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Articles

Selective Isomerization of *cis*-PtL_2(1-alkenyl)$_2$ to *cis*-PtL_2(2-alkenyl)$_2$ Complexes

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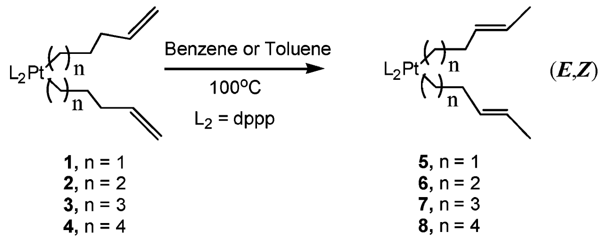
Heating the 1-alkenyl complexes *cis*-[Pt(1-alkenyl)$_2$L$_2$] [alkenyl = 1-pentenyl, 1-hexenyl, 1-heptenyl, and 1-octenyl; L$_2$ = 1,3-bis(diphenylphosphino)propane (dppp) or 1,2-bis(diphenylphosphino)ethane (dppe)] to 100 °C caused a quantitative isomerization to the corresponding 2-alkenyl complexes *cis*-[Pt(2-alkenyl)$_2$L$_2$]. This novel isomerization is strongly dependent on the length of the alkenyl chains as well as the nature of the ligand, L$_2$. The new 2-alkenyl complexes were fully characterized by analytical and spectroscopic methods. An X-ray crystal structure of *cis*-[Pt(2-pentenyl)$_2$(dppp)] confirms this isomerization. Possible reaction mechanisms are discussed.

Introduction

Metal-alkenyl compounds are of interest since they are key intermediates in some catalytic reactions[1] and they have been shown to be useful for generating thin platinum films[2] for microelectronic and catalytic applications[3] using the chemical vapor deposition (CVD) method.[4] Thus metal-alkenyls are an important class of compounds with potential useful applications;[5] however, their chemistry is relatively unexplored. The stability and reactivity of metal-alkenyl compounds depends on various factors but particularly the metal and the other ligands.[5] Recently we have shown that these bis(alkenyl) metal complexes are novel precursors for the preparation of a range of metallacycloalkenes through the ring-closing metathesis ((RCM) reaction.[6,7]

We now find that bis(1-alkenyl)platinum(II) complexes (**1**−**4**) undergo an irreversible and quantitative isomerization in solution to yield the corresponding bis(2-alkenyl)platinum(II) complexes (**5**−**8**) without prior decomposition (see Scheme 1). This is the first example of this type of transformation to the best of our knowledge.[5] However, there are some other similar reports in the literature about the isomerization of related organometallic species. Thus, the acid-catalyzed reversible isomerization of 2-methylallyliridium(III) to the corresponding 2-methylprop-1-enyl complexes has been reported[8] by Deeming et al. Also a facile transformation between parallel and perpendicular alkyne binding modes and subsequent formation of vinyl groups on reaction of alkynes with the heterobinuclear complex [RhMn(CO)$_4$(dppm)$_2$] have been reported.[9] Recently, the isomerization of the 1-alkenyl group in disubstituted alkenylphosphine derivatives of [Rh$_6$(CO)$_{16}$] has been observed.[10] This isomerization occurs within the coordination sphere of the hexarhodium clusters to give the allyl compounds coordinated through the double bond of the rearranged alkenyl moieties. In a similar way, the products obtained by the reactions of μ^3-alkenyl triruthenium carbonyl clusters with alkynes yielded vinylidene-bridging complexes at refluxing temperatures.[11] The isomerization of cyano-olefins by nickel complexes has been found to go through the formation of an intermediate π-methylallyl metal complex.[12]

Scheme 1 . Transformation of (1-Alkenyl)platinum(II) to (2-Alkenyl)platinum(II) Complexes



Experimental Section

All manipulations were carried out under a nitrogen atmosphere unless otherwise stated. The solvents were commercially available

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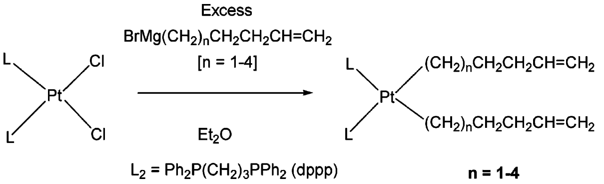
[12] Acosta-Ramirez, A.; Flores-Gaspar, A.; Munoz-Hernandez, M.; Arevalo, A.; Jones, W. D.; Garcia, J. J. *Organometallics* **2007**, *26*, 1712−1720.

10.1021/om0611249 CCC: $37.00



(1)

and distilled from dark purple solutions of sodium/benzophenone ketyl. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DMX-400 spectrometer, and all ^{1}H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents (all at 298 K, C_6D_6). Microanalyses were conducted with a Thermo Flash 1112 Series CHNS-O Analyzer instrument. GC analyses were carried out using a Varian 3900 gas chromatograph equipped with an FID and a 30 m × 0.32 mm CP-Wax 52 CB column (0.25 μm film thickness). The carrier gas was helium at 5.0 psi. The oven was programmed to hold at 32 °C for 4 min and then to ramp to 200 °C at 10 deg/min and hold 5 min. GC-MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60 m × 0.25 mmRtx-1 column (0.5 μm film thickness). The carrier gas was helium at 0.9 mL/min. The oven was programmed to hold at 50 °C for 2 min and then ramp to 250 °C at 10 deg/min and hold 8 min. Pt(COD)Cl$_2$,[13] Pt(PPh$_3$)$_2$Cl$_2$,[14] Pt(dppp)Cl$_2$,[14] and 1-alkenyl Grignard reagents (BrMgCH$_2$CH$_2$(CH$_2$)$_n$CH═CH$_2$; n = 1, 3, 4, 6) were prepared according to literature procedures.[15] The compounds **2**−**4** were prepared in a similar way to that mentioned above[7] (eq 1).

***cis*-[Pt(1-pentenyl)$_2$(dppp)] (1)**. In a Schlenk flask, Pt(COD)Cl$_2$ (406 mg, 1.085 mmol) in diethyl ether (20 mL) was cooled to −78 °C and 1-pentenyl Grignard reagent (2.8 mL of 1.34 M, 3.75 mmol) was added. The solution was brought to ca. 0 °C and then stirred until the solution became clear. To this dppp was added (448 mg, 1.086 mmol) and the reaction mixture stirred for 36 h until a clear solution was formed. The excess Grignard reagent was removed by hydrolyzing the reaction mixture with 5 mL of saturated aqueous NH$_4$Cl at −78 °C. The aqueous layer was washed with 3 × 5 mL of dichloromethane before the organic layer was separated. All the volatiles in the flask were removed under reduced pressure, and the residue obtained was recrystallized from a CH$_2$Cl$_2$/hexane mixture (5 mL:10 mL) at −10 °C for 48 h. The colorless crystalline solid was separated by decanting the mother liquor and dried under vacuum. For **1**: mp 120−122 °C; yield 97%. Anal. Calcd for $C_{37}H_{44}P_2Pt$: C, 59.59; H, 5.95. Found: C, 59.50; H, 5.68. ^{1}H NMR: δ 7.22−7.60 (m, 20H, Ph), 5.48−5.62 (m, 2H, ═CH); 4.67−4.77 (m, 4H, ═CH$_2$), 2.43−2.56 (m, 6H, P−CH$_2$), 0.86−2.08 (m, 12H, −CH$_2$). ^{31}P{^{1}H} NMR: 3.59 (s) ($J_{\mathrm{Pt-P}}$ = 1623 Hz). ^{13}C{^{1}H} NMR: 140.8 (s, *C*H═), 127.3−134.1 (m, Ph), 112.7 (s, ═*C*H$_2$), 40.8, 32.1, 28.2, 24.5, 25.5, 25.6, 20.3.

***cis*-[Pt(2-pentenyl)$_2$(dppp)] (5).** A Schlenk flask was charged with (115 mg, 0.154 mmol) of **1** in toluene (30 mL), and the mixture was heated at 110 °C for 125 h under reduced pressure. The reaction was monitored by ^{1}H NMR. All the volatiles were removed from the pale yellow-brown reaction mixture. The product was recrystallized from a CH$_2$Cl$_2$/hexane mixture (3 mL:5 mL) at −10 °C for 48 h to give pure **5** as a crystalline, colorless solid. Yield: 96 mg (84%). Mp: 143−145 °C. Anal. Calcd for $C_{37}H_{44}P_2Pt$: C, 59.59; H, 5.95. Found: C, 59.66; H, 5.74. ^{1}H NMR: δ 6.76−7.74 (m, 20H, Ph), 5.21−5.58 (m, 4H, ═CH), 1.83−2.13 (m, 6H, P−CH$_2$), 0.68−1.77 (m, 14H, CH$_2$ and CH$_3$). ^{31}P NMR: δ 3.88 (m) ($J_{\mathrm{Pt-P}}$ = 1645 Hz). ^{13}C{^{1}H} NMR: 133.4, 133.5, 133.6 (isomers, ═*C*HCH$_2$−), 126.5−131.6 (m, Ph), 123.9, 124.3, 124.7 (isomers, ═*C*HCH$_3$), 29.6, 27.6, 26.0, 23.2, 17.6, 14.1.

***cis*-[Pt(2-hexenyl)$_2$(dppp)] (6).** Compound **6** was prepared in the same fashion as compound **5** utilizing (108 mg, 0.14 mmol) of **2** in toluene at 110 °C for 60 h. After removing the solvent, the residue crystallized out of 10 mL of *n*-hexane at −10 °C and was recrystallized from a CH$_2$Cl$_2$/*n*-hexane mixture. The yield of the white crystalline solid was 84 mg (78%), mp 96−98 °C (dec). Anal. Calcd for $C_{39}H_{48}P_2Pt$: C, 60.53; H, 6.25. Found: C, 60.64; H, 6.17. ^{1}H NMR: δ 6.95−7.62 (m, 20H, Ph), 5.22−5.59 (m, 4H, ═CH), 1.82−2.19 (m, 6H, P−CH$_2$), 0.73−1.79 (m, 18H, CH$_2$ and CH$_3$). ^{31}P NMR: δ 3.94 (m) (1631 Hz).

***cis*-[Pt(2-heptenyl)$_2$(dppp)] (7).** Compound **7** was prepared in the same fashion as compound **5** utilizing (125 mg, 0.156 mmol) of **3** in toluene at 110 °C for 24 h and recrystallized as described for compound **6**. The yield was 101 mg (81%) of the white crystalline solid, mp 88−90 °C (dec). Anal. Calcd for $C_{41}H_{52}P_2Pt$: C, 61.41; H, 6.54. Found: C, 61.68; H, 6.62. ^{1}H NMR: δ 6.95−7.63 (m, 20H, Ph), 5.27−5.51 (m, 4H, ═CH), 2.02−2.14 (m, 6H, P−CH$_2$), 0.71−1.97 (m, 22H, CH$_2$ and CH$_3$). ^{31}P NMR: δ 3.4 (s) (1625 Hz).

***cis*-[Pt(2-octenyl)$_2$(dppp)] (8).** Compound **8** was prepared in the same fashion as compound **5** utilizing (120 mg, 0.145 mmol) of **4** in toluene at 110 °C for 18 h and recrystallized as described for compound **6**. The yield of the white crystalline solid was 106 mg (88%), mp 82−85 °C (dec). Anal. Calcd for $C_{43}H_{56}P_2Pt$: C, 62.23; H, 6.80. Found: C, 62.41; H, 6.82. ^{1}H NMR: δ 6.96−7.61 (m, 20H, Ph), 5.27−5.41 (m, 4H, ═CH), 2.05−2.17 (m, 6H, P−CH$_2$), 0.75−2.04 (m, 26H, CH$_2$ and CH$_3$); 2.34−3.43 (m, 6H, P−CH$_2$), 0.88−2.35 (m, 14H, CH$_2$). ^{31}P NMR: δ 3.66 (s) (1611 Hz). ^{13}C{^{1}H} NMR: 133.7, 133.8, 133.9 (isomers, ═*C*HCH$_2$−), 127.7−132.2 (m, Ph), 123.8, 124.4, 124.8 (isomers, ═*C*HCH$_3$), 36.7, 33.1, 30.16, 29.6, 27.6, 26.0, 23.1, 18.1, 14.3, 13.8.

***cis*-[Pt(octyl)$_2$(dppp)] (11).** In a Schlenk flask, Pt(COD)Cl$_2$ (306 mg, 0.818 mmol) in diethyl ether (15 mL) was cooled to −78 °C and octyl Grignard reagent (4.7 mL of 0.62 M, 2.863 mmol) was added. The solution was brought to ca. 0 °C and then stirred until the solution became clear. To this was added dppp (338 mg, 0.819 mmol) and the reaction mixture stirred for 36 h until a clear solution formed. The reaction mixture was worked up as described in the preparation of compound **1**. The colorless crystalline solid was obtained from the mother liquor and dried under vacuum for few hours. For **9**: yield 94%, mp 93−95 °C. Anal. Calcd for $C_{45}H_{66}P_2Pt$: C, 62.55; H, 7.70. Found: C, 62.38; H, 7.66. ^{1}H NMR: δ 7.67−7.7 (m, 20H, Ph); 2.05−2.21 (m, 6H, P−CH$_2$); 0.79−1.89 (m, 34H, −CH$_2$). ^{31}P{^{1}H} NMR: δ 3.91 (s) ($J_{\mathrm{Pt-P}}$ = 1619 Hz).

Results and Discussion

Heating compounds **1**−**4** in toluene or benzene at 110 °C results in quantitative isomerization of both 1-alkenyl chains to yield the 2-alkenyl platinum(II) complexes (**5**−**8**) (Scheme 1). These reactions are completely selective, as there is no indication of any further isomerization to 3-alkenyl species or indeed any other organic decomposition products. All the products **5**−**8** were isolated in good yields and fully characterized by analytical and spectroscopic methods (see Experimental Section). These reactions can readily be followed by observing the disappearance of the terminal ═CH$_2$ signal of **1**−**4** in the ^{1}H NMR spectrum and the appearance of a new ═CH signal. Fine structure in the ^{31}P NMR spectra for **5** and **6** (see Figure 1) was observed during the reaction,[16] which we believe is due to the presence of several alkene isomers that differ only slightly in their ^{31}P NMR chemical shifts, as shown in Figure 1. In

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(13) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411−428.

(14) (a) Slack, D. A.; Baird, M. C. *Inorg. Chim. Acta* **1977**, *24*, 277−280. (b) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449−1462.

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(16) The reaction was carried out at 100 °C, and the ^{31}P NMR spectrum was run at room temperature.

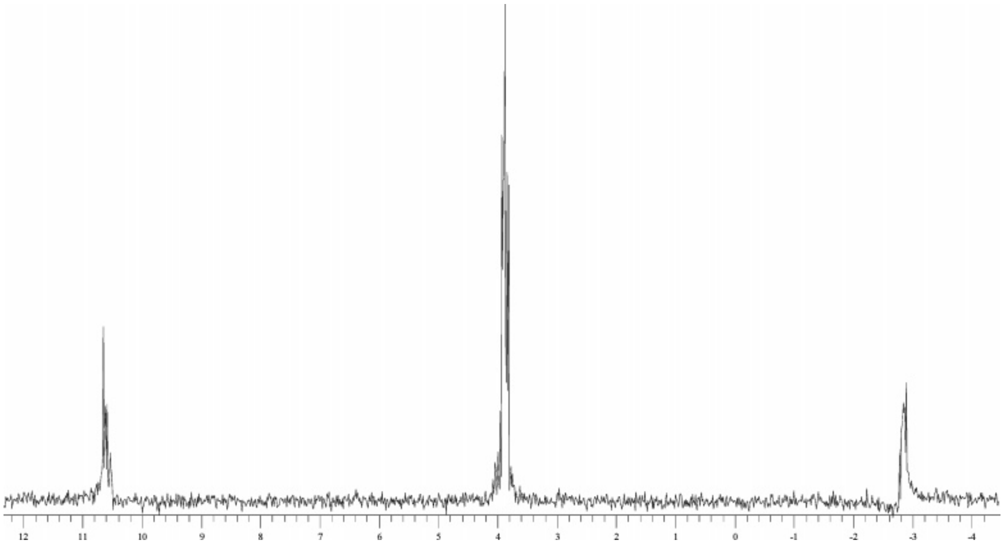

Figure 1. ^{31}P NMR spectrum for bis(2-pentenyl)platinum(II), δ 3.88 ($J_{\mathrm{Pt-P}} = 1645$ Hz).

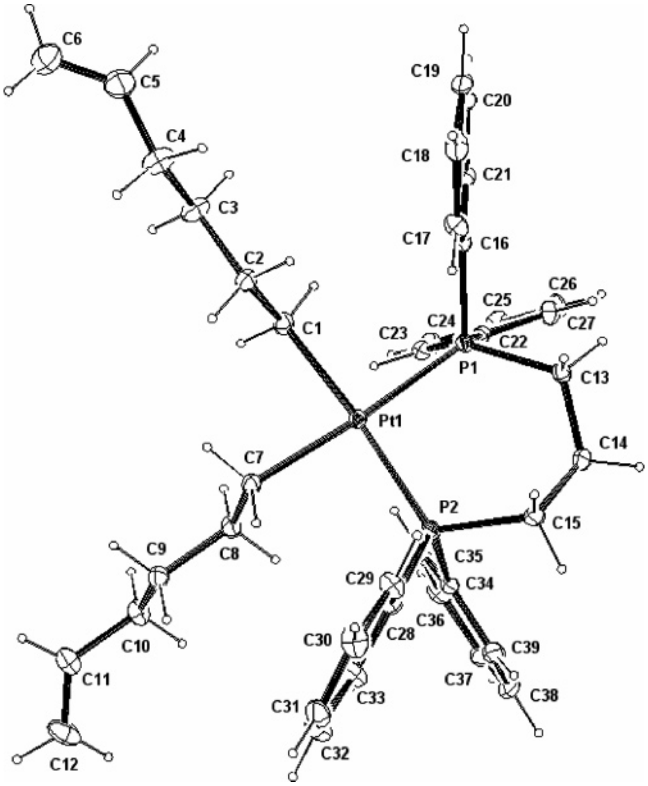

Figure 2. Molecular structure of the major component of compound **2** in the solid state, depicted at the 30% probability level. Selected bond lengths (Å): Pt(1)−P(1) 2.2782(10); Pt(1)−P(2) 2.2805(10); Pt(1)−C(1) 2.120(4); Pt(1)−C(7) 2.118(4); C(5)−C(6) 1.271(7); C(11)−C(12) 1.315(6). Selected bond angles (deg): P(1)−Pt(1)−P(2) 93.95; C(1)−Pt(1)−C(7) 85.03.

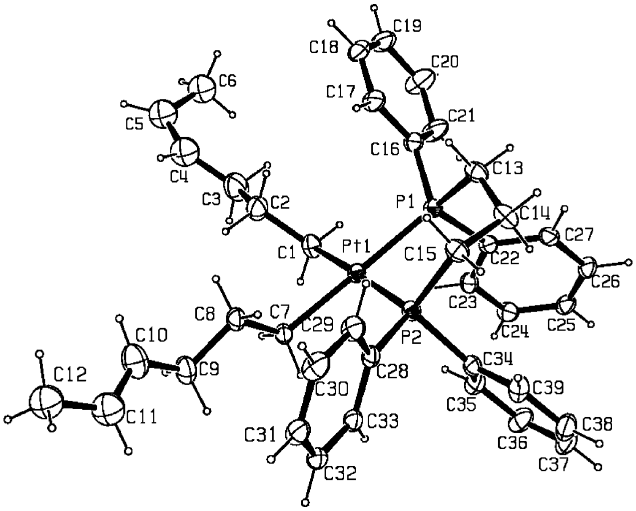

Figure 3. Molecular structure of the major component of compound **6** in the solid state, depicted at the 30% probability level. Selected bond lengths (Å): Pt(1)−P(1) 2.2833(12); Pt(1)−P(2) 2.2877(12); Pt(1)−C(1) 2.109(5); Pt(1)−C(7) 2.104(5); C(5)−C(6) 1.4994(10); C(11)−C(12) 1.4996(10); C(4)−C(5) 1.3200(10); C(10)−C(11) 1.3205(10). Selected bond angles (deg): P(1)−Pt(1)−P(2) 91.17; C(1)−Pt(1)−C(7) 86.3.

contrast, ^{31}P NMR spectra of compounds **7** and **8** showed sharp singlets at δ 3.40 and 3.66 ($J_{\mathrm{Pt-P}} = 1620$ Hz), respectively, indicating that in these cases the presence of isomers, if they are present, did not have any effect on the ^{31}P NMR. The corresponding dppp complex of bis(octyl)platinum(II) (**11**) showed a similar coupling constant, $J_{\mathrm{Pt-P}} = 1619$ Hz at 3.91 ppm. This could be due to the terminal alkene moiety being further away from the metal in **7** and **8**. The range of coupling constants, J(Pt−^{1}H), of platinum with the hydrogen of the adjacent methylene group was found to be 76 to 80 Hz. It was difficult to assign the coupling constants for the rest of the methylene hydrogens, as the signals were seen as a broad multiplet in the ^{1}H NMR. In a similar way, ^{13}C NMR spectra also showed the coupling constants in a range of 638 to 646 Hz for the $^{1}J(^{195}\mathrm{Pt}^{13}\mathrm{C})$ for both the precursors (**1**−**4**) as well as the isomerized products (**5**−**8**). Single crystals of **2** and **6** suitable for X-ray analysis were grown from CH_2Cl_2/hexane solutions. These structures confirmed that **2** is a 1-alkenyl compound and that **6** is a 2-alkenyl compound (see Figures 2 and 3). Interestingly, it also shows that the two alkenyl chains in **6** are different from each other, within the same molecule, with one chain showing that the alkene H atoms are *cis* to each other, whereas the other shows *trans*-positioned H atoms. Bond lengths and angles of **2** and **6** are consistent with those reported for similar compounds.[17]

We also find that 1-alkenes such as 1-pentene, 1-hexene, and 1-octene undergo selective isomerization to their corresponding

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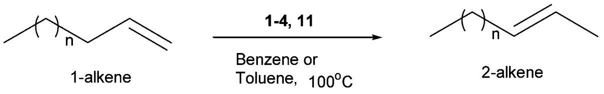
[17] Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

2-alkenes in the presence of **1**−**4** under similar experimental conditions (eq 2). These alkene isomerization reactions are catalytic. In addition, we show that the incoming 1-alkene ends up as the alkyl group in PtL$_2$R$_2$, suggesting that 1-alkene insertion into a Pt−H bond is a key step in these reactions.



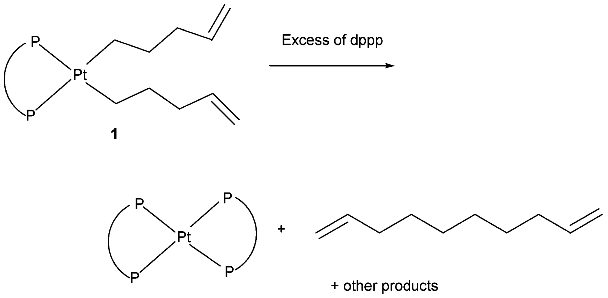
(2)

Also our experiments on the catalytic isomerization of 1-alkenes with bis(octyl)platinum(II) complex **11** as catalyst suggest that the reaction proceeds through an intermolecular interaction (eq 2). Surprisingly, the catalytic activity of metal-alkyl complexes PtL$_2$R$_2$ in this regard is quite comparable with that of compounds **1**−**4**.

An experiment was carried out to determine if PtL$_2$H$_2$ species were involved in the isomerization reaction that could have arisen from two β-H eliminations of PtL$_2$(1-alkenyl)$_2$. The PtL$_2$H$_2$ species could react with 1-alkene to give PtL$_2$R$_2$. However, the attempted *in situ* generation[18] of PtL$_2$H$_2$ and reaction with 1-alkene did not result in the formation of a bis(alkyl)platinum(II) complex, as observed by the ^{31}P NMR.

It is significant to note that this selective isomerization is dependent on the concentration of the solution. In a dilute solution, the isomerization is faster than in a more concentrated one.[19] This may suggest that the isomerization reaction proceeds via an intramolecular process.

During the isomerization of compounds **1**−**4**, the solution changed from colorless to yellow-brown, which is a characteristic color of Pt^0 and some other nanoclusters.[20] To eliminate the possibility that Pt(0) species were catalyzing the isomerization, the reactions were carried in the presence of Hg metal. Since the reaction proceeded in the presence of mercury, we believe that Pt(0) species are not the main species responsible for this catalytic isomerization. The addition of free ligand (dppp) completely retarded the isomerization reaction of **1** under similar experimental conditions, and a new product, Pt(dppp)$_2$ was formed with reductive elimination of 1-decene and 1,9-decadiene (see eq 3); traces of 1-pentene and *n*-pentane were also detected. As Pt(dppp)$_2$ also did not show any isomerization of 1-alkene, the involvement of Pt(0) species was ruled out.



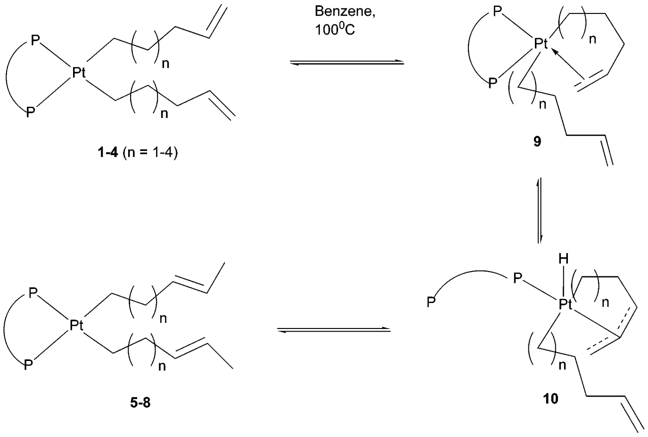
1

+ other products

(3)

Taking all the above into account, we suggest a possible mechanism for these isomerizations (see Scheme 2) involving coordination of the pendant alkene, partial dissociation of the diphosphine ligand, rearrangement to an allyl hydride intermediate, followed by isomerization to give the 2-alkenyl product. In attempts to obtain support for this mechanism, we investigated the ^{1}H and ^{31}P NMR spectra of **4** at high temperature. However, these spectra did not show any peaks corresponding to the intermediates **9** and **10**, nor could any ligand dissociation be detected even though 40% of isomerized product was formed during the measurements.

Scheme 2. Proposed Mechanism for the Internal Isomerization Reactions of the Bis(1-alkenyl)platinum(II) Complexes



1-4 (n = 1-4)

9

5-8

10

It is possible that intermediates **9** and **10** are involved, but they may be too short-lived to be detected. The experiments clearly reveal that the transformation of 1-alkenes and self-isomerization of metal bis(1-alkenyls) are possible and allylic intermediates would seem to be most likely. Under these experimental conditions the isomerization is favored rather than the expected β-hydrogen elimination reaction for these compounds.

We also find that the isomerizations are strongly dependent on the length of the alkenyl chains. Thus, it was found that the longest chain (1-heptenyl) investigated is the fastest to undergo isomerization (see Figure 4). This could be due to strain in the small rings when the alkenyl chains coordinate to the metal, as in **9** in Scheme 2.

A rise in temperature (>150 °C) of benzene solutions of **1**−**4** led to the cleavage of the Pt−C bonds, yielding the corresponding 1-alkenes, 2-alkenes, dienes, etc.

These isomerization reactions were also found to be dependent on the nature of the phosphine ligand system present; thus the chelating effect of diphosphines reduces the amount of decomposition of the 1-alkenyl compounds, even at high temperatures. The PPh$_3$- and P^{t}Bu$_3$-containing metal-alkenyl

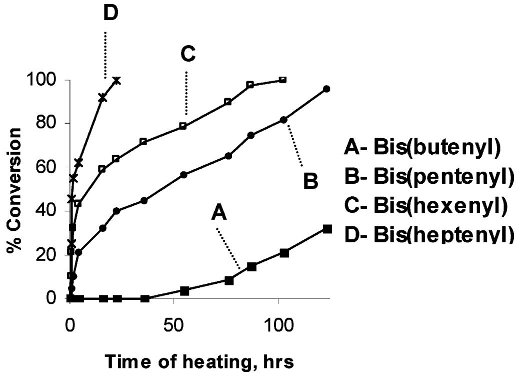


Figure 4. Effect of length of alkenyl chains on isomerization of bis(alkenyl)platinum(II) complexes at 100 °C in benzene.

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[18] Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063.

[19] The two different concentrations of compound **2** (in 5 mL of toluene as solvent) were taken as 7×10^{-4} and 2.8×10^{-3} M for the isomerization reactions, and the time of reaction (product formed) was observed as 110 h (100%) and 110 h (65%), respectively.

[20] (a) Creighton, J. A.; Eadon, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3881. (b) Finney, E. E.; Finke, R. G. *Inorg. Chim. Acta* **2006**, *359*, 2879−2887.

Table 1. Details of Crystallographic Data Collection and Refinement Parameters

	2	**6**
structure formula	$PtC_{39}H_{48}P_2$	$PtC_{39}H_{48}P_2$
fw	773.80	773.80
data collection temp (K)	113(2)	113(2)
cryst syst, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a (Å)	14.1180(2)	10.0956(2)
b (Å)	14.5423(2)	12.8451(2)
c (Å)	18.3322(2)	14.5163(3)
α (deg)	90	77.775(1)
β (deg)	111.156(1)	84.714(1)
γ (deg)	90	70.779(1)
volume (Å^3)	3510.08(8)	1736.70(6)
Z	4	2
D_c, calcd density (g cm^{-3})	1.464	1.480
absorp coeff μ (mm^{-1})	4.114	4.157
F(000)	1560	780
cryst size (mm)	0.08 × 0.16 × 0.18	0.15 × 0.17 × 0.21
θ range for data collection	1.84−26.74	3.42−25.97
limiting indices	±17; ±18; −23,22	−11,12; ±15; ±17
no. of reflns collected/ unique	61 043/7453	42 629/6749
no. of params	380	353
extinction coeff	0.00062(7)	0.0002(3)
goodness-of-fit on F^2	1.092	1.065
final R indices [$I > 2\sigma(I)$]	R1 = 0.0341 wR2 = 0.0595	R1 = 0.0330 wR2 = 0.0802
R indices (all data)	R1 = 0.0514 wR2 = 0.0648	R1 = 0.0409 wR2 = 0.0841
largest diff peak and hole (e Å^{-3})	1.464/−0.915	1.209/−2.821

complexes however decompose rapidly above 80 °C; hence the isomerization could not be detected with these ligands.

Thermal decomposition of the compounds **5**−**8** in dichloromethane at high temperatures (150−170 °C) yielded 85% of the corresponding 2-alkenes as the major products (with 65% *trans*-2-alkene and 35% *cis*-2-alkene), which were analyzed by GC-MS. These yields depended significantly on the experimental conditions for decomposition, i.e., whether in solid state or in solution.

The molecular structures of **2** and **6** were determined by single-crystal X-ray analysis and are illustrated in Figures 2 and 3, respectively. The structural analysis confirms that **6** is the isomerization product of **2**. The main changes in the structural features of complexes **2** and **6** are the differences in some of the bond angles and bond lengths. The Pt−P bonds of compound **2** are slightly shorter than for compound **6**, whereas the Pt−C bonds of **2** are slightly longer than those for **6**. However these bond distances are comparable with the literature reports[17] for related compounds (for Pt−C, 2.118(3)−2.110(3) Å, and Pt−P, 2.263(9)−2.293(7) Å, respectively), while the C═C distances range from 1.271(7) to 1.3200(10) Å. The internal alkene C═C distance in **6** is longer than in **2**. The P−Pt−P and C−Pt−C bond angles in **2** and **6** vary from 93.95(4)° to 91.17(4)° and 85.06(15)° to 86.03(2)°, respectively. Table 1 lists the pertinent crystal data for **2** and **6** (see also the Supporting Information).

Conclusions

The *cis*-[Pt(1-alkenyl)$_2$L$_2$] complexes undergo irreversible selective isomerization reaction to the corresponding *cis*-[Pt(2-alkenyl)$_2$L$_2$] complexes. The rate of isomerization is mainly dependent on the length of the alkenyl chains, the ligand, and the concentration. These complexes also serve as catalysts that selectively isomerize 1-alkenes to their 2-alkene analogues. Currently, we are exploring the interesting properties and reactivity of these compounds. We are also investigating similar compounds with other metal systems.

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Supporting Information Available: Tables of crystallographic data and ^{1}H NMR spectra for **2** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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