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Thermolysis studies on platinacycloalkane complexes

Feng Zheng [a], Akella Sivaramakrishna [a,b,*], John R. Moss [a]

[a] Department of Chemistry, University of Cape Town, Rondebosch 7701, Cape Town, South Africa
[b] Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore 632 014, Tamil Nadu, India

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ABSTRACT

Thermal decomposition studies on platinacycloalkanes of the type $Pt(CH_2)_mL_2$ (where $m = 6,7,8,10$ and L_2 = dppp {1,3-bis(diphenylphosphino)propane}, dppe {1,2-bis(diphenylphosphino)ethane} or $L = PPh_3$, $^tBu_3P$) are described. The results reveal that the organic product distribution depends on various factors such as the nature of ligand, the metal system, the mode of decomposition, the ring size and the temperature. Possible mechanistic pathways for the formation of various products are discussed. These platinacycloalkanes can be used as models for metallacycloalkane intermediates in catalytic reactions.

1. Introduction

Metallacycloalkane complexes have been extensively studied [1] and widely reported [2–21], and are known to be key intermediates in many catalytic reactions. For example, the reactions such as ethylene trimerisation, tetramerisation and oligomerisation to higher linear alkenes proceed through the intermediacy of metallacycloheptanes, metallacyclononanes and other larger size rings [22–28]. Thermolysis of these metallacycloalkanes is also important in generating thin films as well as producing alkenes and other some interesting organic products depending on various factors such as nature of ligands, temperature, metal and solvent [29]. In the literature, thermal decomposition studies on metallacycloalkanes have thus far been restricted to small ring size compounds [3,29]. No kinetic studies have been reported due to the limitation of the amount and stability of the medium and large metallacycloalkane complexes available. Recently, we have discovered a novel route to medium and large, even and odd membered metallacycloalkanes from their metal–alkenyl precursors, using a ring-closing metathesis reaction with Grubbs' catalysts (Scheme 1) [30–33]. In light of this, we have carried out thermolysis studies on a variety of metallacycloalkanes with Pt, Pd, Ir and Rh [34,35]. The purpose of this present article is to assess the stability of the different platinacycloalkanes with different ring sizes and to discuss the range of organic products produced upon their decomposition.

2. Experimental

General Considerations: All manipulations were carried out under a nitrogen atmosphere unless otherwise stated. The solvents were commercially available and distilled from dark purple solutions of benzophenone ketyl. ^1H, and ^{31}P NMR spectra were recorded on a Bruker DMX-400 spectrometer and all ^1H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. 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. The platinacycloalkane compounds **1**–**7** were prepared by ring-closing metathesis (RCM) of bis(1-alkenyl)platinum(II) complexes using Grubbs' 1st generation catalyst. The bis(1-alkenyl)platinum(II) complexes were prepared by the transmetalation reaction of 1-alkenyl Grignard reagents with corresponding dichloroplatinum(II) complexes, and then converted into platinacycloalkenes using the RCM reaction. These

* Corresponding author. Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore 632 014, Tamil Nadu, India. Tel.: +91 416 220 2334.
E-mail address: asrkrishna@vit.ac.in (A. Sivaramakrishna).

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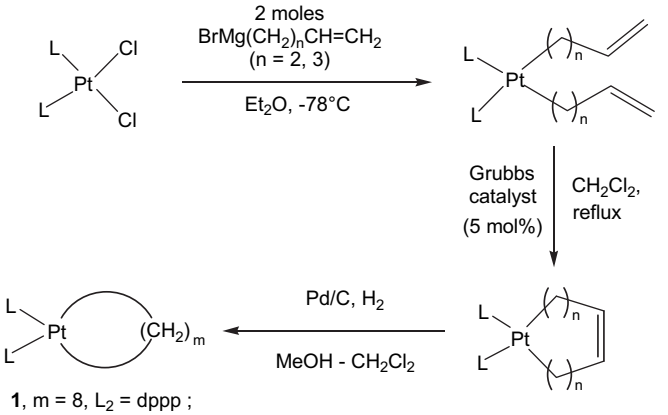


1, m = 8, L_2 = dppp ;
2, m = 8, L_2 = dppe;
3, m = 8, L = Bu^t_3P;
4, m = 7, L_2 = dppp;
5, m = 7, L_2 = dppe;
6, m = 6, L = PPh_3;
7, m = 6, L_2 = dppe;
8, m = 10, L_2 = dppp

Scheme 1. Preparation of platinacycloalkanes.

complexes were then hydrogenated to yield the corresponding platinacycloalkanes (Scheme 1) [30–33].

3. Results and discussion

Our first objective was to identify the decomposition pathways for the metallacycloalkanes although it was not always possible to ascertain all the product-forming reactions, and to assess their relative importance within various combinations of metal, ligand and ring size. The second objective was to establish decomposition rates for an analysis of the comparative thermal stability of different ring sizes and to understand the effect of additional neutral ligands on decomposition pathways.

3.1. Temperature and time effects on thermolysis of 1 and 2

The data for the examination of temperature and time effects on the thermal decomposition of **1** and **2**, using cyclohexane as solvent, were obtained by monitoring the appearance of 1-octene. The studies of temperature effects were carried out by heating **1** and **2** at various temperatures for the same period (2 h). The organic products obtained were analysed by injecting the solution phase, once cooled to room temperature, into a GC.

Thermal decomposition of **1** at 80 °C for 2 h only afforded 1-octene (65%) and *n*-octane (35%). When the temperature was increased to above 120 °C, 2-octenes and 1,7-octadiene were also formed. The amounts of 1-octene as well as the total amount of hydrocarbon products increased with the temperature when heating for the same period. In contrast, decomposition of **2** proceeded much more rapidly, and gave 1-octene (34%), octane (19%), 2-octenes (28%) as well as 1,7-octadiene (16%) and a small amount of cyclooctane (3%) when the thermolysis was carried out at 80 °C for 2 h. The product distribution of **2** at different temperatures varied slightly, but the formation of products remained unchanged. The amount of 1-octene formed was also found to increase with temperature. It is interesting to note that a high temperature is necessary for the thermal decomposition of platinacycles with stable chelating ligands, i.e. dppe and dppp.

The thermal decomposition of **1** and **2** was investigated at 170 °C over a period of time. These experiments were carried out at 170 °C because this temperature resulted in a higher yield of 1-octene.

The amount of 1-octene from the thermal decomposition of **1** increased with decomposition time. A similar result was obtained in the thermal decomposition of **2**. Complex **1** decomposed at a much slower rate than **2**. Formation of 1-octene was complete after 2.5 h for **1**, while for **2**, after 1 h no further formation of 1-octene could be detected. The organic products obtained after decomposition in both cases consisted of a mixture of alkenes, with 1-octene as the major product, while 2-octenes, 1,7-octadiene and octane were present as minor products.

All the decomposition experiments were carried out at 170 ± 5 °C for 2 h which we consider as standard decomposition conditions for the thermolysis of the platinacycloalkanes.

3.2. Kinetic studies

3.2.1. Kinetics of thermal decomposition of *1* and *2*

Kinetic studies were carried out on the thermal decomposition of the platinacycloalkanes **1** and **2** using a similar procedure to that reported by Whitesides and co-workers for the smaller ring compounds [36–38]. The principal reason for choosing these complexes were because of their stability to air and that they have a high decomposition temperature.

The rates of thermal decomposition of platinacyclononanes $L_2Pt(CH_2)_8$ (**1**, L_2 = dppp; **2**, L_2 = dppe) in cyclohexane were examined by GC following the appearance of the total hydrocarbon products from decomposition, which include 1-octene, *n*-octane, 2-octenes, 1,7-octadiene and cyclooctane. Results were obtained by following the total concentration of the products relative to that of an added internal standard (chlorobenzene).

The rate constants for the decompositions were calculated according to Eq.(1) Where, a_0 = [Pt compound]$_0$, x = [total hydrocarbon products]$_t$.

$$\ln[a_0/(a_0 - x)] = kt \quad (1)$$

The examination of rate constants for the thermal decomposition of complexes **1** and **2** was carried out under different conditions and at different concentrations in cyclohexane. The results obtained have been summarized in Table 1.

The decomposition of **1** at 80 °C for 24 h in cyclohexane was found to be first order with a rate constant (7.0×10^{-7} s^{-1}). The extent of decomposition [39] of **1** was, however, ca. 6% even after 24 h which indicates complex **1** is quite stable at 80 °C. Compared with the decomposition for 2 h from which only 1-octene and octane were formed, after decomposition for 4 h at 80 °C, 2-octene was also found. This suggests that the formation of 2-octene might result from isomerisation of 1-octene in a secondary reaction, which was not only dependent on decomposition temperature but also on the heating time.

The decomposition of **1** at 170 °C was first order only over approximately the first 30% of the decomposition for the low concentration, and over ca.20% for the higher concentration (Fig. 1a). Rate constants in the linear region were independent of the initial

Table 1
Rate constants of the thermal decomposition of **1** and **2** in cyclohexane.

Compound	Concentration (mM)	Rate constant	
		80 °C (s^{-1})	170 °C ($k \times 10^4$ s^{-1})
1	23.2	7.00×10^{-7}	–
1	23.2	–	0.471
1	2.32	–	0.485
2	5.74	–	2.01

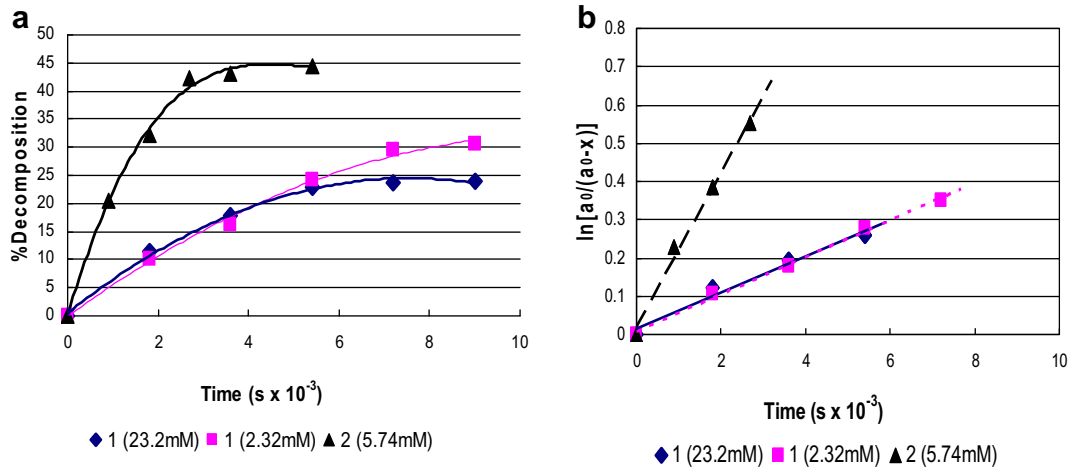


Fig. 1. Representative speciation (a) and first order (b) plots for the thermal decomposition of **1** (23.2 mM ◆ & 2.32 mM ■) and **2** (5.74 mM ▲) at 170 °C.

concentration of the platinum complex (Fig. 1b). The observed rate constant for **2** was 4 times greater than that for **1** (Table 1), which again showed that the thermal stability of platinacyclononane with dppe ligand is lower than that with dppp ligand. The products formed from thermal decomposition of **1** at both concentrations were found to be the same with similar distributions of organic products. Not surprisingly, the product formation and distribution obtained from decomposition of **2** was different which could be due to the stability as a result of the ancillary ligand.

3.2.2. *Kinetics of thermal decomposition of **1** and **2** with added ligands*

The rates of thermal decomposition of platinacyclononanes $L_2Pt(CH_2)_8$ (**1**, L_2 = dppp; **2**, L_2 = dppe) in cyclohexane, with added ligand, were examined by GC following the appearance of the total hydrocarbon products from decomposition. Using the same ligand that is already present in the complexes avoids complications of ligand exchange.

The decomposition of **1** in the presence of added bis(diphenylphosphino)propane (dppp) ligand was carried out in cyclohexane with 0.1–20 ratios of added dppp to **1**. The kinetic behaviour in all cases was first order only over approximately the first 30% of decomposition (Fig. 2a). Rate constants in this region were dependent on the concentration of added dppp and the linear region increased when the concentration of dppp increased (Fig. 2c). The overall rate in this region can be expressed by a two-term rate expression (Eq.(2)) [36], where $k_a = 4.85 \times 10^{-5}$ s^{-1} and $k_b = 1.69 \times 10^{-5}$ s^{-1} at 170 °C, [dppp] (mM): (0.224, 22.4).

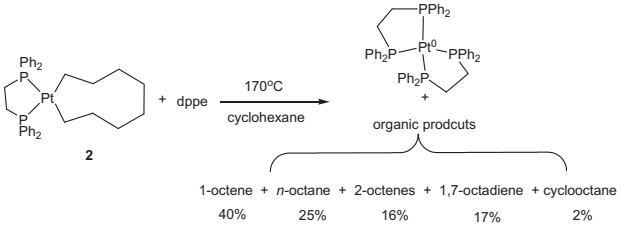
$$-\frac{d[1]}{dt} = (k_a + k_b[dppp]) \quad (2)$$

The thermal decomposition of **2** with added bis(diphenylphosphino)ethane (dppe) was studied in the same way, and showed the same general kinetic features (Fig. 2b). Added dppe ligand also accelerated the reaction; the overall rate in the linear region can be expressed as shown in Eq.(3) by the similar rate expression as Eq.(2), where $k_c = 2.01 \times 10^{-4}$ s^{-1} and $k_d = 4.96 \times 10^{-6}$ s^{-1} at 170 °C, [dppe] (mM): (5.94, 118.8).

$$-\frac{d[2]}{dt} = (k_c + k_d[dppe]) \quad (3)$$

The added phosphine ligand influences the formation of not only the major products (1-octene & *n*-octane), but also the minor products (2-octenes & 1,7-octadiene), particularly for the decomposition of **2**. The same phenomenon was observed in the thermal decomposition of bis(phosphine)platinum(II) metallacyclopentanes [36].

The decomposition of **2** with added dppe ligand in cyclohexane gave a clear golden yellow solution. The organic products from the reaction of **2** with one equivalent of dppp at 170 °C are shown in Eq.(4) and the metal-containing product was identified as $[Pt^0(dppe)_2]$ by ^{1}H and ^{31}P NMR spectroscopy. The major singlet at δ 4.49 in ^{31}P NMR spectrum shifted to δ 32.35 after 2 h, and agreed with the literature report; no sign of Pt–H bonds or hydridic hydrogen were observed [40,41]



(4)

These results are in good agreement with the reported reaction of dppe with $[PtPh_2(dppe)]$ (Eq.(5)) [42].

$$[PtPh_2(dppe)] + dppe \xrightarrow{490K} [Pt(dppe)_2] + Ph_2 \quad (5)$$

In contrast, an intense red residue was formed when complex **1** decomposed without added dppp, which was insoluble in cyclohexane and we believe it is to be due to $Pt_n(L)_m$ clusters [43].

3.2.3. *Kinetics of thermal decomposition of **5** and **8***

Kinetic studies were carried out on the thermal decomposition of the complexes of the type $Pt(CH_2)_n(dppp)$ (**5**, $n = 7$; **8**, $n = 10$) in order to examine the effects of different ring sizes on the thermal stability of platinacycloalkanes. The rates of decomposition of **5** and **8** in toluene-d^8 at 90 °C were determined by following the disappearance of ^{31}P peak of the starting platinacycloalkanes using ^{31}P{^{1}H} NMR spectroscopy [44,45].

Thermal decomposition of **5** at 90 °C was much slower than that of **8**. The decomposition of **8** was complete after heating for 5 h, which was indicated by the total disappearance of the starting material peak in the ^{31}P NMR spectrum. However, the decomposition of **5** was complete after 48 h. Whitesides and co-workers have found that five- and six-membered platinacycloalkanes are

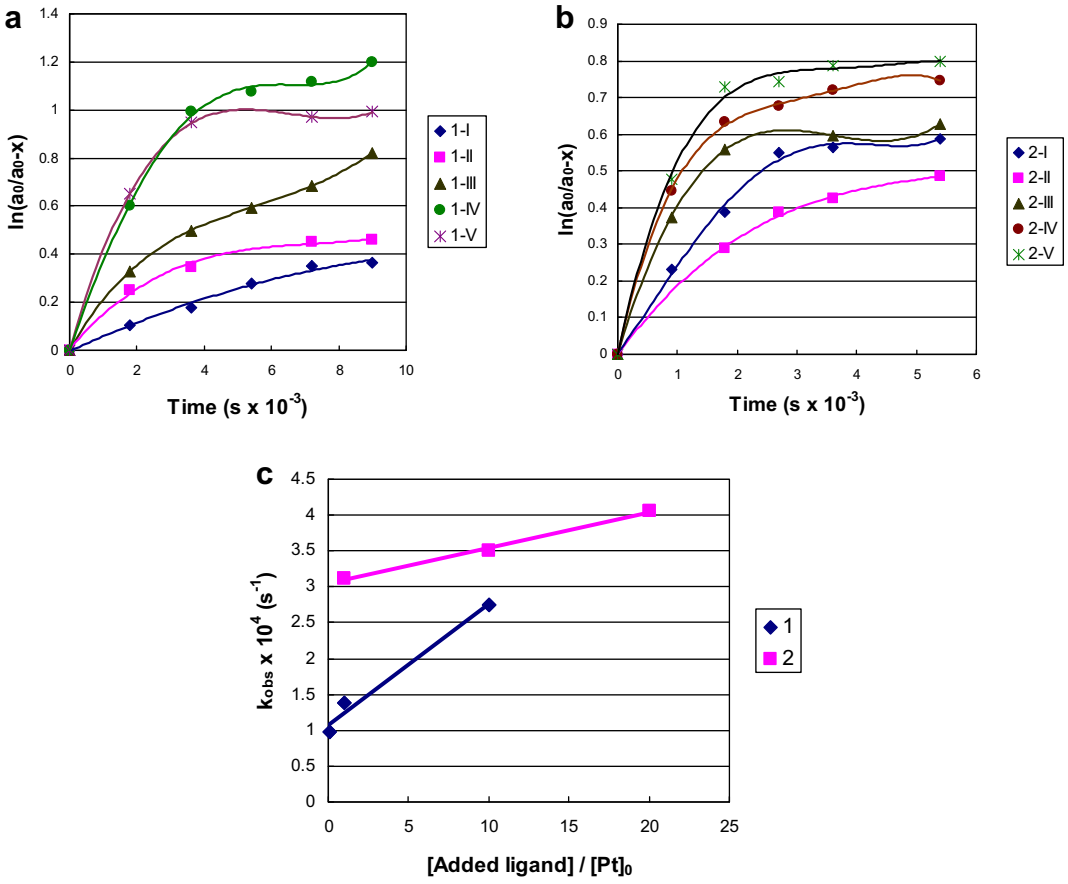


Fig. 2. a: The rate of thermal decomposition of **1** depends on the concentration of dppp in solution. Data are for runs in cyclohexane, having $[\mathbf{1}]_0 = 2.32$ mM and these values for [dppp] (mM): 1–I, 0.0; 1–II, 0.224; 1–III, 2.24; 1–IV, 22.4; 1–V, 44.8. b: The rate of thermal decomposition of **2** depends on the concentration of dppp in solution. Data are for runs in cyclohexane, having $[\mathbf{2}]_0 = 5.74$ mM and these values for [dppp] (mM): 2–I, 0.0; 2–II, 0.594; 2–III, 5.94; 2–IV, 59.4; 2–V, 118.8. c: Observed rate constants (k_{obs}) for the thermal decomposition of **1** (◆) and **2** (■) as a function of the ratio of added ligand to Pt complex. These curves are derived from the data of a and b.

markedly more stable than the platinacycloheptane [36]. In this study, we found that the eight-membered platinacycloalkane **5** is significantly more stable than the larger and conformationally more mobile eleven-membered ring **8**.

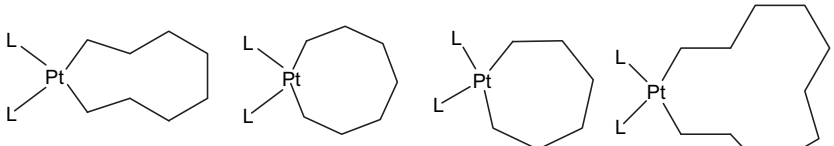
3.3. Products of decomposition of platinacycloalkanes

The non-kinetic decomposition studies of platinacycloalkanes **1**–**6** (Chart 1) were carried out both in solvent and solvent free under the standard conditions. Heating a *ca.* 10 mg solid sample or 0.5 mL of 0.02 M sample solution in cyclohexane or toluene at 170 °C for 2 h resulted in formation of a mixture of alkene and *n*-alkane products (see Table 2) accompanied by transformation of the solid, or solution, from its original pale yellow colour to an intense red colour.

Two methods of product extraction were used for the solvent free thermal decomposition of complex **1** in order to draw comparisons. The first method was to collect the volatile products using trap-to-trap distillation, and the second one was addition of appropriate solvent to extract the products. The products obtained were found to be same using either method, however, the relative amount of individual product that could be recovered by the former method was clearly less than the later one.

Besides this, it was practically difficult to handle a trap-to-trap distillation when the amount of metallacycle complex was so small that it could only result in a trace of volatile products. For the results reported here, we used the method of adding an appropriate solvent to extract the volatile products when the thermal decomposition was carried out under solvent free conditions.

The results presented in Table 2 show that the overall decomposition patterns for the platinacycloalkanes are independent of the ring size. These complexes can decompose thermally in several ways to give a range of organic products, including 1-alkenes,



1, L_2 = dppp;
2, L_2 = dppe;
3, L = Bu^t_3P

4, L_2 = dppp;
5, L_2 = dppe

6, L = PPh_3;
7, L_2 = dppe

8, L_2 = dppp

Chart 1. Platinacycloalkane complexes **1**–**8**.

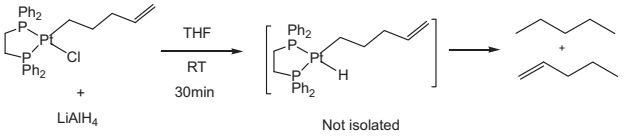
Table 2
Products for the thermal decomposition of the platinacycloalkanes **1**–**7** at 170 °C for 2 h.

Complex	Medium	Products observed (%)[a]				
		1-alkene	2-alkenes	1,*n*-diene	*n*-alkane	Cycloalkane
1	Solid	49	21	4	26	–
	Cyclohexane	46	17	4	33	–
	CH_2Cl_2	27	21	4	44	4
2	Solid	41	21	13	23	2
	Cyclohexane	37	21	12	28	2
3	Solid	54	20	9	17	–
	Cyclohexane	51	24	5	20	–
	CH_2Cl_2	32	26	6	28	8
4	Solid	45	14	9	32	–
	Toluene	43	22	<1	35	–
5	Solid	50	20	2	28	–
	Toluene	43	13	3	40	–
6	solid	41	27	13	20	–
7	solid	44	23	9	24	–

[a] Products were analysed by GC and GC–MS within the error limits of ±3% for each determination.

2-alkenes, *n*-alkanes and dienes (only complex **2** decomposed in dichloromethane to give cycloalkane).

The formation of 1-alkenes and 2-alkenes is known from the decomposition of metallacyclopentanes [46], -hexanes and –heptanes [36], which was in agreement with our observations of the decomposition of these larger ring-size metallacycloalkanes. Assuming that the reaction pathway to form 1-alkene takes place via the β-hydride elimination, the hydridoalkenylplatinum(II) complex should be a key intermediate. Attempts were made to isolate this intermediate and we carried out a reaction of (dppe)PtCl (1-pentenyl) with $LiAlH_4$ in THF at room temperature. The reaction was monitored by ^1H NMR, but no hydride signal could be observed. The reaction solution was then injected to the GC, *n*-pentane (24%) and 1-pentene (76%) were identified (Eq.(6)), which suggests that the alkenyl hydride intermediate is not stable under these conditions and if formed, undergoes reductive elimination to give 1-pentene as the major product.

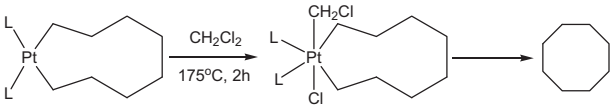


(6)

Attempts to isolate the hydridoalkenylplatinum(II) complex by reacting a chloride hydridoplatinum(II) complex with Grignard reagent at −78 °C also failed as no hydride signal was obtained from ^1H NMR after reaction. The products formed were 1-alkene and *n*-alkane which were analysed by GC–MS [47].

Due to the absence of any direct evidence, it is suggested that formation of the alkenyl hydride intermediate might take place rapidly and perhaps reversibly, or the formation of 1-alkene may not involve such an intermediate. An alternative pathway might be via a concerted metal-assisted hydride transfer route [48–50]. The formation of 2-alkenes could probably be caused by the occurrence of isomerisation either during or after decomposition. In addition, the corresponding *n*-alkane was also obtained as one of the major products (>20%) in all cases.

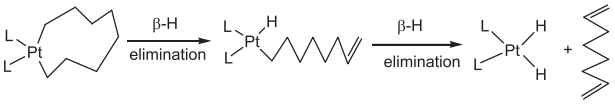
The thermolysis products of **1**–**5** obtained in solvent and solvent free conditions were compared to determine the influence of solvent on the decomposition pathways. The product formation patterns were similar although the relative yields of the products were different in the different decomposition media. The decomposition of **1** and **3** were carried out in three media, *i.e.* solvent free, in cyclohexane and in dichloromethane. Under both solvent free conditions and in non-halogenated solvent, only linear C_8 products were formed. In contrast, small amounts of cyclooctane were also obtained when the decomposition of these two complexes was carried out in dichloromethane. In a solvent capable of oxidative addition, like dichloromethane, formation of cyclobutane and C_5 materials from the decomposition of platinacyclopentanes was reported by Whitesides and co-workers [38]. We propose that cyclooctane could be formed in the same way as reported for the formation of cyclobutane [38]. Platinum(IV) intermediates were produced by oxidative addition of dichloromethane to platinum(II) metallacycles, which then generated cyclooctane by reductive elimination (Eq.(7)). The products with one more carbon than the metallacyclic group were not observed in this study. In addition, it was observed that the decomposition residue in dichloromethane for complex **1** formed white needles with a melting point at 155–160 °C. This residue was identified by ^1H and ^{31}P NMR, as the starting dichloride platinum(II), $PtCl_2L_2$.



(7)

A trend of increasing formation of *n*-alkane was observed when complexes **1** and **3** decomposed in different media: solvent free < in solvent (cyclohexane < dichloromethane). The same phenomenon was found from the decomposition of complexes **2**, **4** and **5**, whereas the relative yield of *n*-alkane is slightly less under solvent free conditions than in solvent. The chosen solvents for the decomposition studies were cyclohexane, dichloromethane and toluene.

Nevertheless, the fact that *n*-alkane formed under solvent free conditions indicates that the hydrogen-atom responsible for producing the saturated alkane is not only from the solvent but could be from other sources. The most likely sources are considered to involve two components: 1) platinum hydride species produced by releasing diene from platinacycles (Eq.(8)) [45] and 2) hydrogen transferred from coordinated ligand, e.g. *ortho* activation of the phenyl group of PPh_2 [51–53].

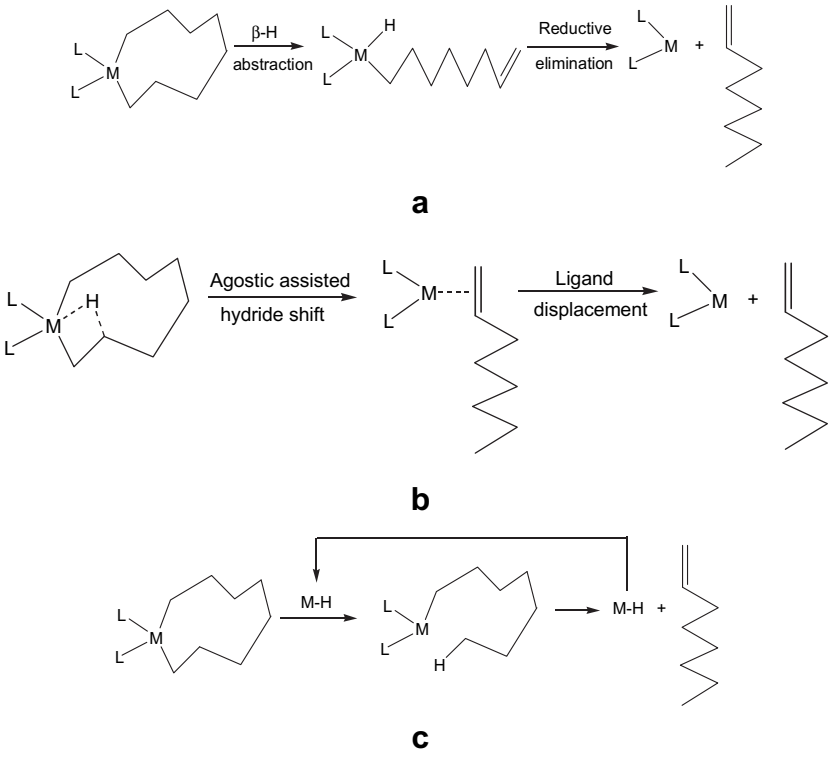


(8)

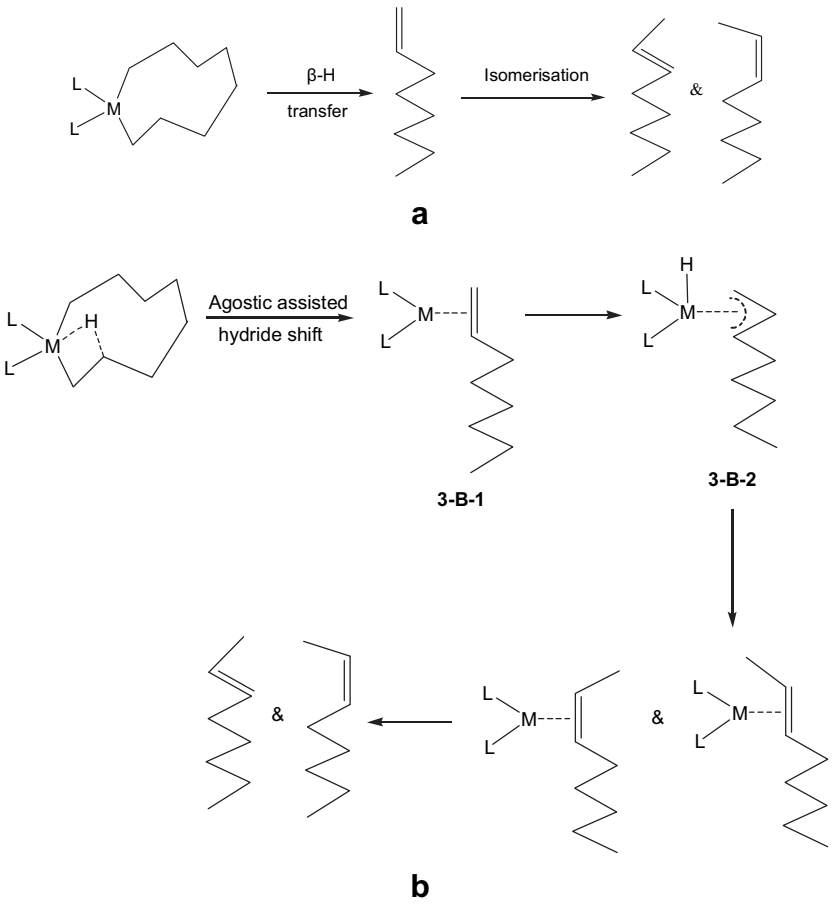
The thermal decomposition of platinacycloheptanes **6** and **7** was first reported by Whitesides and co-workers: decomposition of platinacycloheptanes in dichloromethane at 60 °C afforded 1-alkene and 2-alkenes only [36]. In contrast, many more products formed when these complexes decomposed at higher temperature (170 °C) in this study. Higher thermolysis temperatures are required for the stable platinacycle complexes, especially for those with chelating ligands, which might make available additional reaction pathways.

3.4. The mechanisms of the thermal decomposition of metallacycloalkanes

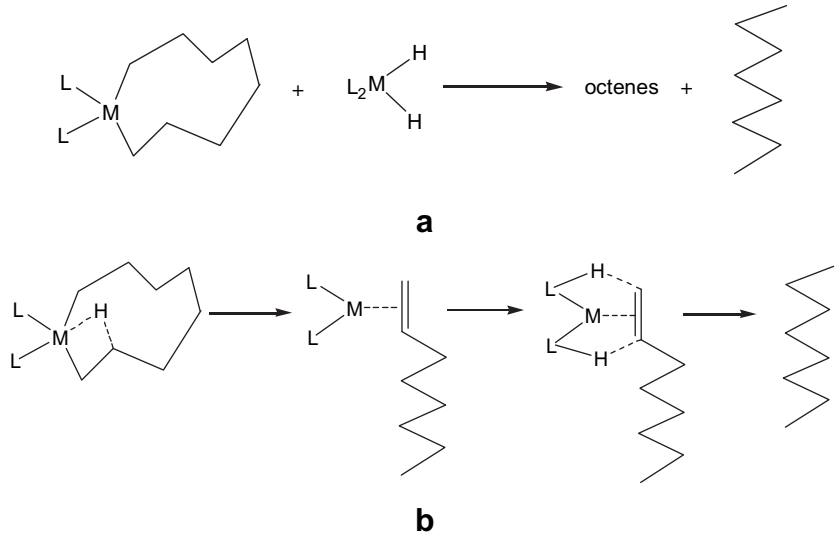
The decomposition pathways of metallacycloalkanes documented so far are not only relevant to those of alkyl complexes, also relevant to decomposition of metallacycles in catalytic reactions e.g. ethylene oligomerization [22–28]. We try to draw a detailed mechanism based on these decomposition pathways to interpret



Scheme 2. Possible mechanisms for the formation of 1-octene from a metallacyclononane.



Scheme 3. Possible mechanisms for the formation of 2-alkenes from a metallacyclononane.



Scheme 4. Possible mechanisms for the formation of *n*-alkane from a metallacyclononane.

the formation of various products by α- and β-hydride elimination, ligand–hydrogen abstraction, reductive elimination and homolytic M–C bond cleavage. Some of the discussions on the mechanisms that follow are based on the literature, and the rest is a consequence of our recent studies.

3.4.1. The formation of 1-alkene

The best documented reaction pathway to produce 1-alkene is via β-hydride elimination from metal–alkyl complexes. This could also be the possible decomposition mechanism for the formation of 1-alkene from metallacycloalkanes with flexible medium to lager ring size, even though this pathway is reported to be hindered in the small metallacycloalkanes. β-Hydride elimination is formally meant as β-hydride abstraction by the metal, followed by reductive elimination of the resultant alkenyl hydride species (Scheme 2a) [54]. The alternative mechanism for generation of 1-alkene is via a concerted metal-assisted hydride transfer from C_2 to C_n of the metallacycloalkane which was supported by the calculations for Ti and Cr catalytic trimerisation systems (Scheme 2b) [48–50]. Nowadays, these two mechanisms are termed as "β-hydride transfer" due to the difficulty of distinguishing them in various metallacyclic systems. Furthermore, Miller and Whitesides demonstrated an intermolecular chain reaction pathway for the formation of 1-alkene, in which a hydridoplatinum intermediate was involved [45] (Scheme 2c).

3.4.2. The formation of 2-alkenes

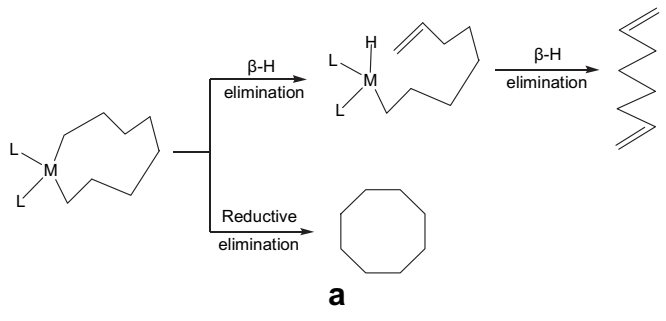
While a reaction pathway such as that shown in Scheme 2 accounts well for the formation of 1-alkenes, R–CH=CH_2, some authors pointed out that the appearance of an internal alkene, R–CH=CH–R′, could result from the isomerisation of the initially formed 1-alkene (Scheme 3a) [55]. And some reported that it could be presumably explained by a metal hydride-catalyzed intramolecular isomerisation before the olefin is released into solution [36]. The proposed mechanism is outlined in Scheme 3b [56]: β-hydride elimination followed by metal-assisted hydrogen shifts to form a viable intermediate **3-B-1** which could rise for 1-alkene or 2-alkenes depending upon the regioselectivity of hydrogen migration through the formation of **3-B-2** [57]. Our experiments suggest that the metal–alkenyl and metal–alkyl compounds can also isomerize 1-alkenes to the corresponding internal 2-alkenes catalytically in solution [58].

3.4.3. The formation of n-alkane

For the thermal decomposition of metal–alkyl complexes, it has been suggested that with only a single alkyl ligand, alkanes should not form unless an intermolecular reaction (Eq.(9)) occurs [52].

$$M{-}H + M{-}R \rightarrow 2M + RH \quad (9)$$

Similarly, the formation of alkane from the decomposition of metallacycloalkane complexes should only occur with an extra hydrogen source other than the metallacyclic moieties such as solvent, metal–hydride species and hydrogen transferred from coordinated ligand. Therefore, the mechanism of the formation of *n*-alkane could be proposed in three ways: intermolecular hydrogen abstraction (Scheme 4a), intramolecular hydrogen abstraction (Scheme 4b) and the combination of intermolecular and intramolecular hydrogen abstraction. Thermal decomposition studies of **1** in CD_2Cl_2 gave *n*-octane as the major product but with no incorporation of deuterium observed by GC–MS.



Scheme 5. Possible mechanisms for the formation of dienes and cycloalkane from a metallacyclononane.

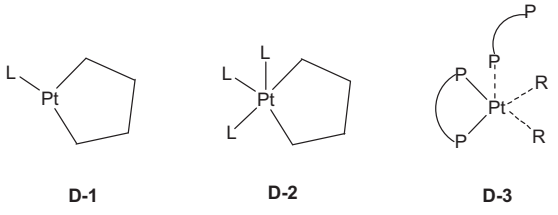
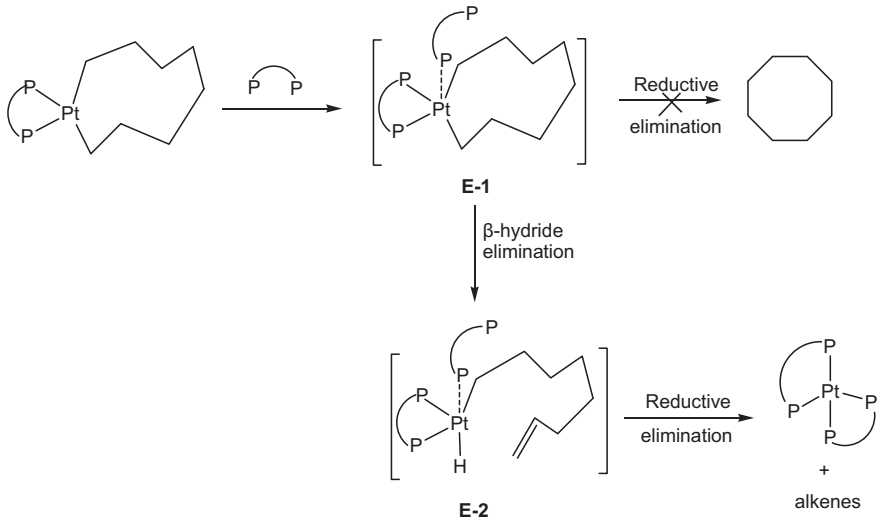


Chart 2. Possible intermediate species in the presence of additional neutral ligands.



Scheme 6. Proposed mechanism for the decomposition of platinacyclononanes with added ligand.

3.4.4. The formation of diene and cycloalkane

Smaller amounts of dienes and cycloalkanes were also produced from certain metallacycles. Dienes might be formed via β-hydride elimination from an alkenyl hydride species and a reductive elimination pathway could result in C–C bond formation to give cycloalkane (Scheme 5).

3.5. General factors affecting the thermal decomposition of platinacycloalkanes

Information from the thermal decomposition of small metallacycles have shown that the thermal stability of these complexes is quite dependent on the nature of metal, size of the ring, solvent and supporting ligands [29]. These factors also played a significant role in the current thermal studies on various mediums to large metallacycles.

3.5.1. Additional neutral ligands

The notable effect of the presence of free phosphine ligands (dppp and dppe) on the thermolytic behaviour of complexes **1** and **2** is the facilitation of decomposition in every case. This effect is also found in the decomposition of some bis(phosphine)platinacyclopentanes with added ligand [36].

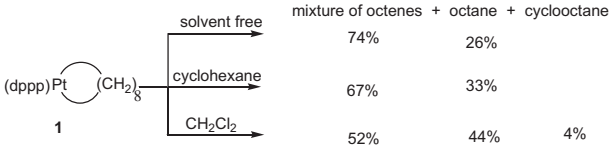
There is no clear mechanism for such reactions so far. According to Whitesides and co-workers [36], this acceleration by added ligand might be due to either inhibition of the formation of a three-coordinate intermediate **D-1**, or to promotion of the formation of a five-coordinate intermediate **D-2** (Chart 2).

Braterman and co-workers also reported that reductive elimination of biaryl was enhanced by added phosphines in the thermolysis reactions of PtL_2Ar_2 due to their electrodonor capability [1,40,41,53,59]. Again, a five-coordinate intermediate **D-3** was proposed according to their evidence from the DSC results.

The complexes **1** and **2** with the chelating ligands dppp and dppe, however, do not involve a three-coordinate intermediate during the thermal decomposition as they ensure retention of configuration. The mechanism of the decomposition of **1** (or **2**) with additional ligand is easily rationalized using the hypothesis that a five-coordinated intermediate **E-1** could be formed initially followed by β-hydride elimination to form a metal–hydride intermediate **E-2**, and the reductive elimination of alkenes could be then facilitated by the added phosphine ligand (Scheme 6). The five-coordinate metal–hydride species **E-2** is presumably the favoured intermediate due to the fact that no (or no more) cyclooctane was formed with added ligand, which indicated reductive elimination from the initial intermediate **E-1** to form cyclooctane might be blocked.

3.5.2. Changes of decomposition medium

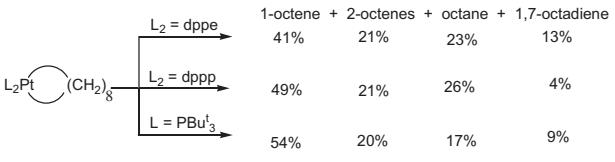
The effects of decomposition medium on the hydrocarbon products of the platinacyclononane **1** were observed (Eq.(10)). The relative amount of the mixture of octenes including 1-octene, 2-octenes and 1,7-octadiene is significantly higher for the solvent free decomposition than those decomposed in solvent. Decomposition in the halogenated, highly co-ordinating and polar solvent, dichloromethane, was found to favour formation of *n*-octane and cyclooctane. On the other hand, the formation of octane showed different trends compared to octenes.



(10)

3.5.3. Changes of supporting ligands

The thermal stability of metallacycles is dependent on the ancillary ligand systems. The order of stability for Pt complexes is as follows: $PPh_3 < P^tBu_3 <$ diphos (diphos = dppe, dppp, dmpe, dcpe). The role of the supporting ligands seems to hold the balance in the decomposition pathways of certain metallacycle systems. For instance, all platinacyclononane complexes (**1**, L_2 = dppp; **2**, L_2 = dppe; **3**, L = P^tBu_3) produced 1-octene as major products upon solvent free decomposition, whereas the relative amount of 1-octene increased in the order of the ligands: dppe < dppp < P^tBu_3 (Eq.(11)).



(11)

4. Conclusions

Some useful results pertinent to the thermal decomposition of metallacycloalkanes emerged from the current study. The rate of decomposition of platinacycloalkanes in cyclohexane is increased by adding dppp and dppe ligands respectively. The effect of the additional ligands could be that of facilitating the reductive elimination of alkenes from a five-coordinated metal–hydride intermediate. The relative amount of 1-octene formed from the thermal decomposition of platinacyclononanes is dependent on the decomposition temperature and time. The formation of the total products including 1-octene, 2-octenes, *n*-octane, 1,7-octadiene and cyclooctane is first order for about the first 30% of the decomposition. These results taken together demonstrate that changes of decomposition medium, ring size, supporting ligands and metal centres have significant effects on the decomposition pathways; moreover, these factors seem to have a cooperative effect in the decomposition of certain metallacycloalkanes. The possible decomposition pathways involved in the thermolysis of these metallacycloalkanes could be: β-hydride transfer or an intermolecular chain reaction to form 1-alkene; intermolecular or intramolecular isomerisation for 2-alkenes; the formation of *n*-alkane by an intermolecular hydrogen abstraction, or alternatively an intramolecular hydrogen abstraction from supporting ligands. The thermolysis data in this study suggest that the medium to large metallacycloalkanes can be useful models for the intermediates in selective catalytic oligomerisation reactions, particularly ethylene trimerisation and tetramerisation reactions.

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