the stronger platinum–carbon bond for platinum(II)–olefin complexes,[28] the abundant diastereomer seems to have a stronger platinum–olefin bond also in this case.

Diastereomeric Difference in the *N*-Methyl-(*S*)-proline Moiety. It was reported that a Karplus type[29] dihedral angle dependence held for the three-bond vicinal coupling constant $^3J_{\mathrm{PtC}}$ in the Pt–N–C–C fragments.[30] The failure to observe the ^{195}Pt satellite for the pyrrolidine ring carbons, C(β) and C(γ), strongly suggests that the dihedral angles in the corresponding four-atom fragments are approximately 90° for all the complexes.

The carbon chemical shifts of the *N*-methyl-(*S*)-proline moiety (Table V) are a good measure of diastereomeric difference in the interaction of two chiral moieties. Since trans disubstitution of ethylene gives no energetic gain in the coordinated state by such distortions as sliding and/or twisting other than tilting,[31,32] it is reasonable that the *trans*-2-butene diastereomers show no chemical shift difference, except a very small difference in C(α) (note that appreciable differentiations occurred for propene diastereomers which showed a similar magnitude of small enantioselection).

The existence of considerable differences in δ_{CO} and $\delta_{\mathrm{C}(\beta)}$ between the diastereomers of styrenes, with no difference in $\delta_{\mathrm{C}(\delta)}$, seems to support the postulation concerning the preferred orientation of phenyl groups (Figure 7). Differences are again observed for the *tert*-butylethylene diastereomers, which would reflect the different mode of coordination and diastereomeric discrimination for this complex: (i) the order of carbonyl carbon shielding is abundant diastereomer < less abundant diastereomer, (ii) a substantial difference exists in $\delta_{\mathrm{C}(\delta)}$, and (iii) no difference is observed for $\delta_{\mathrm{NCH_3}}$.

Notwithstanding the presence of the chemical shift differences in the amino acid moiety, it should be emphasized that the observed orientation of asymmetric induction (*R*) appears in conflict with the picture of steric control[33] via a repulsive interaction between the bulky groups, i.e., the vinylic substituent and the pyrrolidine ring (Figure 7). We previously suggested that a certain kind of molecular orbital reflected the diastereotopic atomic arrangement of the platinum(II)–olefin complexes.[12] A stereoelectronic factor, as was found in the bonding characteristics of the platinum–olefin coordination bond, should be important in the present enantioselection.

Diastereomeric Difference in the Olefin Exchange Reaction. It is likely that the difference in the thermodynamic stability affects the reactivity of the diastereomers. The rate of the inversion of coordinated styrenes in the complex *trans*(*N*,-olefin)-[PtCl(*S*-Pro)(*p*-$YC_6H_4CH{=}CH_2$)] is quite sensitive to the nature of the para substituent Y, increasing as the electron-donating ability decreases.[13] This fact was claimed to be consistent with the view of a stronger platinum–styrene bond for a more electron-donating Y.[17] In view of the parallelism between the substituent effect and the diastereomeric difference in the styrene complexes, the observed trend indicates that the following relationship also holds within the respective diastereomeric pairs: the weaker the platinum–olefin bond, the faster the reaction rate.

Conclusions

(1) Substantial differences were found for the first time in $^1J_{PtC}$ for coordinated carbons and δ_{Pt} between the diastereomeric complexes of platinum(II) which contain chirality in both the coordinated olefin (*R* or *S*) and the *N*-methyl-(*S*)-proline chelate ligand.

(2) The observed trend in ^{13}C and ^{195}Pt NMR properties was interpreted as an indication of the stronger platinum–olefin bond for the abundant diastereomers, which should enhance their thermodynamic stability.

(3) Although phenyl and *tert*-butyl groups have both been recognized as highly "bulky" substituents, contrasting features were found in the NMR properties of styrene and *tert*-butylethylene diastereomers. Sliding appears to be the distinctive distortion in the diastereomeric discrimination of the former, in contrast to twisting and/or tilting in that of the latter.

(4) The ^{13}C chemical shifts of the *N*-methyl-(*S*)-proline moiety reflected well the diastereomeric difference of its interaction with vinylic substituents and were consistent with the postulated conformational preference of coordinated olefins.

(5) The rate of the exchange reaction with free olefins was faster for the less abundant diastereomers for all the styrene complexes. The observed trend is in accord with a view that the weaker the platinum–olefin bond, the faster the reaction rate.

Registry No. *trans*(*N*,*R*-olefin)-[PtCl(*N*-Me-*S*-Pro)($CH_3CH{=}CH_2$)], 68833-21-6; *trans*(*N*,*R*-olefin)-[PtCl(*N*-Me-*S*-Pro)($CH_3CH{=}CHCH_3$)], 62839-86-5; *trans*(*N*,*R*-olefin)-[PtCl(*N*-Me-*S*-Pro)(*t*-$C_4H_9CH{=}CH_2$)], 68833-22-7; *trans*(*N*,*R*-olefin)-[PtCl(*N*-Me-*S*-Pro)(*p*-$ClC_6H_4CH{=}CH_2$)], 68833-23-8; *trans*(*N*,*R*-olefin)-[PtCl(*N*-Me-*S*-Pro)($C_6H_5CH{=}CH_2$)], 68833-24-9; *trans*(*N*,*R*-olefin)-[PtCl(*N*-Me-*S*-Pro)(*p*-$CH_3OC_6H_4CH{=}CH_2$)], 68833-25-0; *trans*(*N*,*S*-olefin)-[PtCl(*N*-Me-*S*-Pro)(*t*-$C_4H_9CH{=}CH_2$)], 68853-54-3; *trans*(*N*,*S*-olefin)-[PtCl(*N*-Me-*S*-Pro)(*p*-$ClC_6H_4CH{=}CH_2$)], 68853-55-4; *trans*(*N*,*S*-olefin)-[PtCl(*N*-Me-*S*-Pro)($C_6H_5CH{=}CH_2$)], 68853-56-5; *trans*(*N*,*S*-olefin)-[PtCl(*N*-Me-*S*-Pro)(*p*-$CH_3OC_6H_4CH{=}CH_2$)], 68853-57-6; *trans*(*N*,*S*-olefin)-[PtCl(*N*-Me-*S*-Pro)($CH_3CH{=}CH_2$)], 68853-58-7; *trans*-(*N*,*S*-olefin)-[PtCl(*N*-Me-*S*-Pro)($CH_3CH{=}CHCH_3$)], 68853-59-8; ^{13}C, 14762-74-4; ^{195}Pt, 14191-88-9.

References and Notes

(1) Mislow, K.; Raban, M. *Top. Stereochem.* **1967**, *1*, 1.
(2) Bogdanović, B. *Angew. Chem.* **1973**, *85*, 1013. Scott, J. W.; Valentine, Jr., D. *Science* **1974**, *184*, 943. Morrison, J. D.; Masler, W. F.; Neuberg, M. K. *Adv. Catal.* **1976**, *25*, 81.
(3) Paiaro, G. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 319.
(4) N-Methylation gave about tenfold solubility for the corresponding (*S*)-proline complexes.
(5) Pine, S. H.; Sanchez, B. L. *J. Org. Chem.* **1971**, *36*, 829.
(6) Buyle, R. *Chem. Ind.* (*London*) **1966**, 380.
(7) Fujita, J.; Konya, K.; Nakamoto, K. *Inorg. Chem.* **1970**, *9*, 2794.
(8) Goggin, P. L.; Goodfellow, R. J.; Haddock, S. R.; Taylor, B. F.; Marshall, I. R. H. *J. Chem. Soc., Dalton Trans.* **1976**, 459.
(9) Konya, K.; Fujita, J.; Nakamoto, K. *Inorg. Chem.* **1971**, *10*, 1699.
(10) Scott, A. I.; Wrixon, A. D. *Tetrahedron* **1971**, *27*, 2339. Ball, R. G.; Payne, N. C. *Inorg. Chem.* **1976**, *15*, 2494.
(11) Boucher, H.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6253.
(12) Shinoda, S.; Sudo, Y.; Yamaguchi, Y.; Iwayanagi, T.; Saito, Y. *J. Organomet. Chem.* **1976**, *121*, 93.
(13) Konya, K.; Fujita, J.; Kido, H.; Saito, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2161.
(14) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; Chapter 4.
(15) Spectra were analyzed with a JEOL NMR simulation program.
(16) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon: New York, 1965; Vol. 1, Chapter 8.
(17) Cooper, D. G.; Powell, J. *Inorg. Chem.* **1976**, *15*, 1959.
(18) Pregosin, P. S.; Sze, S. N.; Salvadori, P.; Lazzaroni, R. *Helv. Chim. Acta* **1977**, *60*, 2514.
(19) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1969**, 53.
(20) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 1653.
(21) Brause, A. R.; Kaplan, F.; Orchin, M. *J. Am. Chem. Soc.* **1967**, *89*, 2661. Fritz, H. P.; Schwarzhans, K. E.; Sellmann, D. *J. Organomet. Chem.* **1966**, *6*, 551.
(22) Nyburg, S. C.; Simpson, K.; Wong-Ng, W. *J. Chem. Soc., Dalton Trans.* **1976**, 1865.
(23) Ball, R. G.; Payne, N. C. *Inorg. Chem.* **1977**, *16*, 1871.
(24) Pedone, C.; Benedetti, E. *J. Organomet. Chem.* **1971**, *29*, 443.
(25) Gel'fman, M. I.; Karpinskaya, N. M.; Razumovskii, V. V. *Zh. Neorg. Khim.* **1970**, *15*, 2766.
(26) Herberhold, M. "Metal π-Complexes"; Elsevier: Amsterdam, 1974; Vol. 2, Part 2, Chapter 6.
(27) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135. Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299. Gansow, O. A.; Vernon, W. D. "Topics in Carbon-13 NMR Spectroscopy", Levy, G. C., Ed.; Wiley: New York, 1976; Vol. 2, pp 269–341.
(28) Iwayanagi, T.; Saito, Y. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 459.
(29) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.
(30) Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1975**, *14*, 3007.
(31) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.
(32) Benedetti, E.; Corradini, P.; Pedone, C. *J. Organomet. Chem.* **1969**, *18*, 203.
(33) Lazzaroni, R.; Salvadori, P.; Bertucci, C.; Veracini, C. A. *J. Organomet. Chem.* **1975**, *99*, 475.