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Synthesis, structure and reactivity of *cis*-[PtL_2(1-alkenyl)$_2$] complexes

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Abstract

The synthesis and characterization of several new bis(1-alkenyl)platinum(II) complexes have been carried out. The structure of *cis*-[Pt(dppp)(($CH_2)_6CH{=}CH_2)_2$] has been determined by X-ray crystallography. The stability and reactivity of the compounds, *cis*-[$PtL_2((CH_2)_nCH{=}CH_2)_2$] ($n = 3$ or 4 and L_2 = 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)ethane (dppe), L = PPh_3) is strongly dependent on the nature of ligand systems. It is found that the insertion of carbon monoxide into the metal–carbon bonds of the platinum alkenyl complexes is possible. Other reactions including transmetalation, intermolecular alkenyl migrations, oxidative addition of methyl iodide are described and the thermal decomposition of the bis(alkenyl) complexes are also reported.

Keywords: Bis(alkenyl) complexes; Structure; Reactivity; Insertion reactions; Oxidative addition; Transmetalation

1. Introduction

Metal–alkenyl complexes are an important class of compounds. These compounds have been implicated as potential model compounds for intermediates in a number of catalytic cycles as well as other applications [1]. Metal–alkenyl complexes have been shown to act as precursors for the preparation of thin metal films, which can in turn be applied in the micro-electronics and catalysis industries [2]. Recently we have shown that bis(1-alkenyl)platinum complexes undergo a novel ring closing metathesis (RCM) reaction to give medium to large metallacycles [3–5]. Selective and quantitative isomerization of *cis*-[PtL_2(1-alkenyl)$_2$] to *cis*-[PtL_2(2-alkenyl)$_2$] complexes has also been observed [6]. In order to explore the reactivity pathways for these complexes, we have investigated some novel reactions of platinum alkenyl complexes. The present paper also explores the influence of the nature of phosphine ligands on the reactivity aspects of the title compounds.

2. Experimental

2.1. Materials and methods

All manipulations were carried out under a nitrogen atmosphere unless otherwise stated. Commercially available solvents were distilled from Na metal/benzophenone ketyl before use.

2.1.1. Nuclear magnetic resonance spectroscopy

^{1}H, ^{13}C 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 deuterated solvents (all at 298 K, C_6D_6).

2.1.2. Elemental analysis

Microanalyses were conducted with a Thermo Flash 1112 Series CHNS-O Elemental Analyzer instrument.

2.1.3. GC–MS analysis

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

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thickness). The carrier gas used 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 °C/min and then hold for 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 mm Rtx-1 column (0.5 μm film thickness). The carrier gas was helium at a flow rate of 0.9 ml/min. The oven was programmed to hold at 50 °C for 2 min and then ramp to 250 °C at 10 °C/min and then hold for 8 min.

2.1.4. Infrared spectroscopy

Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR Spectrometer.

2.1.5. Materials

All chemicals were obtained commercially and unless otherwise stated, were used as received without further purification. 1-Alkenyl Grignard reagents ($BrMgCH_2CH_2(CH_2)_nCH{=}CH_2$; $n = 1, 3, 4, 6$) [7], $Pt(COD)Cl_2$ [8], $Pt(dppe)Cl_2$, [9] $Pt(dppp)Cl_2$, [9] and $Pt(PPh_3)_2Cl_2$ [9] were prepared according to the literature procedures. Bis(1-octenyl)(dppp)platinum(II) (**1**), bis(1-hexenyl) *cis*- bis(triphenylphosphine)platinum(II) (**2**), bis(1-hexenyl)(dppp)platinum(II) (**3**), bis(1-pentenyl)*cis*-bis(triphenylphosphine)platinum(II) (**4**) and bis(1-pentenyl)(dppp)-platinum(II) (**5**) were prepared as reported earlier [4].

*2.1.6. Crystallographic data for compound **1***

Single crystals of compound **1** were obtained by recrystallization and slow evaporation from Et_2O at room temperature. Intensity data for the compound **1** was collected at 113 K on a Nonius Kappa CCD diffractometer using graphite- monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). $C_{43}H_{56}P_2Pt$, $M = 829.91$, triclinic, $P\bar{1}$, $a = 12.59740(10)$, $b = 12.98700(10)$, $c = 14.5363(2)$ Å, $\alpha = 110.3300(10)°$, $\beta = 90.6480(10)°$, $\gamma = 117.1230(10)°$, $V = 1943.33(3)$ Å^{-3}, $Z = 2$, $\mu = 3.720$ mm^{-1}, unique reflections = 55624/7391 [$R(\text{int}) = 0.0467$], $R_1 = 0.0210$, $wR_2 = 0.0433$ [$I > 2\sigma(I)$].

2.2. Synthesis of the metal complexes

*2.2.1. Preparation of bis(1-pentenyl)(dppe)platinum(II) (**6**)*

$Pt(COD)Cl_2$ (506 mg, 1.352 mmol) in diethyl ether (20 ml) was cooled to −78 °C and of 1-pentenyl Grignard reagent (2.8 ml, 1.34 M, 3.75 mmol) was added. The solution was warmed to 0 °C and then stirred until the solution became clear. To this, solution dppe (539 mg, 1.353 mmol) was added and stirred for 30 h until a clear solution was formed. The excess Grignard reagent was removed by hydrolyzing the reaction mixture with saturated aqueous NH_4Cl (5 ml) at −78 °C. The aqueous layer was washed with dichloromethane (2 × 5 ml), dried with anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure and the residue recrystallized from a CH_2Cl_2/hexane mixture (3 ml: 5 ml) at −10 °C for 48 h. The pale yellow crystalline solid was separated by decanting the mother liquor and dried under vacuum for 3 h. For compound **6**. Yield: 96%. M.p. 84–85 °C. *Anal.* Calc. for $C_{36}H_{42}P_2Pt$: C, 59.09; H, 5.79. Found: C, 58.98; H, 5.69%. IR (ν_{max}/cm^{-1}) in CH_2Cl_2: 1605(m), 1636(s); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.36–7.91 (m, 20H, Ph); 5.55–5.72 (m, 2H, =CH); 4.68–4.82 (m, 4H, $=CH_2$); 1.96–2.22 (m, 4H, P-CH_2); 1.21–1.88 (m, 12H, –CH_2);^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.01 (s, 2C);133.16–133.29 (m, 12C); 129.98 (s, 8C) 127.55–128.32 (m, 4C); 112.40 (s, 2C); 32.08–32.56 (m, 2C); 30.88 (s 2C); 29.03–29.79 (m, 2C); 22.57 (d, $J = 6.67$ Hz 2C) 21.60 (d, $J = 6.58$ Hz), $^{31}P\{^1H\}$ 45.76 (s) ($J_{Pt–P} = 1641$ Hz).

2.2.2. Carbonylation of compound 6

Compound **6** (262 mg, 0.358 mmol) was dissolved in toluene (25 ml) of. After bubbling CO through the contents of the flask for 5–6 min, the solution was stirred at room temperature under ambient pressure of carbon monoxide (balloon). After 72 h, the solvent was removed under the reduced pressure. The residue was filtered and recrystallized from a CH_2Cl_2/hexane mixture (2:1 v/v) to give compound **10a**. Yield: 62%. M.p. 118–126 °C. *Anal.* Calc. for $C_{38}H_{42}O_2P_2Pt$: C, 57.94; H, 5.37. Found: C, 58.16; H, 5.42%. IR (ν_{max}/cm^{-1}) in CH_2Cl_2: 1608(m), 1680(s). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.24–7.91 (m, 20H, Ph); 5.54–5.69 (m, 2H, CH); 4.61–4.80 (m, 4H, $=CH_2$); 1.98–2.40 (m, 4H, P–CH_2); 1.16–1.86 (m, 12H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.78 (s, 2C); 140.92 (s, 2C); 133.21–133.58 (m, 12C); 129 (s, 8C); 126.71–128.37 (m, 4C); 112.30 (s, 2C); 31.55 (m, 2C); 30.87 (s, 2C) 25.10 (d, $J = 8.66$ Hz); 24.14 (d, $J = 8.71$ Hz) $^{31}P\{^1H\}$ 46.00 (s) ($J_{Pt–P} = 2320$ Hz).

*2.2.3. Carbonylation of compound **1***

A similar procedure was followed by taking compound **1** (61 mg, 0.073 mmol) in a round bottom flask containing toluene (15 ml). The reaction was carried out and worked-up as described above to give compound **10b** as colourless crystals. Yield: 86%. M.p. 104–105 °C. *Anal.* Calc. for $C_{45}H_{56}O_2P_2Pt$: C, 61.01; H, 6.37. Found: C, 61.16; H, 6.42%. IR (ν_{max}/cm^{-1}) in CH_2Cl_2: 1605(m), 1676(s). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.21–7.97 (m. 20H, Ph); 5.40–5.70 (m, 2H, =CH); 4.63–4.73 (m, 4H $=CH_2$); 1.99–2.15 (m, 6H, P–CH_2); 1.23–1.92 (m, 24H, CH_2).

*2.2.4. Reaction of $Pt(1\text{-pentenyl})_2\ (PPh_3)_2$ (**4**) with $[Cp^*IrCl_2]_2$*

Compound **4** (232 mg, 0.271 mmol) and $[Cp^*IrCl_2]_2$ (0.104 mg, 0.135 mmol) were transferred into a Schlenk flask containing toluene (5 ml). The mixture was heated for 3 h at 85–90 °C. A colourless precipitate was formed during the reaction. The solvent was removed in vacuo. The mixture was treated with diethylether (5 ml). The insoluble crystalline solid was found to be a mixture of $[Pt(PPh_3)_2Cl_2]$ and $[IrCp*(PPh_3)Cl_2]$. The products **13** and

14 from the solution were separated by using a *p*-TLC with CH_2Cl_2 as an eluent. The pale yellow band was extracted and compound **13** was obtained as a yellow oily substance (48 mg). The oil was treated with *n*-hexane (3 ml) and on cooling a yellow solid resulted which was shown to be compound **13**, bis(1-pentenyl)(tetramethylcyclopentadienyl)iridium(III)- (triphenylphosphine) Yield: 50%. M.p. 66–68 °C. *Anal.* Calc. for $C_{37}H_{46}IrP$: C, 62.24; H, 6.49. Found: C, 62.43; H, 6.59%. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.99–8.10 (m, 15H, Ph); 5.63–5.94 (m, 2H, =CH); 4.88–5.13 (m, 4H, $=CH_2$); 4.19 (s, 1H, Cp*–H); 0.76–2.12 (m, 12H, CH_2); $^{31}P\{^1H\}$ 25.88 (s).

2.2.5. Reaction of $Pt(1\text{-pentenyl})_2$ (dppp) (**5**) with $[Cp^*IrCl_2]_2$

Compound **5** (202 mg, 0.272 mmol) and $[Cp^*IrCl_2]_2$ (0.105 mg, 0.136 mmol) were taken in to a Schlenk flask containing toluene (15 ml). The mixture was heated for 13 h at 85–90 °C. The colourless precipitate that formed during the reaction was found to be compound **11**, (η^3-dimethylallyl)[1,3-bis(diphenyl phosphino)propane]-platinum(II)chloride. Yield: 68%. M.p. 144–146 °C. *Anal.* Calc. for $C_{32}H_{35}P_2PtCl$: C, 53.97; H, 4.95. Found: C, 54.16; H, 4.88%. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.23–7.78 (m, 20H, Ph); 3.30–3.87 (m, 3H, allylic-H); 2.17–2.67 (m, 4H, P–CH_2); 1.09–1.17 (m, 6H, CH_2); $^{31}P\{^1H\}$ −1.32 (s) ($J_{Pt–P} = 3828$ Hz). All the solvent was removed from the solution and the obtained pale yellow solid was recrystallized from 1:1 *n*-hexane-diethylether mixture to yield the compound **12**. Yield: 75%. M.p. 108–112 °C. *Anal.* Calc. for $C_{14}H_{22}IrCl$: C, 40.23; H, 5.31. Found: C, 40.46; H, 5.36%. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.43 (s, 1H, Cp–H); 3.95 (m, 1H, CH); 2.95 (m, 1H, **CH**–CH_3); 2.20 (m, 2H, –CH_2), 1.81 (s, 12H, Cp–CH_3), 1.52–1.61 (m, 2H, CH_2); 0.92–1.06 (m, 3H, CH_3).

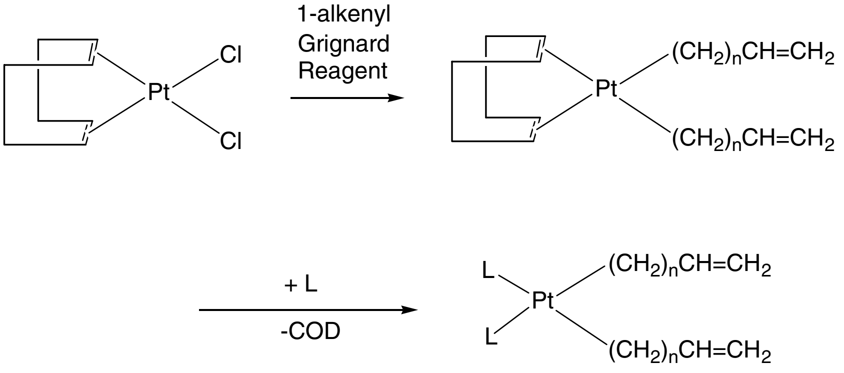
2.2.6. Reaction of $Pt(1\text{-pentenyl})_2$ (dppp) (**6**) with MeI

Compound **6** (304 mg, 0.415 mmol) and 118 mg of MeI (0.832 mmol) were taken in to of CH_2Cl_2 (5 ml). After stirring at room temperature for 72 h, a pale yellow precipitate was formed. The precipitate was washed with diethylether (5 ml) and recrystallized from CH_2Cl_2–hexane mixture (1:1). The product was found to be compound **9b**. The product **9a** was isolated from the solution. After removing the solvent, the compound was recrystallized from a mixture of toluene (2 ml) and hexane (1 ml). The liquid product was found to be 5-iodo-1-pentene. For compound **9a**, (1-pentenyl)(methyl)[1,2-bis-(diphenylphosphino)ethane] platinum(II). Yield: 52%. M.p. 110–112 °C. *Anal.* Calc. for $C_{32}H_{36}P_2Pt$: C, 56.72; H, 5.35. Found: C, 56.66; H, 5.62%. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.18–7.92 (m, 20H, Ph); 5.69–5.86 (m, 1H, =CH); 4.77–4.98 (m, 2H, $=CH_2$); 1.85–2.29 (m, 4H, P–CH_2); 1.15–1.67 (m, 6H, CH_2); $^{31}P\{^1H\}$ δ 45.96, 45.91 (d), 45.76, 45.70 (d) (1685 and 1635 Hz).

3. Results and discussion

3.1. Synthesis and characterization of compounds

The bis(alkenyl)–platinum complexes were prepared in high yields by reacting the appropriate Grignard reagents with $Pt(COD)Cl_2$. Several derivatives of these compounds were synthesized using various ligand systems, mainly, PPh_3, dppe and dppp (Scheme 1). All the data gathered for compounds (**1**–**6**) are consistent with the proposed formulations. The ^1H NMR spectra exhibit signals which are characteristic of species containing a vinylic functionality, while the ^{31}P NMR spectra showed sharp singlets with their respective platinum satellites. Single crystals of compound **1** were obtained by recrystallization from Et_2O at room temperature. Crystallographic data are listed



1, L_2 = dppp, n = 6;
2, L = PPh_3, n = 4;
3, L_2 = dppp, n = 4;
4, L = PPh_3, n = 3;
5, L_2 = dppp, n = 3;
6, L_2 = dppe, n = 3.

Scheme 1.

Table 1
Selected bond distances (Å) and angles (°) of compound **1**

Bond distances			
Pt(1)–C(61)	2.119 (3)	C(56)–C(55)	1.526 (4)
Pt(1)–C(51)	2.120 (3)	C(65)–C(66A)	1.5207 (7)
Pt(1)–P(1)	2.2766 (7)	C(57)–C(58)	1.292 (5)
Pt(1)–P(2)	2.2873 (7)	C(68A)–C(67A)	1.211 (7)
Bond angles			
C(61)–Pt(1)–C(51)	85.05 (10)	C(51)–Pt(1)–P(1)	89.86 (8)
C(61)–Pt(1)–P(2)	91.98 (7)	C(61)–Pt(1)–P(1)	174.78 (7)
P(1)–Pt(1)–P(2)	92.97 (2)	C(51)–Pt(1)–P(2)	173.58 (7)

in Section 2, and selected bond distances and angles are given in Table 1.

The molecular structure of compound **1** (Fig. 1) shows square-planar coordination geometry around the platinum. The Pt–C and Pt–P bonds of compound **1** are similar and comparable with the literature reports of similar compounds [10] (2.119(3)–2.120(3) Å and 2.2766(7)–2.2873(7) Å, respectively), while the C$=$C distances range from 1.211(7) to 1.292(5) Å. The P–Pt–P, P–Pt–C and C–Pt–C bond angles in compound **1** are observed as 92.97(2), 89.86(8) to 91.98(7) and 85.05(10), respectively.

3.2. Reactivity of metal–alkenyl complexes

Generally, metal alkenyl complexes can show two distinct reaction pathways: (i) reaction at the M–C bond (ii) coordination of the pendant alkene. It is interesting to note that these special features impart novel chemistry to these compounds [1a].

The interaction of metal–alkenyls with electrophilic reagents such as acids and halogens gives the corresponding hydrocarbons or 1-haloalkenes resulting from the cleavage of metal–carbon bonds and the hydrogenation and hydroformylation reactions of some metal alkenyl compounds have been reported with the Lewis acid $TiCl_4$ [1b], we explored other novel reactions with various substrates. The group 10 metal-catalyzed cross-coupling reactions are very important in organic synthesis through oxidative addition, transmetallation, and reductive elimination steps [11]. Some of these reactions may have considerable potential in chemical synthesis, since they provide a method for the formation of new C–C bonds by reductive elimination or formation of C–X bonds. The effect of the length of the alkenyl chains, the influence of the solvent as well as the nature of ligand systems on the reactivity of the title compounds will be discussed.

3.3. Thermal decomposition and rearrangement reactions

Although thermal decomposition pathways of metal–alkenyl complexes may be similar to those of metallacycles or metal alkyl complexes, the products formed can differ considerably because of the pendant alkene functionality. The thermal stability of the metal–alkenyl complexes is dependent on the solvent system, thus halogenated solvents readily cleave the M–C bond to form metal halides irrespective of the ligand system. Bis(alkenyl) metal complexes can give various products on decomposition (Scheme 2).

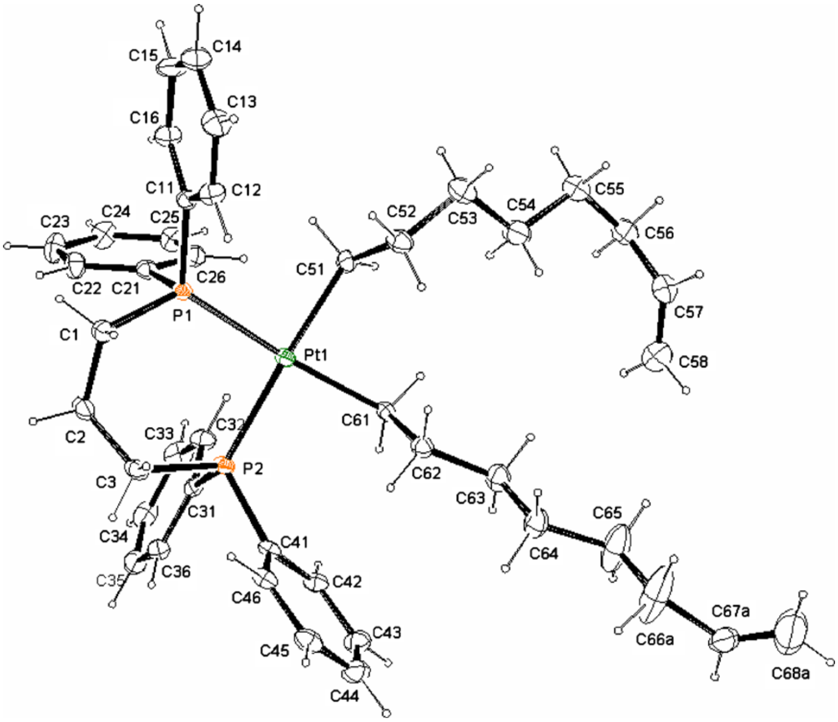
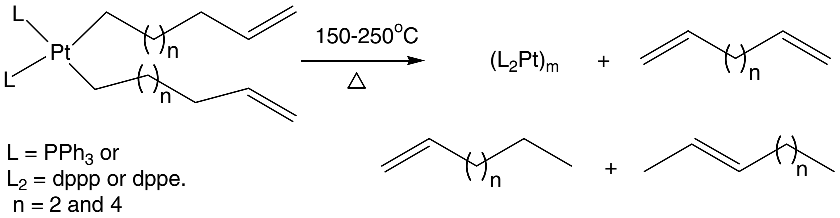


Fig. 1. Molecular structure and atom labeling scheme for compound **1**. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Atom C67 was disordered over two positions: C67A with Site Occupancy 0.535 and C67B with Site Occupancy 0.465.



Scheme 2.

Our present experiments show that the organic products depend on the nature of the ligands, and this may relate to the stability and reactivity of the metal–alkenyl compounds in solution. Thus the triphenylphosphine complexes, $Pt(PPh_3)_2\{(CH_2)_nCH{=}CH_2\}_2$ were found to yield an intense red colour on decomposition which we believe to be due to $[(PPh_3)2Pt]_m$ clusters. In contrast, the $PtL_2[(CH_2)_3CH{=}CH_2]_2$ complexes (where $L_2 =$ dppp or dppe) were found to be quite stable up to 100 °C [6]. The diphosphine ligands have generally been found to increase the thermal stability of the complexes significantly. It is also believed that metal alkenyl species may be important intermediates in the decomposition of metallacycloalkanes through β-hydride elimination [12,13].

Table 2
Thermal decomposition of bis(1-hexenyl)(dppp)platinum(II) (**3**), at 175 °C

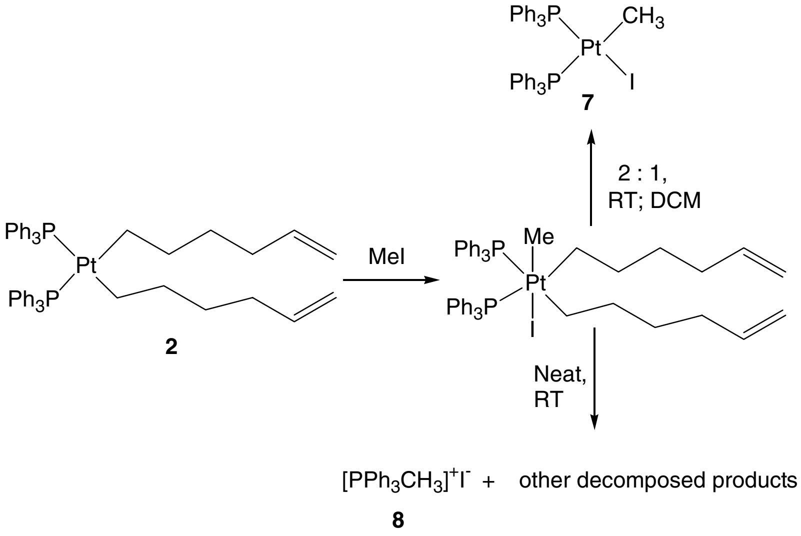
Medium	Observed products (%)*				
	n-Hexane	1-Hexene	2-Hexene (*cis*- + *trans*-isomers)	Cyclohexane	1,5-Hexadiene
Solid					
1 h	25	8	41	14	11
3 h	2	0	63	22	12
10 h	1	0	63	18	8
24 h	0	0	71	21	8
CH_2Cl_2	14	0	83	3	1

By GC–MS analysis.

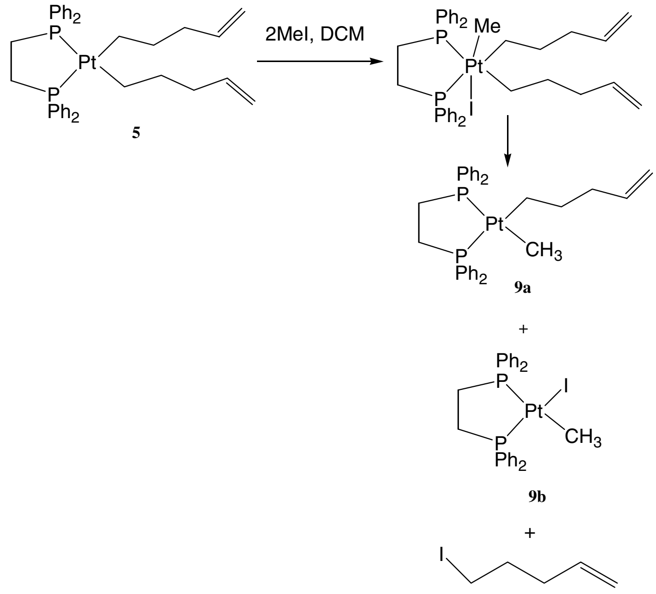
Several interesting trends were noted in the products isolated from the thermolysis reactions. First, all the decomposition reactions showed the presence of 2-alkene and cycloalkane as major components. Second, the organic product distributions are quite dependent on the time of heating as well as the medium of reaction whether in the solid state or in solution (Table 2). It can be seen that there is a significant decrease in the quantities of 1-alkene species with increasing the time of heating, with the exception of PPh_3 derivatives, which is in agreement with earlier reports [6]. Further thermal studies will be carried out to try and understand the mechanistic aspects for the formation of the organic products in these reactions.

3.4. Oxidative addition

The oxidative addition of organic molecules to unsaturated transition metal complexes is a fundamental process in organometallic chemistry and catalytic reactions [14]. It was found that the bis(alkenyl)platinum(II) complexes undergo oxidative addition reactions with methyl iodide to yield different products, depending on the experimental conditions (Schemes 3 and 4). It is presumed that the reaction proceeds via the formation of hexacoordinate platinum(IV) species by oxidative addition as reported earlier



Scheme 3.



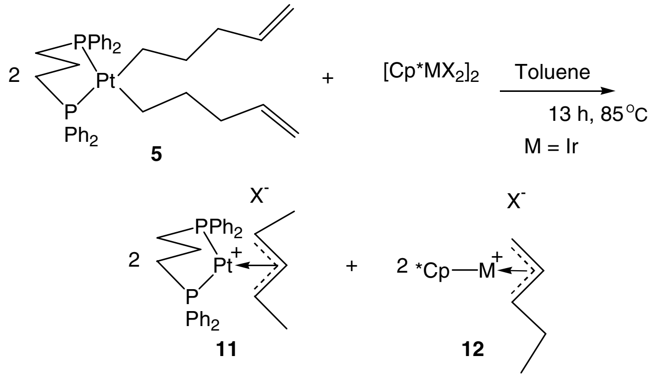
Scheme 4.

[15]. The organic products were found to be 1-alkenes, 2-alkenes and α,ω-dienes. Attempts to isolate these intermediate hexacoordinate platinum(IV) species were unsuccessful.

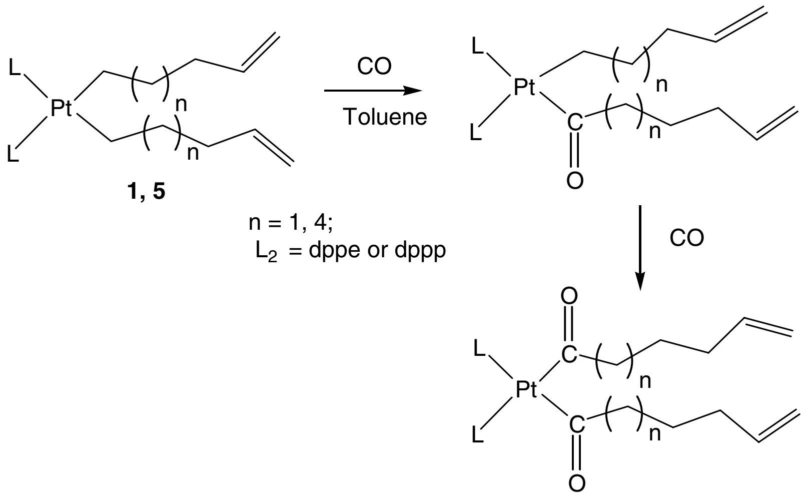
Surprisingly, the oxidative addition of MeI to compound **2** afforded different products depending on the experimental conditions and ligand systems (Scheme 3). It is of interest to note that when MeI was allowed to react with **2** in 2:1 molar ratio, a 70% of known compound Pt$(PPh_3)_2$MeI (**7**) [16] was isolated. The major organic products were found to be 1-hexene (56%), 2-hexene (23%), 1,5-hexadiene (5%) as well as other unidentified products. In contrast, the presence of excess MeI showed the quantitative formation of the known methylphosphonium iodide salt (**8**). The decomposed products could not be identified or isolated. The formation of the new compound **9a** (15%) and known compound **9b** (41%) [16] were evident when the ligand was dppe in the presence of 1:2 MeI (Scheme 4). The formation of 5-iodo-1-pentene (32%) was also confirmed. It is of interest to note that the addition of MeI allowed the formation of a new metal–carbon bond and breaking of already existing metal–carbon bond simultaneously, this is significant. The nature of ligand systems show a marked effect in oxidative addition reactions, which may be due to differences in steric, electronic and chelating effects in the ligands.

3.5. Carbonylation

Carbon monoxide insertion into M-alkyl as well as M-acyl bonds to form M-acyl as well as α-ketoacyl complexes



Scheme 6.



Scheme 5.

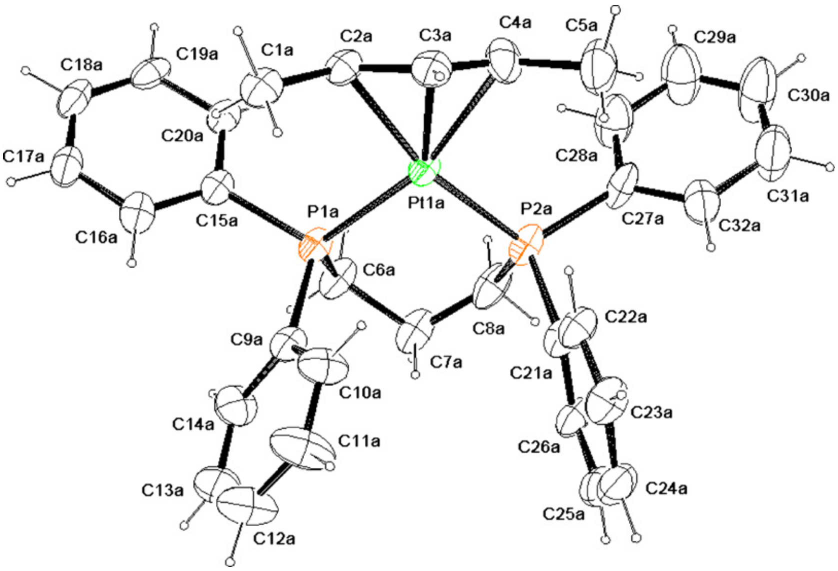


Fig. 2. Molecular structure and atom labeling scheme for the cationic part of the compound **11**, showing one of the two unique molecules (A and B) with the atom-numbering scheme; the suffix a denotes the crystallographically independent molecule A. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii.

is well known in the literature [14,17]. It was found that the reaction of carbon monoxide with the bis(pentenyl)platinum(II) complex $L_2Pt[(CH_2)_3CH{=}CH_2]_2$ ($L_2 = $ dppe) afforded the expected di(acyl) inserted products **10a** while the reactions with other bis(pentenyl) complexes gave unidentified products ($L_2 = $ COD). The ^{1}H NMR spectra of the reaction mixture ($L = PPh_3$ and $L_2 = $ dppp) showed very complex signals indicating the presence of the monoacyl intermediate, which was identified by the characteristic ^{31}P NMR spectrum. However, the reaction smoothly proceeds to the formation of compound **10a** over time. This was evidenced by the ^{13}C NMR which shows a signal in the region of δ 206.8 ppm for the carbonyl carbon as well as a signal at δ 31.5 ppm corresponding to the carbon α to the carbonyl carbon. The IR spectral analysis of the reaction mixture also indicated the presence of bands corresponding to the coordinated CO, which may be due to the replacement of PPh_3 with CO ligands, when $L = PPh_3$. A solution of compound **1** in toluene was subjected to carbonylation with carbon monoxide gas at room temperature. This resulted in the insertion of CO into the Pt–C σ bond to afford the di-acyl product as a colourless crystalline solid after 48 h (Scheme 5). Two strong IR bands at 1605 cm^{-1} (C=C) and 1676 cm^{-1} (C=O) were observed in the spectrum of compound **10b**.

3.6. Transmetalation reactions

Transmetalation is a fundamental step in cross-coupling chemistry [11]. Various transmetalation reactions of group 10 metal halide complexes with organoboronic acid or organometallic reagents have received recent attention [18,19]. Clarke and Heydt have reported the importance of ligand steric effects on transmetalation reactions of some organometallic complexes [20].

The diphosphine ligand system allowed the quantitative formation of allylic metal complexes after reaction of compound **5** with the dimeric sandwich compounds of iridium (Scheme 6). Products **11** and **12** were isolated from diethylether solution and characterized by spectroscopically. Compound **11** was also characterized by X-ray analysis, but the structure was not fully refined.[1]

The Pt–P bonds of compound **11** are found to be 2.261(2) and 2.265(2) Å, while the Pt–C bond distances range from 2.156(10)–1.266(3) Å (Fig. 2). Strikingly, the distance between central allylic carbon (C_3) and metal is the shortest. The allylic carbon–carbon distances (C_2–C_3 and C_3–C_4), ranging from 1.349(18) to 1.427(16), showed the nature of double bond and the other C_1–C_2 and C_4–C_5 distances are found to be single bonds. The P–Pt–P, P_1–Pt–C_2 and C–Pt–C bond angles in compound **11** are observed as 94.69(11), 98.0(3) and 66.9(5), respectively.

In contrast, the PPh_3 ligand system shows a different trend in the reactivity by forming unexpected compounds **13** and **14** (Scheme 7). The compound can be easily assigned in the ^{31}P NMR, showing a signal at 26.4 ppm

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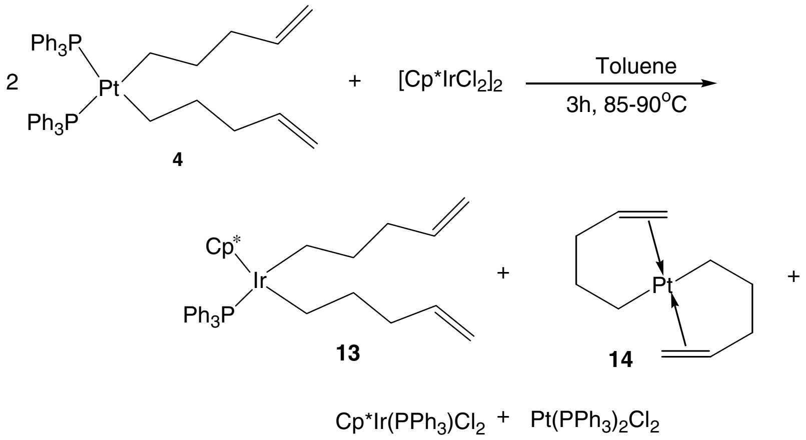
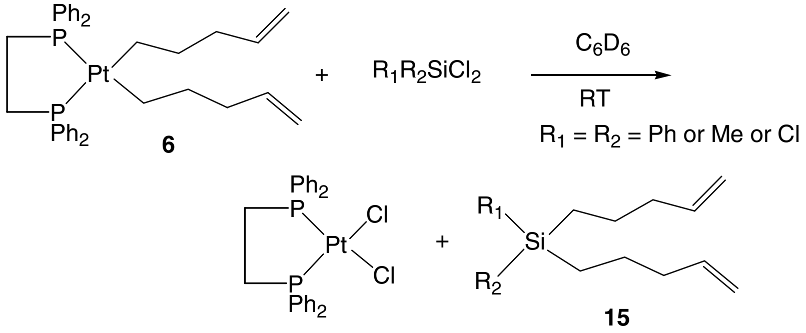
[1] The cationic part of the structure was completely solved, but we failed to solve the counter anion because there were unidentified discrete solvent molecules in this structure. However, the positions for the atoms of cationic part of the compound 11 molecules were unambiguously placed and refined with reasonable anisotropic displacement parameters. The final R factor of 0.0591 is acceptable. We therefore report this structure here. The parameters for crystal data collection and structure refinements are in Table 1. The bond lengths, angles, torsion angles and other molecular parameters are in Table 2–6 (see supporting information for the tables and other details about the data collection).



Scheme 7.



Scheme 8.

without any satellites. $Pt(PPh_3)_2Cl_2$ and $Cp{*}Ir(PPh_3)Cl_2$ were also recovered from the reaction mixture as insoluble solids from a benzene solution. All these products were isolated and characterized. Data for compound **14** was in agreement with the literature [21].

3.7. Alkenyl group migration reactions

The reaction of platinum(II)-alkenyls with halosilanes yielded the corresponding alkenyl silane products (Scheme 8), with quantitative migration of the alkenyl chains from the platinum to the silicon center. In all the reactions, the products were isolated and identified. The characterization of compound **15** is in agreement with previously reported data [22].

4. Conclusions

Various reactions of bis(alkenyl) platinum complexes have been carried out and shown to yield interesting products. The chelating effect of diphosphine ligands is shown to affect the stability as well as the reactivity aspects of these title compounds significantly. It was also found that these compounds decomposed in the presence of halogenated solvents under light or heat. The length of alkenyl chains did not influence the reactivity of the alkenyl complexes. Studies are in progress which should yield information regarding further reactivity aspects and mechanisms of reactions of these platinum(II) alkenyls and other metal alkenyl compounds. Furthermore the scope of other insertion reactions in the presence of, oxygen, sulphur dioxide, carbon dioxide and elemental sulphur will be explored which may lead to produce some interesting organic products.

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Appendix A. Supplementary material

CCDC 631341 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.08.036.

References

[1] (a) A. Sivaramakrishna, H. Clayton, C. Kaschula, J.R. Moss, Coord. Chem. Rev. 251 (2007) 1294;
(b) L. Hermans, S.F. Mapolie, Polyhedron 16 (1997) 869.

[2] C.D. Tagge, R.D. Simpson, R.G. Bergman, M.J. Hosteler, G.S. Girolami, R.G. Nuzzo, J. Am. Chem. Soc. 118 (1996) 2634.

[3] K. Dralle, N.L. Jaffa, T. le Roex, J.R. Moss, S. Travis, N.D. Watermeyer, A. Sivaramakrishna, Chem. Commun. (2005) 3865.

[4] A. Sivaramakrishna, H. Su, J.R. Moss, Angew. Chem., Int. Ed. (Eng.) 46 (2007) 3541.

[5] A. Sivaramakrishna, H. Su, J.R. Moss, Dalton Trans., accepted for publication.

[6] (a) A. Sivaramakrishna, H. Su, J.R. Moss, Organometallics, in press;
(b) F. Zheng, A. Sivaramakrishna, J.R. Moss (2007) (unpublished results).

[7] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6522.

[8] H.C. Clark, L.E. Manzer, J. Organomet. Chem. 59 (1973) 411.

[9] D.A. Slack, M.C. Baird, Inorg. Chim. Acta 24 (1977) 277.

[10] F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, 1992.

[11] A.D. Meijere, F. Dieterich, Metal Catalyzed Cross-Coupling Reactions, Wiley, New York, 2004, and the references therein.

[12] (a) R.H. Grubbs, A. Miyashita, Fundamental Res. Homogeneous Catal. 3 (1979) 151;
(b) R.J. Puddephatt, Coord. Chem. Rev. 33 (1980) 149;
(c) R.J. Puddephatt, Comments Inorg. Chem. 2 (1982) 69;
(d) E. Lindner, Adv. Heterocyclic Chem. 39 (1986) 237.

[13] J. Cámpora, P. Palma, E. Carmona, Coord. Chem. Rev. 193–195 (1999) 207.

[14] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organo Transition Metal Chemistry, University Press, Mill Valley, CA, 1987.

[15] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.

[16] (a) S. Otto, A. Roodt, J.G. Leipoldt, S. Afr. J. Chem. 48 (1995) 114;
(b) K.A. Hooton, J. Chem. Soc. [Sect.] A: Inorganic, Physical, Theoretical (1970) 1896.

[17] (a) J.B. Sheridan, S.H. Han, G.L. Geoffroy, J. Am. Chem. Soc. 109 (1987) 8097;
(b) F. Calderazzo, Angew. Chem., Int. Ed. Engl. 16 (1977) 299.

[18] T. Nishikata, Y. Yamamoto, N. Miyaura, Organometallics 23 (2004) 4317.

[19] K. Osakada, H. Onodera, Y. Nishihara, Organometallics 24 (2005) 190.

[20] M.L. Clarke, M. Heydt, Organometallics 24 (2005) 6475.

[21] C.D. Tagge, R.D. Simpson, R.G. Bergman, M.J. Hostetler, G.S. Girolami, R.G. Nuzzo, J. Am. Chem. Soc. 118 (1996) 2634.

[22] A.C. Church, J.H. Pawlow, K.B. Wagener, Macromolecules 35 (2002) 5746.