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Stereochemical Nonrigidity in a Chelated Platinum(0)-Diolefin Complex

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Summary: Stereochemical nonrigidity has been observed in the Pt(0) complex $[Pt\{(\eta\text{-}ViMe_2Si)_2O\}(P^tBu_3)]$ (**1a**) *by NMR spectroscopy. The activation parameters have been measured by DNMR3 analysis of the spectra over a range of temperatures. It is concluded that the vinylsiloxane ligand is undergoing a facile dissociation–reassociation process, although a related nondissociative mode involving a rotation about the alkene C–C axis cannot be completely dismissed.*

Introduction

The dynamic sterochemical behavior of alkene ligands coordinated to transition metals has been a fruitful subject for study.[1] For a single, coordinated alkene the major dynamic processes that have been described, but not necessarily observed, are rotation about either the metal–alkene axis or the alkene C–C axis, dissociation and reassociation of the alkene, and changes in the mode of alkene coordination (π to σ for example). Peng and Gladysz[2,3] have recently discussed these different processes and described the equilibration of a pair of chiral rhenium diastereoisomers in terms of a novel nondissociative mechanism whereby the metal moves through the π nodal plane of the alkene via a carbon–hydrogen "σ-bond complex".

The first example of rotation of a coordinated ethene ligand was reported by Cramer[4] for $CpRh(C_2H_4)_2$. Stereochemical nonrigidity, on the NMR time scale, has also been observed by Stone[5] for a series of Pt(0)–diethylene complexes where rotation about the metal–alkene is the most plausible explanation for the dynamic behavior. Johnson[6,7] demonstrated for an osmium complex that, of the two rotation modes proposed by Cramer,[4] rotation about the metal–alkene axis (Figure 1(i)) was favored over the alternative rotation about the C–C axis (Figure 1(ii)). There are many reports of rotations about metal–alkene axes, and for most compounds[1,8] the activation energies lie in the range of 8–14 kcal mol^{-1}.

(i) (ii)

Figure 1. The two possible modes of coordination alkene rotation: (i) rotation about the metal–alkene axis; (ii) rotation about the alkene C–C axis.

There have been no authenticated examples of rotation about the alkene C–C axis. Ligand dissociations are, however, well-known, and many examples have been examined, mostly through exchange reactions between bound and free alkenes.[8,9] In some cases the kinetics of dissociation have been obtained by examining the rate of exchange between the bound and free alkenes. Cramer[10] observed a very high lability for the alkene ligand in Zeise's salt ($K[C_2H_4PtCl_3]$), where the exchange rate in methanol containing HCl was greater than 70 s^{-1} even at 200 K. Consiglio and co-workers[11] demonstrated that diastereisomers of some pseudotetrahedral cationic ruthenium complexes, $[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH(CH_3)PPh_2\}(CH_2{=}CHR)]PF_6$, interconverted by alkene dissociation–reassociation. Recently Toyota and Oki[12] have measured the activation parameters for dissociation of alkene from Pt(II) complexes and found values of $\Delta H^{\ddagger} = 17.6 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.7 \pm 1.3$ cal mol^{-1} K^{-1}. The activation parameters for alkene dissociation are therefore generally higher than those for rotation. If that were not the case, rotation would be rarely observed, as dissociation–reassociation of the alkene would, in most cases, give a stereochemical outcome that would mask the rotational equilibria.

Our interest in the dynamic properties of coordinated alkenes was stimulated by the observation that the SiMe signals in the proton NMR spectrum of chelated Pt(0)–vinylsiloxane complex **1a** (R = ^{t}Bu)[13,14] were considerably broadened at ambient temperature. This strongly suggested that the coordinated disiloxane ligand was undergoing some kind of dynamic process. The aim of this work was to elucidate that process as far as possible. The stereochemical nonrigidity we have observed in the chelated Pt(0)–vinylsiloxane complex **1a** (R = ^{t}Bu) is in a molecule where rotation about the metal–alkene axis is

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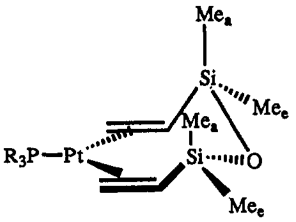

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Figure 2. Structure of the chelated vinylsilane–platinum complex.

not possible. An understanding of the dynamic processes occurring in this compound could be important in helping to understand why this and related compounds are efficient hydrosilylation catalysts.[13,14]

Results and Discussion

The X-ray crystal structure of **1a** (R = ^{t}Bu) has been determined,[14] and the geometry is as shown in Figure 2 with the ligand and platinum center together in a pseudochair structure with two pseudoaxial methyl groups, Me$_a$, and, diastereoisomeric with Me$_a$, two pseudoequatorial groups, Me$_e$.[16] The ^{13}C, ^{1}H, ^{31}P, and ^{29}Si NMR spectra are compatible with the structure, and data are given in Table 1.

All of the resonances in the ^{1}H NMR spectrum of **1a** are in the expected regions and are of natural line width, with the notable exception of the SiMe protons, which at 295 K in CDCl$_3$ or C$_6$D$_6$ appear as two broad singlets of equal intensity. Similarly, at 295 K the ^{13}C NMR spectrum of the vinyl carbon atoms and the phosphine carbon atoms is entirely compatible with those reported by Stone[5] and again the only broadened lines are the two singlets of equal intensity from the SiMe carbon nuclei. The NMR spectral data for two vinylsiloxane–platinum complexes, [Pt{(η-ViMe$_2$Si)$_2$O}(P-^{t}Bu$_3$)] (**1a**) and [Pt{(η-ViMe$_2$Si)$_2$O}(PCy$_3$)] (**1b**), are given in Table 1.

As the temperature is raised, the ^{1}H and ^{13}C spectra of **1a** (R = ^{t}Bu) show similar behavior. The SiMe resonances start as a pair of broad singlets, broaden, coalesce (321 K for ^{1}H; 325 K for ^{13}C in both CDCl$_3$ and C$_6$D$_6$), and eventually give rise to a sharp singlet. All other resonances in the spectra of **1a** are essentially temperature invariant with the Pt–C, Pt–H, Pt–P, Pt–Si, P–Si, and P–C couplings being maintained at all temperatures. Thus, the dynamic process is an intramolecular degenerate exchange in which the only stereomutation is between the two sets of methyl groups on silicon.

Superficially, the stereomutation appears to be directly analogous to the familiar cyclohexane chair–chair interconversion, but closer examination shows that to be a misleading comparison. The interconversion of axial and equatorial substituents in cyclohexanes is fundamentally a process involving rotation about C—C bonds. The stereomutation of the methyl groups in **1a** by a cyclohexane-type ring flip would require rotation about the C=C *double bond*, which is highly unlikely. Similarly, models show that there is some conformational freedom for rotation about the vinyl—Si and Si—O bonds but "flipping" that fragment does not interconvert the methyl group environments. The only way to exchange the axial and equatorial methyl environments is to change the coordination of the platinum from one face of the vinyl group to the other for each of the alkene residues.

Table 1. NMR Spectral Data for R$_3$PPt(CH$_2$=CHSi(CH$_3$)$_2$)$_2$O in CDCl$_3$ at 298 K

1a (R = *t*-Bu)

^{1}H NMR

	SiMe (a)	SiMe (b)	P(^{t}Bu)$_3$	HC=CH$_2$
δ/ppm	–0.28	0.33	1.47	2.5 complex m
integration	3H	3H	27H	6H
peak width/Hz	8.00	8.00		
$\lvert J\rvert_{\mathrm{PH}}$/Hz			11.48	

^{13}C NMR

	SiMe (a)	SiMe (b)	C	CH$_3$	CH	CH$_2$
δ/ppm	–1.83	1.72	40.9	24.2	45.3	48.9
$\lvert J\rvert_{\mathrm{PC}}$/Hz			9.5	5.2	11.1	6.5
$\lvert J\rvert_{\mathrm{PtC}}$/Hz			34.8	15.9	103.6	178.6

^{29}Si NMR

δ/ppm	5.13
$\lvert J\rvert_{\mathrm{PtS}}$/Hz	40
$\lvert J\rvert_{\mathrm{PSi}}$/Hz	3.9

^{31}P NMR

δ/ppm	22.9
$\lvert J\rvert_{\mathrm{PtP}}$/Hz	3731

1b (R = C$_6$H$_{11}$)

^{1}H NMR

	SiMe (a)	SiMe (b)	P(C$_6$H$_{11}$)$_3$	HC=CH$_2$
δ/ppm	–0.29	0.33	complex multiplets at 1–2	

^{13}C NMR

	SiMe (a)	SiMe (b)	C1	C2	C3	C4	CH	CH$_2$
δ/ppm	–1.72	1.55	37.0	30.0	27.7	26.7	41.6	44.9
$\lvert J\rvert_{\mathrm{PC}}$/Hz			32.0	0	10.4	0	10.3	6.3
$\lvert J\rvert_{\mathrm{PtC}}$/Hz			33.7	22.0	0	0	110.0	163.1

^{29}Si NMR

δ/ppm	3.4
$\lvert J\rvert_{\mathrm{PtSi}}$/Hz	43
$\lvert J\rvert_{\mathrm{PSi}}$/Hz	3.9

^{31}P NMR

δ/ppm	22.9
$\lvert J\rvert_{\mathrm{PtP}}$/Hz	3498

The two most reasonable mechanisms for the process are (a) a stepwise, nondissociative rotation of each alkene fragment about the carbon–carbon axis (as in Figure 1(ii) and in Scheme 1 as **1** $\rightleftharpoons$ **3** $\rightleftharpoons$ **1′**) and (b) a stepwise dissociation–reassociation mechanism (Scheme 1; **1** $\rightleftharpoons$ **2** $\rightleftharpoons$ **3** $\rightleftharpoons$ **2′** $\rightleftharpoons$ **1′**). The two mechanisms are related and could be considered to be the extremes on a continuum where the major differences are in the extent of Pt–alkene bonding in the transition state.

The rotational, nondissociative mechanism is appealing, as this rotation mode has not been observed to date. However, the dissociative pathway must also be considered, despite the maintenance of Pt–C and P–C coupling, because spin correlation is not lost during this mechanism since bonding is always maintained to at least one end of the bidentate ligand.

A number of experiments were carried out in an attempt to elucidate the mechanism. Although not definitive, the evidence favors the dissociative route, as described in Scheme 1.

A total line-shape analysis of the ^{1}H SiMe resonances (in CDCl$_3$) was performed using DNMR3.[15] A good

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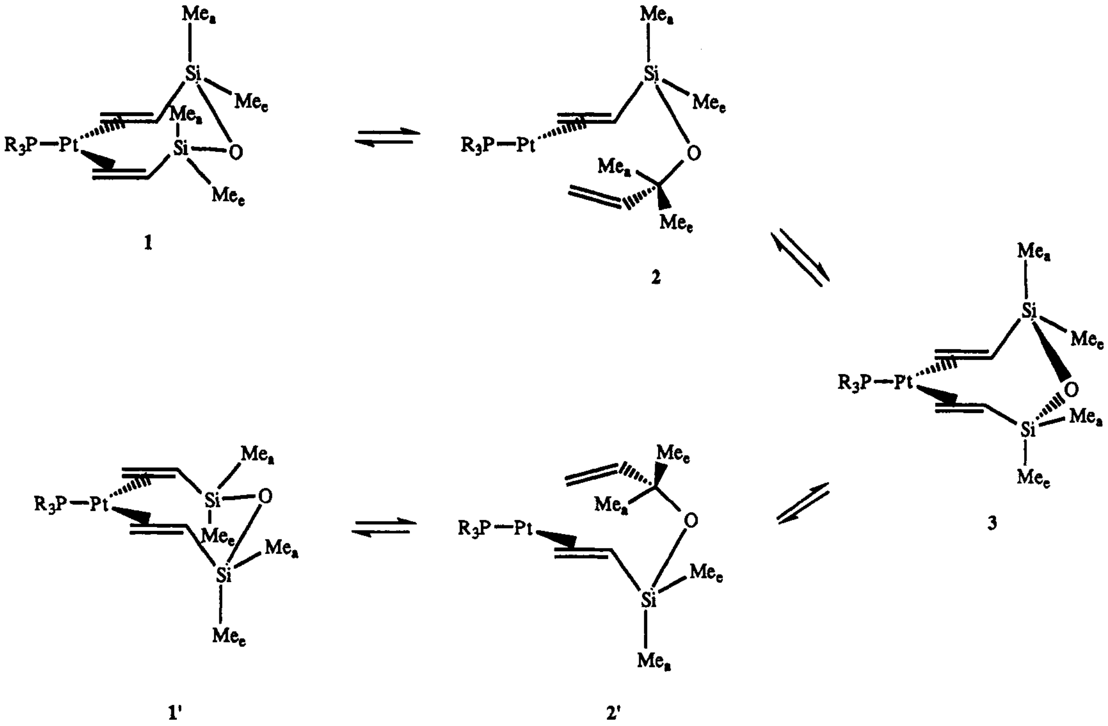
[15] DNMR3; QCPE, Bloomington, IN, 1970; No. 165.

Scheme 1. Dissociative Route for Methyl Group Stereomutation in 1a[a]



[a] The nondissociative route is 1 ⇌ 3 ⇌ 1′.

straight line was obtained for a plot of ln k vs $1/T$, where k is the calculated rate constant of exchange. The activation parameters obtained (calculated for 298 K where appropriate) for the methyl group interconversions were $\Delta G^{\ddagger} = 15.3$ kcal mol^{-1}, $\Delta H^{\ddagger} = 15.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = +1.8$ cal mol^{-1} K^{-1}, $E_a = 16.3$ kcal mol^{-1}, and log $A = 13.2$ (the errors in E_a are estimated to be ± 0.5 kcal mol^{-1}). The activation parameters are in quite close agreement with the values of $\Delta H^{\ddagger} = 17.6 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.7 \pm 1.3$ cal mol^{-1} K^{-1} reported by Toyota and Oki[12] for alkene dissociation from Pt(II). The free energy of activation is significantly higher at 16.3 kcal mol^{-1} than the rotational barriers measured by Stone[5] (10–13.6 kcal mol^{-1}).

It is also interesting to note that, despite the accessible values for the activation parameters of **1a**, the similar complex **1b** (R = cyclohexyl) does not show stereochemical nonrigidity. The two sets of SiMe groups in **1b** are always sharp pairs of singlets of equal intensity in both the proton and carbon NMR spectra, even in $C_6D_5CD_3$ at 380 K. The two phosphine ligands ^{t}Bu$_3$P and $(C_6H_{11})_3P$ have similar cone angles and electronic properties, and we ascribe the effect of the $(C_6H_{11})_3P$ ligands as being due to longer range steric interactions inhibiting dissociation. From molecular models this appears feasible, whereas there does not appear to be any extra inhibition to rotation about the C–C axis with $(C_6H_{11})_3P$.

A useful test for dissociative processes with nonchelating ligands is to add free ligand and see if there is exchange at the same rate.[1] When the ligand $(ViSiMe_2)_2O$ was added to **1a**, a separate, sharp singlet for the free ligand methyl groups was observed when the two complex SiMe groups were in the region of intermediate exchange. However, at 368 K in $C_6D_5CD_3$ only one SiMe resonance was observable in both the carbon and proton NMR spectra. At this temperature the vinyl regions of complex and free ligand were still distinct, but some broadening was observed. This experiment shows that exchange with free ligand is occurring, probably through vacant coordination sites at platinum, but the intramolecular stereomutation process is faster. Complexes such as **1** are efficient hydrosilylation catalysts, and we suggest that this is related to the relative ease of dissociation of the vinyl ligand, leaving a vacant site for coordination of unsaturated molecules or for oxidative addition.

Thus, we have observed a novel dynamic process in which the divinylsiloxane ligand shows potential as a probe for conformation dynamic behavior in metal–alkene complexes.

Experimental Section

Compounds **1a** and **1b** were prepared and purified as described by Chandra and co-workers.[14]

NMR measurements were made on a JEOL FX90Q spectrometer operating at 89.56 MHz for ^{1}H, 22.5 MHz for ^{13}C, 17.76 MHz for ^{29}Si, and 36.26 MHz for ^{31}P. The spectra are summarised in Table 1 and are for 5% solutions in $CDCl_3$. Very similar spectra were obtained for solutions in C_6D_6. Variable-temperature measurements were carried out using the same instrument. The temperature was measured using a calibrated thermocouple and found to be reproducible to ±0.5 K. Activation parameters were obtained by using DNMR3[15] to simulate ^{1}H and ^{13}C spectra for a series of rate constants for methyl group exchange (k/s^{-1}) and comparing the simulated with the actual spectra. From these data a plot of ln k vs $1/T$ gave $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

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(16) We have assumed the solution structure to be the same as that in the solid phase. The alternative geometry (structure 3, Scheme 1) with the two SiMe$_2$ groups on opposite sides of the plane of the two vinyl groups is much more highly strained according to molecular models and appears to be unlikely. The mechanistic agruments advanced, with minor modifications, can be applied to 3, and the conclusions would remain unaffected should 3 be shown to be the solution structure.