Stereochemical non-rigidity in a macrocyclic vinylsiloxane-based tris(alkene)nickel(0) complex ☆

Anthony G. Avent, Michael F. Lappert *, Calum MacBeath

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BNL 9QJ, UK

Abstract

A series of variable temperature saturation transfer NMR spectroscopic experiments show that the complex [Ni(CH$_2$=CHSi(Me)$_2$OSi(Me)$_2$CH=CHSi(Me)$_2$OSi(Me)$_2$CH=CH$_2$)] (1) undergoes slow chemical exchange with minor conformers in benzene-d$_6$ at 298 K. The latter are proposed intermediates in an intramolecular process causing epimerization of the fused bicyclic molecule to take place. The implications of these results for interpreting dynamic processes in the monocyclic complex [Pt(LL)(P^{t}Bu$_3$)] and the Karstedt hydrosilylation catalyst [{Pt(LL)}$_2$(μ-LL)] are discussed [LL = {Me$_2$(CH$_2$=CH)Si}$_2$O].

Keywords: Ni(0) triene complexes; Divinyltetramethyldisiloxane; Dynamic processes; Hydrosilylation

1. Introduction

The problem of fluxionality in η-alkene complexes has attracted much attention, since Cramer's discovery in 1964 of the dynamic behaviour of the rhodium(I) complex [Rh(η-C$_5$H$_5$)(η-C$_2$H$_4$)$_2$] [1]. The line shape changes observed in its variable temperature (VT) ^{1}H NMR spectra were attributed to rotation about the C$_2$ axis through the metal, I; this process was considered to be energetically more favourable than rotation about the alkene C–C axis, II.

This proposal was supported by studies on [Os(CO)NO(η-C$_2$H$_4$)(PPh$_3$)$_2$][PF$_6$], which has each end of the bound C$_2$H$_4$ in a chemically distinct environment [2]. The VT ^{13}C NMR spectrum in (CD$_3$)$_2$O showed that the separate 1:1 signals for the C$_2$H$_4$ carbons observable at -80°C gave way to a single resonance at 20°C. An alkene–metal dissociative pathway was ruled out, since ^3J(^{1}H-^{31}P) was maintained in the ^{1}H NMR spectrum throughout the temperature range.

A dissociative process was demonstrated for [PtCl$_3$(η-C$_2$H$_4$)]$^-$ [3]. In the presence of an excess of C$_2$H$_4$, there was a single CH$_2$ ^{1}H NMR spectral signal, the rate of C$_2$H$_4$ exchange being > 70 s^{-1} at -75°C; using free C$_2$D$_4$ + [PtCl$_3$(η-C$_2$H$_4$)]$^-$, C$_2$H$_4$/C$_2$D$_4$ exchange was rapid and the rate dependent on ethene concentration.

Activation parameters, deduced from VT ^{1}H NMR spectra, have been evaluated for numerous Pt(II) complexes: cis-[Pt(diket)(X)(η-alkene)] and cis-[PtCl$_2$(L)-(η-alkene)] [diket = (CH$_3$CO)$_2$CH or (CF$_3$CO)$_2$CH, X = Cl or Br and alkene = C$_2$H$_4$, C$_3$H$_6$, cis- or trans-C$_4$H$_8$-2 or C$_2$Me$_4$] [4], $\Delta G^\dagger$ for alkene–Pt dissociation being greater than $\Delta G^\dagger$ for Pt–alkene rotation (I) (45–70 KJ mol^{-1}) [4].

A dissociative pathway was established for the epimerisation of [Ru(η-C$_5$H$_5$){Ph$_2$CH(Me)CH(Me)PPh$_2$}(η-CH$_2$=CHR)][PF$_6$] [e.g., R = H, Me, COOMe or C(O)Et], high $\Delta G^\dagger$ values being found for those alkenes having electron-withdrawing groups R (e.g. COOMe) [5], these bonding most strongly to the metal. Similarly in trans-[PtCl$_2${ONC$_5$H$_4$(COOMe)-4}(η-CH=CH^{i}Pr)], the rate of racemisation (monitored by focussing on the double doublet ^{1}H NMR signal due to the ^{i}Pr protons; $\Delta G^\dagger$ 77 KJ mol^{-1} at 323 K in CDBr$_3$) was shown to involve an alkene–Pt dissociative pathway [6].

☆ Dedicated to Prof. H. Brunner, as a mark of esteem and friendship, on the occasion of his 60th birthday.

* Corresponding author.
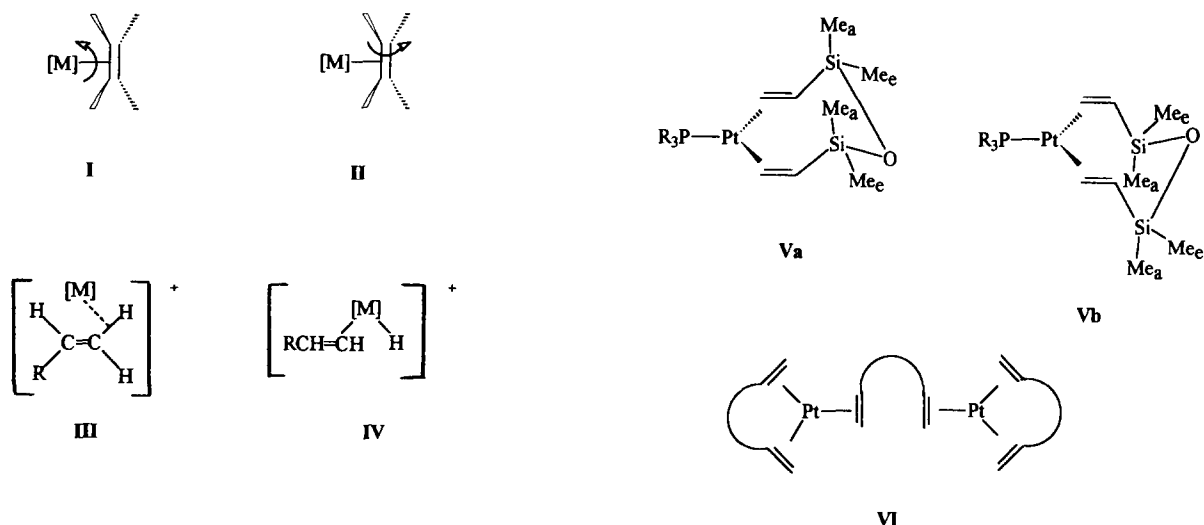
A recent study on the interconversion of the (*RS, SR*)/(*RR, SS*) diastereoisomers of [Re(η-C$_5$H$_5$)-(NO)(PPh$_3$)(η-CH$_2$=CHR)][BF$_4$] (e.g., R = Ph) at 95–100°C in a chlorocarbon established the mechanism to be non-dissociative (e.g., no incorporation of deuterated alkene), with retention of configuration at Re and with no *E/Z* scrambling of deuterium labels [7]. Thus it was suggested that Re moves through the π-nodal plane of the alkene via a C–H σ-bonded complex **III** and/or a vinyl hydride oxidative adduct **IV**.

Our interest in alkene–metal complexes derives from a study of the Speier hydrosilylation catalyst H$_2$[PtCl$_6$]-.xH$_2$O in its Karstedt modification, i.e., in "solution" in (Me$_2$ViSi)$_2$O (=LL; Vi = CHCH$_2$), solution **A**. It was shown that **A** contained Pt(0), as evident from its ^{195}Pt NMR spectral shift and from the isolation therefrom of various Pt(0) derivatives; e.g., addition of P^{t}Bu$_3$ gave the X-ray characterised [Pt(LL)(P^{t}Bu$_3$)] (**V**) (R=^{t}Bu here and in **VI, IX–XI**) [8]. From solution **A** (or an alternative substrate), the crystalline complex *rac*-[{Pt(LL)}$_2$(μ-LL)] (**VI**) was isolated and structurally characterised [9]. The systems (i) *cis*-[PtCl$_2$(η-CH$_2$=CHPh)$_2$]/LL → **VI**, and (ii) **VI** + excess LL or
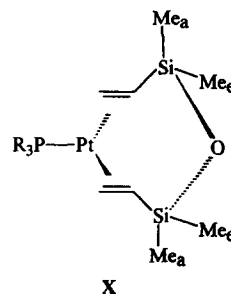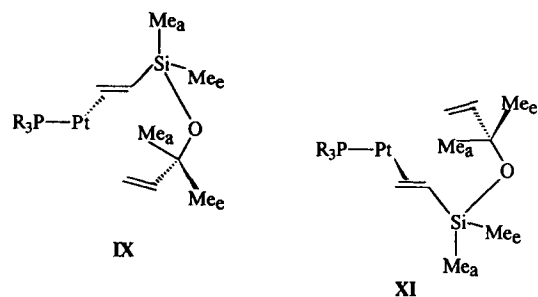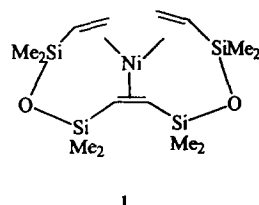
Table 1
NMR spectral data for Complex 1 recorded in d$_6$ benzene at 298 K

^{1}H NMR Assignment	δ (ppm)	^{13}C{^{1}H} NMR Assignment	δ (ppm)
H$_d$	4.04(2H, d)	C$_c$	77.86
H$_c$	3.83(2H, s)	C$_b$	69.69
H$_c$	5.41(2H, s) [a]	C$_a$	68.34
H$_c$	3.46(2H, q) [a]	Me$_d$	1.88
H$_b$	3.20(2H, t)	Me$_c$	1.48
H$_a$	3.05(2H, d)	Me$_b$	−1.24
Me$_d$	0.55(6H, s)	Me$_a$	−1.43
Me$_c$	0.48(6H, s)	^{29}Si{^{1}H} NMR	
Me$_b$	−0.10(6H, s)	Assignment	δ (ppm)
Me$_a$	−0.27(6H, s)	Si$_b$	5.22
		Si$_a$	3.80

[a] These peaks are due to minor conformers and the integration values are on a different scale.

I

II

III

IV

Va

Vb

VI
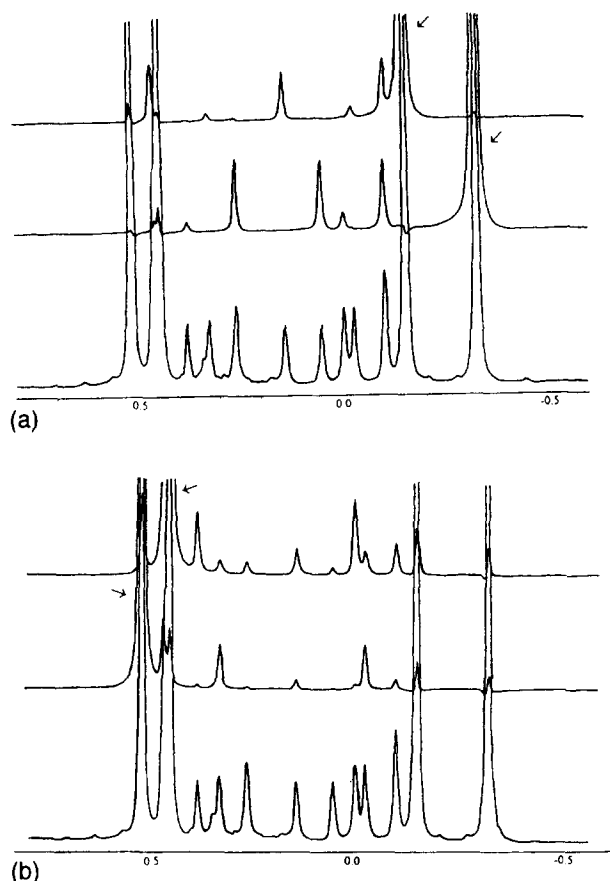

VII

VIII

1

IX

XI

X

Fig. 1. Saturation transfer studies at 298 K. Fig. 1(a) shows the effect of irradiation of the equatorial methyl groups. Fig. 1(b) shows the effect of irradiation of the axial methyl groups. The arrows indicate which peaks are being irradiated. The lower spectrum in each case shows the "normal" appearance of the methyl region.

$PhCH=CH_2$ were studied by multinuclear NMR spectroscopy, showing that the three-coordinate Pt(0) complexes $[\overline{Pt(LL)}(LL)]$ (VII) or $[\overline{Pt(LL)}(\eta\text{-}PhCH=CH_2)]$
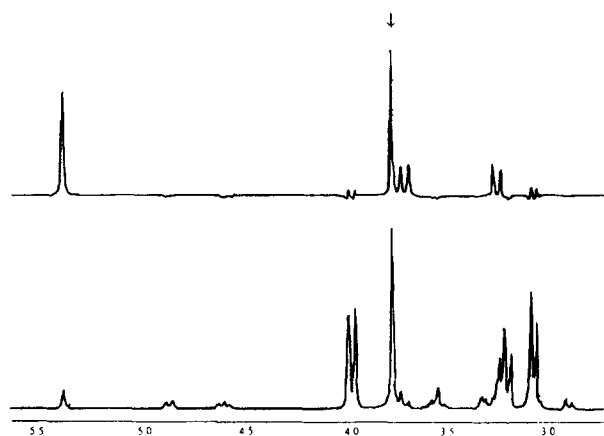

Fig. 2. Saturation transfer studies at 298 K. The upper spectrum shows the effect of irradiation of the singler at δ 3.83. The lower spectrum shows the "normal" appearance of the vinyl region. The arrow indicates which peak is being irradiated.

(VIII) were readily formed [10]. Using the metal vapour synthesis technique, Ni atoms when condensed with LL at $-110°C$ yielded the cyclotrienenickel(0) complex 1 [11].

For these multidentate vinyl ligands the further possibility exists of processes that are both dissociative and intramolecular. For example, complex V was shown (by multinuclear VT NMR spectroscopy and DNMR total line shape analysis of the SiMe ^1H resonances) to undergo an intramolecular exchange process whereby the Me groups on the silicon were exchanging ($V_a \leftrightarrow V_b$) with $\Delta G^{\ddagger}$ 298 K 64.3 KJ mol^{-1} [12]. The preferred dissociative mechanism involved the sequence $V_a \leftrightarrow IX \leftrightarrow X \leftrightarrow XI \leftrightarrow V_b$, although the alternative $V_a \leftrightarrow X \leftrightarrow V_b$ was not totally discounted.

Another example is the Ni(0) complex, $[Ni_2(\eta^4,\eta^4\text{-}DMOD)(^iPr_2PC_2H_4P^iPr_2)_2]$ (DMOD = 3,6-dimethylene-1,7-octadiene), in which each each Ni atom is coordinated to two vinyl groups [13]. In this case a fluxional process was found that could be explained by a sequence in which each vinyl in turn dissociated from the metal, flipped over, and recoordinated through its opposite face.
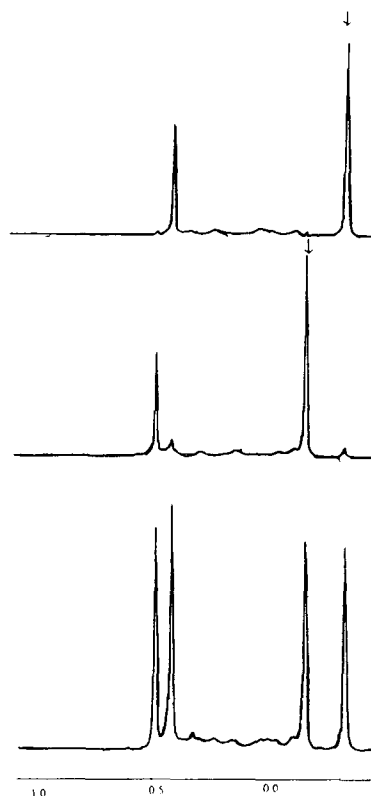

Fig. 3. Saturation transfer studies at 323 K. The upper two spectra show the effect of irradiation of the peaks due to the equatorial methyl groups of the major isomer. The arrows indicate which peaks are being irradiated. The lower spectrum shows the "normal" appearance of the methyl region.

2. Results and discussion

Our objective was to investigate the dynamic behaviour of the trienenickel(0) complex **1** in solution, and thereby contribute to an understanding of the fluxional processes relating the η^2-alkene-metal moieties. In particular, evidence was sought for the existence of one or other intermediates postulated in earlier studies.

Details of the ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra in benzene-d_6 at 298 K, with assignments are listed in Table 1. The data are consistent with the notion that **1** in solution retains the structural integrity established for the solid by X-ray crystallography [11], comprising a fused bicyclic structure with both rings in the chair conformation, each silicon having an equatorial and an axial methyl methyl group and the three η^2-alkenes being co-planar with the central nickel atom. Thus **1** is a d^{10} Ni(0) 16-electron complex, having the local trigonal planar configuration favoured by other nickel(0) alkene complexes [14].

The major resonances in the ^{1}H NMR spectrum of complex **1** were in the appropriate region for a (Me$_2$ViSi)$_2$O complex, with the vinylic protons at δ 3.05–4.04 and four major methyl proton signals at δ −0.27 − 0.55. Nuclear Overhauser effect studies were carried out in order to assist in the assignment of the latter.

Complex **1** showed two ^{29}Si{^{1}H} NMR spectral signals, which were at a higher frequency than the δ −2.3 for free (Me$_2$ViSi)$_2$O, consistent with deshielding of the silicon nucleus upon the ligand's coordination to a metal. The ^{13}C{^{1}H} NMR spectrum was unexceptional, but 2D heteronuclear shift correlation experiments were used to asign the individual ^{13}C{^{1}H} and ^{29}Si{^{1}H} signals, Table 1.

It is noteworthy that each of the ^{1}H NMR spectral signals of complex **1** were of natural line width. This contrasts with the corresponding observations on Pt(0) complexes such as [Pt(LL)(P^{t}Bu$_3$)] (**V**) [8] or [{Pt(LL)}$_2$(μ-LL)] (**VI**) [9], which showed broad methyl signals; this effect for **V** was attributed to the coordinated vinylsiloxane ligand undergoing the intramolecular exchange process $V_a \leftrightarrow V_b$, involving the interconversion of the axial and equatorial methyl groups [12].

A possible interpretation of this difference appeared initially to be that in **1** there was no such intramolecular process involving the coordinated macrocyclic triene ligand. However, a series of saturation transfer experiments on complex **1** showed that when each of the four major ^{1}H signals in the methyl region was in turn irradiated at 298 K, there was a reduction in the intensity of the minor signals in this region, Figs. 1a and 1b. These observations indicate that the latter are derived from conformers of complex **1**.
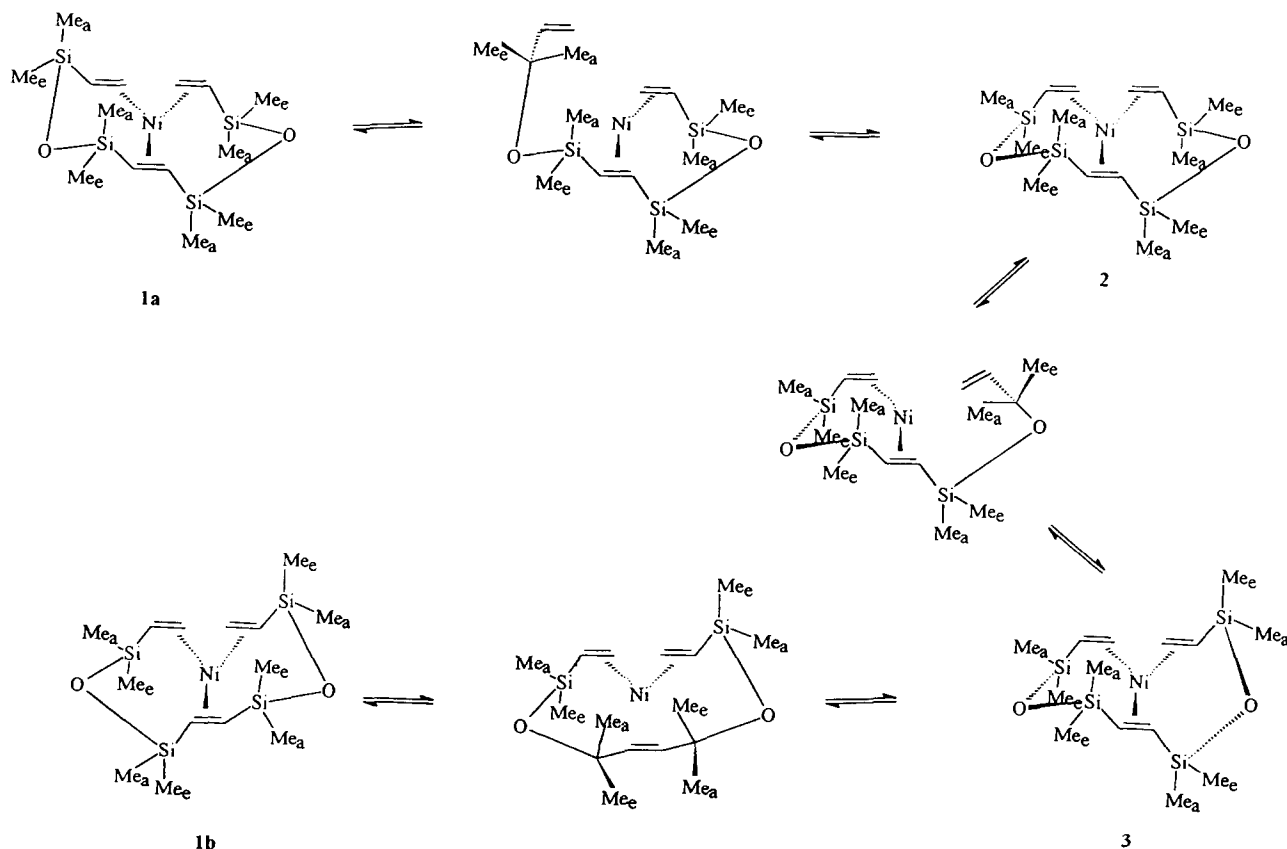
Scheme 1.The dissociative mechanism for the epimerzation of complex **1**.

Similarly, irradiation of the singlet at δ 3.83 due to the CH=CH protons of **1** at 298 K reduced the intensity of two other sets of signals in the alkenyl region: the singlet at δ 5.4 and the AB quartet in the range δ 3.18 to 3.75, Fig. 2. This observation is likewise attributed to an exchange process involving complex **1** and two minor conformers. Plausible structures for the latter are the asymmetric and symmetric molecules **2** and **3** respectively. In **2**, the CH=CH protons are inequivalent as is consistent with the AB quartet pattern.

A third series of experiments involved irradiating at 323 K in turn each of the equatorial methyl protons of **1** at δ -0.27 and δ -0.10, causing the intensities of the signals due to the axial methyl protons at δ 0.48 and δ 0.55 to be reduced, Fig. 3. These saturation transfer experiments demonstrate that at 323 K there was exchange between the axial and equatorial methyl groups of the major component, complex **1**, shown in Scheme 1 as the degenerate interchange of *gem*-methyl groups between the identical structures **1a** and **1b**. At this higher temperature, the rate of the **1a** $\leftrightarrow$ **1b** exchange was significantly faster than that at 298 K and hence the labile structures **2** and **3** were not so prominent.

The above three sets of experiments are brought together in terms of Scheme 1. Thus, starting from **1a**, dissociation then rotation about the C–C axis of the freed CH_2=CH group and reassociation leads to **2**. A second such tandem sequence converts **2** into **3**, while inverting the coordinating face of the CH=CH-centred ligand of **3** transforms **3** into **1b**. Structures **4**, **5** and **6** represent notional transients or transition states between **1a** and **2**, **2** and **3**, and **4** and **1b** respectively.

The shift of the CH=CH ^{1}H NMR spectral signal from δ 3.83 in **1** to δ 5.4 in **3** is attributed to the strain imposed by the less favourable conformation of the latter, which may be reflected in a longer Ni–CH=CH bond in **3** than in **1**.

An alternative to the dissociative pathway shown for the transformations **1a** $\to$ **2** and **2** $\to$ **3** would involve a non-dissociative CH_2=CH bond rotation. In principle, the two alternatives might be distinguished by establishing whether upon addition of the metal-free ligand [LL'L] to **1** there is exchange between [Ni(LL'L)] (i.e. **1**) and [LL'L]. This option was not available to us, as we have not yet obtained [LL'L]. However, we were able to examine the effect of adding two equivalents of $(Me_2ViSi)_2O$ (LL) to **1**. The ^{1}H NMR spectrum of this mixture showed that in addition to the signals previously observed for **1**, others at δ 5.6–6.1 were due to the vinyl protons of LL and that at δ 1.00 was due to the methyl protons of LL. Upon selectively irradiating the former at 298 and 318 K, no change was observed in the intensity of any signal due to bound vinyls of complex **1**, and hence exchange between **1** and [LL] is ruled out. This, however, is not surprising since it is

unlikely that even the tripodal [LL'L] ligand, let alone [LL] would exchange with the ligated [LL'L] of complex **1** because of their multidentate character.

In conclusion, we favour the dissociative process of Scheme 1 for the following reasons. First, we have provided evidence for the presence of the conformers **2** and **3** of **1**. Second, **2** and **3** correspond precisely to the transient intermediates **IX** and **XI** that were postulated but not identified in the [Pt(LL)(P^{t}Bu$_3$)] $V_a \leftrightarrow V_b$ system [12]. Third, for the crystalline Karstedt hydrosilylation catalyst [{Pt(LL)}$_2$(μ-LL)] **VI**, a dissociative pathway leading to the three-coordinate Pt(0) complexes [Pt(LL)(LL)] **VII** or [Pt(LL)(η-CH$_2$=CHPh)] **VIII** was established [10]. Finally, a non-dissociative "flipping" mechanism of the sort recently proposed by Peng and Gladysz for their Re(η-CH$_2$=CHR) system [7], is less likely for **1** because it would require inverting the entire bicyclic system of the tridentate [LL'L] ligand of **1** through the CC vector of the CH=CH bond, a process which would be energetically prohibitive.

Acknowledgement

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