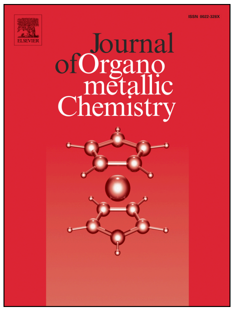

Synthesis, structure and thermolysis of *cis*-Dialkylplatinum(II) complexes – Experimental and theoretical perceptions

Sadhana Venkatesh, Chinduluri Sravani, Sannapaneni Janardan, Pothini Suman, E. Veerashekhara Goud, B.B. Pavankumar, Vardi Leninkumar, Haamid R. Bhat, Akella Sivaramakrishna, Kari Vijayakrishna, Prakash C. Jha, Gregory S. Smith

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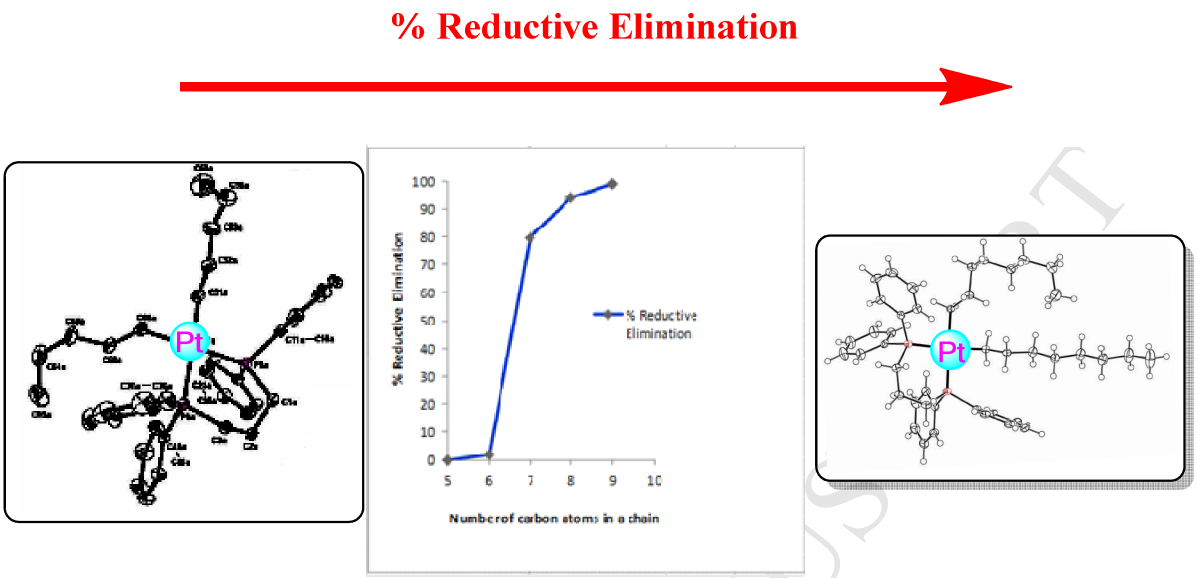
Graphical Abstract



Reaction Pathways in Platinum-Dialkyl Complexes – Reductive elimination is more preferred than β-hydride elimination with longer chain lengths

Synthesis, Structure and Thermolysis of *cis*-Dialkylplatinum(II) Complexes - Experimental and Theoretical Perceptions

Sadhana Venkatesh,[a] Chinduluri Sravani,[a], Sannapaneni Janardan,[a] Pothini Suman,[a] E. Veerashekhara Goud,[a] B.B. Pavankumar,[a] Vardi Leninkumar[a], Haamid R. Bhat,[b] Akella Sivaramakrishna*,[a] Kari Vijayakrishna,[a] Prakash C. Jha,[b] and Gregory S. Smith,[c]

[a]Department of Chemistry, School of Advanced Sciences, VIT University, Vellore 632 014, Tamil Nadu, India

[b]School of Chemical Sciences, Central University of Gujarat, Sector-30, Gandhinagar, Gujarat, India

[c]Department of Chemistry, University of Cape Town, Rondebosch 7701, Cape Town, South Africa

E-Mail: asrkrishna@vit.ac.in; Tel (O) # +91 416 2202351; Fax # +91 416 2243092

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ABSTRACT: The formation of new C-C bonds by metal complexes always stimulates great interest because these fundamental reaction types possess numerous potential applications in organic synthesis. These reactions are well documented for a variety of transition metal complexes. Herein we report synthesis and characterization of a series of platinum-dialkyl complexes (**1**-**10**) of the type [Pt(L_2)R_2], (where L_2 = dppp (1,3-bis(diphenylphosphino)propane or L = PPh_3; R = *n*-butyl to *n*-nonyl) with a view to understand the organic product distribution patterns on thermolysis. The single crystal X-ray structures of the complexes [Pt(dppp){$CH_2(CH_2)_3CH_3$}$_2$] (**1**) and [Pt(dppp){$CH_2(CH_2)_6CH_3$}$_2$] (**7**) are reported. Thermal decomposition studies of these complexes show interesting behaviour; the longer chain dialkyls *i.e.* C_7-C_9 complexes undergo reductive elimination whereas the shorter chain dialkyl complexes and C_3-C_6 prefer only the β-hydride elimination reaction. Possible mechanistic aspects are discussed. Theoretical calculations reveal the strongest delocalizations in both complexes involve the interaction of Pt–C bond pair electron density with the trans positioned Pt–P antibonding orbital and vice-versa.

Keywords: platinum(II)-dialkyl complex, synthesis, structure, thermolysis, reductive elimination, β-hydride elimination.

INTRODUCTION

Reductive elimination of C–H, C–C and C–X bonds is a key step in numerous metal-catalysed reactions [1]. Among them, catalytic reactions involving of Group 10 metals has been extensively studied for the formation of new C-C bonded products, where the alkyl or aryl groups consist of a variety of substituents with pronounced electronic effects [2-4]. This is of interest to understand the factors influencing the direct reductive elimination reactions in metal-alkyl complexes [5]. A comprehensive DFT study revealed the reductive elimination barrier in alkyl-, vinyl-, or arylpalladium(II) complexes is dramatically affected by the nature of ancillary ligands [6].

In general, metal-alkyls are a very important class of compounds in organometallic chemistry as key intermediates in a variety of catalytic reactions [7]. The most striking feature of metal-alkyls, with shorter alkyl chains, is that they can undergo β-hydride elimination at ambient temperatures prior to either the reductive elimination or α-hydride elimination reactions. These reactions are also shown by related compounds such as metal-alkenyls and metallacycloalkanes [8]. The β-hydride elimination is also a fundamental termination step in many catalytic reactions [9]. In the past, Whitesides and co-workers studied thermal decomposition reactions of some platinum(II)-dialkyl compounds PtL_2R_2 (where R = Me, Et and L_2 = PPh_3, Bu_3P), and suggested mechanistic pathways [10].

Current studies of the fundamental chemistry at platinum centres are essential to intrinsic modes of platinum reactivity, particularly those that possess longer alkyl chains. Herein we report the preparation of platinum-dialkyl complexes (**1-10**) of the type $[Pt(L_2)R_2]$, containing two metal-carbon σ- bonds with short and long alkyl chains (where L_2 = dppe and dppp; R = *n*-butyl to *n*-nonyl). In addition, we also report a surprising competition between two different decomposition pathways *i.e.* β-hydride elimination *vs* reductive elimination associated with a slight change in the length of the alkyl chains. These studies could play a crucial role in the design and rational development of novel reagents/ catalysts for the selective reductive elimination reactions of C-X (X = carbon or any heteroatom) [11].

EXPERIMENTAL SECTION

General Methods. 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. Reagents were purchased from Sigma-Aldrich. GC analyses were carried out using a Varian 3900 gas chromatograph equipped with an FID and a 30 m x 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. (COD)$PtCl_2$[12], $(PPh_3)_2PtCl_2$[13], (dppp)$PtCl_2$[14], (dppm)$PtCl_2$, alkyl Grignard reagents ($BrMgCH_2CH_2(CH_2)_nCH_2CH_3$; n = 1, 2, 3, 4, 5) were prepared according to literature procedures [15].

Instrumentation. NMR spectra were recorded on a Bruker DMX-400 spectrometer operating at 500.13 and 202.46 MHz, respectively, for ^{1}H and ^{31}P spectra. Spectra are reported in δ (ppm) relative to TMS, as determined from standard residual solvent-proton (or carbon) signals for ^{1}H and ^{13}C, relative to external (capillary) H_3PO_4 for ^{31}P. Melting points were measured in sealed capillaries using a Büchi melting point instrument and are uncorrected. GC-MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph and Perkin-Elmer Clarus 600 C equipped with MSD and a 60 m x 0.25 mm Rtx-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. Elemental analyses were performed with a Thermo Flash 1112 Series CHNS–O analyzer instrument, upon crystalline samples that had been dried in vacuo.

Single Crystal X-Ray Analysis. A microscope was used to identify suitable crystals of the same habit. The crystallographic data for all the single crystals was collected at 113 K on a Nonius Kappa CCD diffractometer using graphite- monochromated Mo-Kα radiation (λ = 0.71073 Å). Space groups were determined on the basis of systematic absences and intensity statistics. The structures were solved by direct methods and refined by full-matrix least-squares refinement on F^2. Anisotropic displacement parameters were determined for all non-hydrogen atoms. Hydrogen atoms were placed at idealized positions and refined with fixed isotropic displacement parameters.

Synthesis of *cis*-Pt(*n*-pentyl)$_2$(dppp) (1): A Schlenk flask was charged with Pt(COD)Cl$_2$ (501 mg, 1.34 mmol) and diethyl ether (25 mL). The mixture was cooled to T = -78°C and *n*-pentyl Grignard reagent (3.25 mL, 1.24 M, 4.02 mmol) was added. The solution was brought to around 0°C and then stirred until the solution becomes clear. To this, dppp (552 mg, 1.34 mmol) was added and stirred for 1h until a clear solution is 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 2 x 5 mL of dichloromethane and the organic layer was separated by a separating funnel. The solvent was removed under reduced pressure and the residue recrystallized from a CH$_2$Cl$_2$/hexane mixture (3:5) at -10°C for 48 h. The colorless crystalline solid was separated by decanting the mother liquor and dried under vacuum for several hours. For **1**: m.p. 152-154°C (dec); Yield 96%; Anal. Calcd for $C_{37}H_{48}P_2Pt$: C, 59.27; H, 6.45. Found: C, 59.46; H, 6.63; ^{1}H NMR: δ 7.24-8.17 (m, 20H, Ph); 2.43-2.56 (m, 6H, P-CH$_2$CH$_2$), 0.66-2.59 (m, 22H, -CH$_2$ and –CH$_3$); ^{31}P{^{1}H} = δ 3.38 (s) (J_{Pt-P} = 1665 Hz).

Synthesis of*cis*-Pt(*n*-pentyl)$_2$(PPh$_3$)$_2$ (2): A similar procedure was followed using Pt(COD)Cl$_2$ (406 mg, 1.085 mmol) in diethyl ether (20 mL), *n*-pentyl Grignard reagent (2.6 mL, 1.24 M, 3.26 mmol) and PPh$_3$ (570 mg, 2.173 mmol) was added and stirred for 36 h until a clear solution is formed. The reaction mixture was worked up as described above. For **2**: m.p. 162-164°C; yield 97%; Anal. Calcd. for $C_{46}H_{52}P_2Pt$: C, 64.10; H, 6.08. Found: C, 64.14; H, 6.11; ^{1}H NMR: δ 7.22-7.82 (m, 30H, Ph), 0.86-2.08 (m, 22H, -CH$_2$ and –CH$_3$); ^{31}P{^{1}H} = δ 26.92 (s), J(Pt-P) = 1724.24 Hz.

Synthesis of *cis*-Pt(*n*-hexyl)$_2$(dppp) (3): A similar procedure was followed using (dppp)PtCL$_2$ (0.502 g, 0.71 mmol) in dry diethyl ether (30 mL) and MgBr(CH$_2$)$_5$CH$_3$ (4.0 ml, 1.0 M, 4.0 mmol) under N$_2$ at -78^{o}C. The obtained pale yellow solid was dried under vacuum for 1 hour to give **3** as a pale yellow solid (0.34 g, 62%), m.p. 90–95^{o}C. Anal. Calcd. for $C_{39}H_{52}P_2Pt$: C, 60.22; H, 6.74; Found: C, 59.60; H, 6.81. ^{1}H-NMR (CDCl$_3$): δ 7.60 – 7.14 (m, 20H, Ph), 2.46-2.60 (m, 6H, P-CH$_2$CH$_2$), 0.73 – 2.38 (m, 26H, -CH$_2$ and –CH$_3$). ^{31}P NMR (CDCl$_3$): δ 3.44 (s), J(Pt-P) = 1623 Hz.

Synthesis of *cis*-Pt(*n*-hexyl)$_2$(PPh$_3$)$_2$ (4): The same procedure was followed by using (COD)PtCl$_2$ (0.3 g, 0.8 mmol) in dry diethyl ether (30 mL), MgBr(CH$_2$)$_5$CH$_3$ (3.2 mL, 1.0 M, 3.2 mmol) and PPh$_3$ (0.42 g, 1.6 mmol). After evaporating the solvent, the product **4** was obtained as a pale yellow crystalline solid, this was dried under high vacuum for 1 hour. Yield (0.54 g, 76%), m.p. 116–120 ^{o}C. Anal. Calcd. for $C_{48}H_{56}P_2Pt$: C, 64.78; H, 6.34%; Found: C, 64.02; H, 6.83. ^{1}H-NMR (CDCl$_3$): δ 7.82 – 7.13 (30H, m, Ph), 0.94 – 1.40 (m, 26H, -CH$_2$ and –CH$_3$). ^{31}P NMR (CDCl$_3$): δ 27.18 (s), J(Pt-P) = 1726.33 Hz.

Synthesis of *cis*-Pt(*n*-heptyl)$_2$(dppp) (5): (dppp)PtCl$_2$ (700 mg, 1.032 mmol) was reacted with *n*-heptyl Grignard reagent (2.06 ml, 4.126 mmol) in diethyl ether (40 ml). The reaction mixture was worked up as described above. The oil was recrystallized from a 50:50 mixture of hexane and diethyl ether (20 ml) to give **5** as colorless crystalline solid, which were dried under vacuum for 1 hour. Yield 80%; m.p. 97-99°C; Anal. Calcd. for $C_{41}H_{56}P_2Pt$: C, 61.10; H, 7.00, Found: C, 61.09; H, 7.24; ^{1}H NMR (300 MHz, CDCl$_3$): 7.17-7.61 (m, 20H, Ph), 2.28-2.42 (m, 6H, P-CH$_2$CH$_2$), 0.78-2.23 (m, 30H, -CH$_2$ and –CH$_3$); ^{31}P NMR (CDCl$_3$): δ 3.46 (s), J(Pt-P) = 1623.03 Hz.

Synthesis of *cis*-Pt(*n*-heptyl)$_2$(PPh$_3$)$_2$ (6): (COD)PtCl$_2$ (600 mg, 1.600 mmol) was reacted with *n*-heptyl Grignard reagent (2.06 mL, 4.126 mmol) in 35 mL of diethyl ether. After the reaction, PPh$_3$ (839 mg, 3.200 mmol) was added. The obtained oily mass was recrystallized from a 50:50 mixture of hexane and diethyl ether (25 mL) to give **6** as colorless crystalline solid, which was dried under vacuum for 1 h. Yield (84%); m.p. 99-102°C; Anal. Calcd. for $C_{50}H_{60}P_2Pt$: C, 65.42; H, 6.59, Found: C, 65.55; H, 6.55; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.01-7.68 (m, 30H, Ph), 0.73-1.95 (m, 30H, –CH$_2$ and -CH$_3$); ^{31}P NMR (CDCl$_3$): δ 27.18 (s), J(Pt-P) = 1716.33 Hz.

Synthesis of *cis*-Pt(*n*-octyl)$_2$(dppp) (7): (COD)PtCl$_2$ (342 mg, 0.914 mmol) in diethyl ether (30 mL), 3.1 mL of *n*-octyl Grignard reagent (0.88 M, 2.74 mmol) and dppp (377 mg, 0.914 mmol) were used to prepare **7** as described above. For **7**: mp 78-80°C; yield 94%; Anal. Calcd for $C_{43}H_{60}P_2Pt$: C, 61.93; H, 7.25. Found: C, 62.23; H, 7.28; ^{1}H NMR: δ 6.92-7.64 (m, 20H, Ph); 2.08-2.19 (m, 6H, P-CH$_2$CH$_2$); 0.83-2.05 (m, 34H, -CH$_2$ and –CH$_3$); ^{31}P{^{1}H} 3.88 (s) (J_{Pt-P} = 1618 Hz).

Synthesis of *cis*-Pt(*n*-octyl)$_2$(PPh$_3$)$_2$ (8): (COD)PtCl$_2$ (336 mg, 0.898 mmol) in diethyl ether (30 mL) was reacted with 3.1 mL of 1-octenyl Grignard reagent (0.88 M, 2.694 mmol). To this, PPh$_3$ (471 mg, 1.796 mmol) was added and stirred for 36 h until a clear solution is formed. The reaction mixture was worked up as described above. For **8**: mp 110-112°C; yield 92%; Anal. Calcd for $C_{52}H_{64}P_2Pt$: C, 66.01; H, 6.82. Found: C, 66.13; H, 6.88; ^{1}H NMR: δ 7.12-7.96 (m, 30H, Ph); 0.83-2.05 (m, 34H, -CH$_2$ and –CH$_3$); ^{31}P{^{1}H} 27.84 (s) (J_{Pt-P} = 1634 Hz).

Synthesis of *cis*-Pt(*n*-nonyl)$_2$(dppp) (9): Pt(COD)Cl$_2$ (256 mg, 0.684 mmol) in diethyl ether (30 mL) was cooled and 1.85 mL of *n*-nonyl Grignard reagent (1.12 M, 2.05 mmol) was added. The solution was brought to around 0°C and then stirred until the solution becomes clear. To this, dppp (282 mg, 0.684 mmol) was added and stirred for 36 h until a clear solution is formed. The reaction mixture was worked up as described above. For **9**: m.p. 68-70°C; yield 94%; Anal. Calcd. for $C_{45}H_{64}P_2Pt$: C, 62.70; H, 7.48. Found: C, 62.84; H, 7.52; ^{1}H NMR δ 7.02-7.64 (m, 20H, Ph, 2.12-2.21 (m, 6H, P-CH$_2$CH$_2$); 0.76-2.08 (m, 38H, -CH$_2$ and –CH$_3$); ^{31}P{^{1}H} 3.94 (s) (J_{Pt-P} = 1634 Hz).

Synthesis of *cis*-Pt(*n*-nonyl)$_2$(PPh$_3$)$_2$ (10): (COD)PtCl$_2$ (286 mg, 0.764 mmol) in diethyl ether (30 mL) was cooled to T = -78°C and 2.05 mL of *n*-nonyl Grignard reagent (1.12 M, 2.29 mmol) was added. The solution was brought to around 0°C and then stirred until the solution becomes clear. To this, PPh$_3$ (401 mg, 1.53 mmol) was added and stirred for 36 h until a clear solution is formed. The reaction mixture was worked up as described above. For **10**: mp 92-94°C; yield 90%; Anal. Calcd. for $C_{54}H_{68}P_2Pt$: C, 66.58; H, 7.04. Found: C, 66.68; H, 7.16; ^{1}H NMR: δ 6.86-7.88 (m, 30H, Ph); 0.68-2.16 (m, 38H, -CH$_2$ and –CH$_3$); ^{31}P{^{1}H} = δ 27.4 (s) (J_{Pt-P} = 1684 Hz).

Synthesis of *cis*-Pt(*n*-hexyl)Cl(dppp) (11): **3** (1.245 g, 1.6 mmol) was added to a mixture of 250 mL of CH$_2$Cl$_2$ and 100 mL of methanol. To this, acetyl chloride (125 mg, 1.6 mmol) in 125 mL of CH$_2$Cl$_2$ was added drop-wise over 2 h using an ice-cold bath under constant stirring. Then the formed precipitate was filtered and all the volatiles were removed from the filtrate by rotavap. The product **11** was recrystallized from the solvent mixture of 1:1 CH$_2$Cl$_2$ and methanol. Yield = 0.536 g (46%). mp 198–200°C (dec.). ^{1}H NMR: δ 7.28–7.96 (m, 20H, Ph), 2.65–3.11 (m, 6H, P–

CH_2CH_2), 0.66–1.38 (m, 13H, CH_2 and CH_3); ^{31}P NMR: δ −1.5 (s) ($J_{Pt\text{-}P}$ = 3842 Hz). Anal. calcd for $C_{33}H_{39}P_2PtCl$: C, 54.43; H, 5.40. Found: C, 54.56; H, 5.48.

Synthesis of *cis*-Pt(*n*-hexyl)(*n*-octyl)(dppp) (12): 11 (282 mg, 0.3873 mmol) and dry diethyl ether (30 mL) were taken in a Schlenk flask and 1.5 mL of *n*-octyl Grignard reagent (0.92 M, 0.78 mmol) was added to the flask at -78°C. The solution was brought to around 0°C and then stirred until the solution becomes clear. The reaction mixture was worked up as described for compound **1**. For **12**: mp 106-108°C (dec.); yield 82%; ^1H NMR: δ 6.96‐7.84 (m, 20H, Ph), 2.32‐2.52 (m, 6H, P-CH_2CH_2), 0.65‐2.38 (m, 30H, -CH_2 and -CH_3); ^{31}P NMR: δ 2.56, 2.69 ppm and 4.23, 4.12 ppm ($J_{Pt\text{-}P}$ = 1675 and 1689 Hz). Anal. calcd for $C_{41}H_{56}P_2Pt$: C, 61.10; H, 7.00. Found: C, 61.16; H, 7.11.

General procedure for thermolysis:

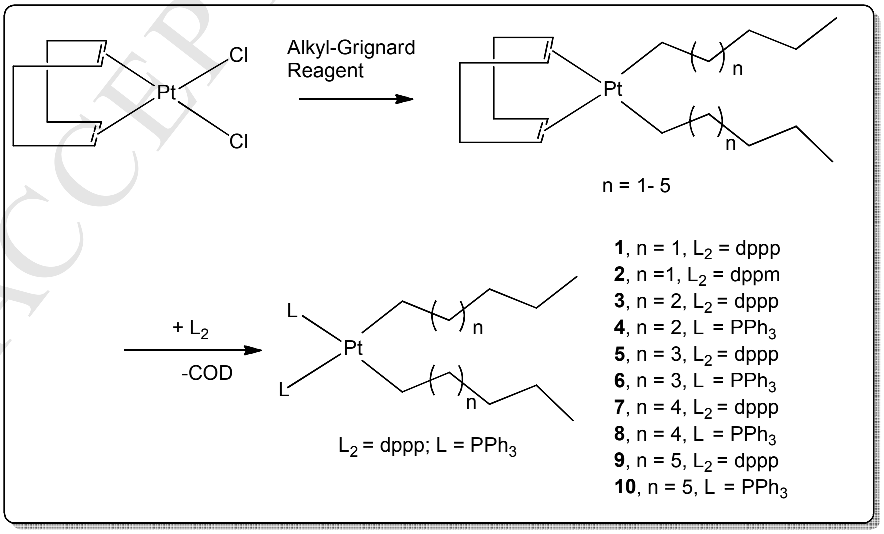
Thermolysis reactions were carried out in dry, sealed and evacuated vertical Schlenk tubes of 1-cm o.d. and 10-cm lengths. The platinum complexes were dissolved in DCM and transferred into the tube; the solvent was removed under vacuum and dried at least for 6 hours before thermolysis. The samples were then immersed in a thermostated oil bath constant at 170±5 ºC. The tubes were removed at intervals (2 h) and quenched by immersion in liquid nitrogen. Decomposition products were extracted by 0.5 mL pentane containing 20 µL of chlorobenzene as internal standard and analyzed by GC/GCMS. Products were identified by comparison of retention times to those of authentic samples. Product yields were determined by response relative to the internal standard (chlorobenzene).

4. Computational Details

All the calculations were based on density functional theory (DFT) and Gaussian 09 package was exploited to carry out these calculations [16]. The optimization of the geometries was done by employing Becke’s hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang and Parr (B3LYP)[17-19] and the standard 6-31G* basis set function of DFT for all atoms except the Platinum (Pt) atom for which effective core potential (ECP) of Wadt and Hay pseudopotential with a double- ζ basis set LANL2DZ has been employed. For the structural calculations of transition metal complexes, the relativistic LANL2DZ pseudopotential is the typical basis set and is identified to give close agreement between optimized and experimentally determined structures for organoplatinum complexes [20]. In order to see the identity of each stationary point found as a global minimum, frequency calculation was performed too by employing the same level of theory. The population analysis has been performed by the natural bond orbital (NBO) method [21] at B3LYP/631G* level of theory using NBO 3.1 version of Gaussian 09 program package.

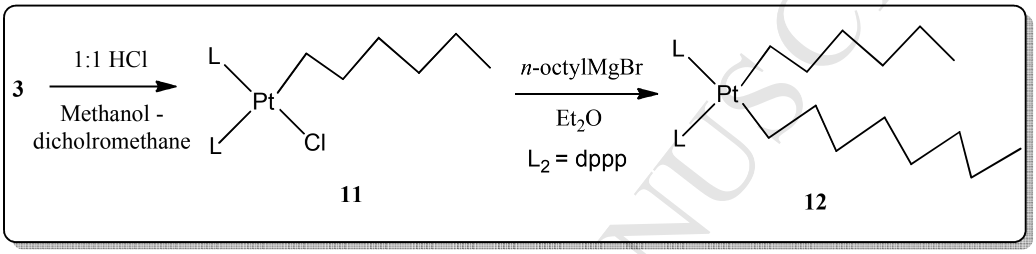
RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of Platinum-Dialkyl complexes. The dialkyl-platinum(II) complexes **1-10** were obtained by the transmetalation reaction of alkyl Grignard reagents with either [Pt(COD)Cl_2] or [Pt$L_2$$Cl_2$]($L_2$ = dppp or L = PPh_3) precursors as shown in Scheme 1. Complexes **1-10** were obtained as colorless solids in high yield after recrystallization from CH_2Cl_2/diethyl ether. These new compounds were found to be quite stable at room temperature and the thermal stability of the complexes follows the order PPh_3 < dppp due to the chelating effect. The ^{31}P{^{1}H} NMR spectra of all the compounds displayed a singlet around 3.4 ppm for **1**, **3**, **5**, **7**, **9** compounds and 26.4 ppm for **4**, **6**, **8**, **10** compounds respectively with Pt satellites. The average coupling constants ($^1J_{Pt-P}$) of these compounds were found to be 1620 Hz for **1**, **3**, **5**, **7**, **9** and 1800 Hz for **4**, **6**, **8**, **10** respectively, which are quite similar to their bis(1-alkenyl)platinum(II) analogs [22]. All new compounds described in Scheme 1 were characterized by analytical and spectroscopic methods.



Scheme 1. Preparation of various platinum-dialkyl complexes

Careful reaction of **3** with either 1 mole of acetyl chloride solution in a solvent mixture of methanol-dichloromethane (1:1) yielded the mono-hexyl compound **11**. The reaction of **11** with the *n*-octyl Grignard reagent gave compound **12**, which now contains two different alkenyl chains of the type [(dppp)Pt(*n*-hexyl)(*n*-octyl)] (Scheme 2). The unsymmetrical nature of this molecule is clearly seen in the ^{31}P NMR spectrum which shows two doublets, each with platinum satellites showing the signals at 2.56, 2.69 ppm and 4.23, 4.12 ppm ($J_{\text{Pt-P}}$ = 1675 and 1689 Hz).



Scheme 2: Preparation of [(dppp)Pt(*n*-hexyl)(*n*-octyl)]

Crystallographic Characterization of Platinum-Dialkyls. The molecular structures of **1** and **7** are shown in Fig.1 and Fig.2 respectively [23]. To the best of our knowledge, these are the first examples of structurally characterized dipentyl or dioctylplatinum(II) compounds reported in the literature. The main structural features of complex **1** and **7** are given in some of the bond angles and bond lengths. The Pt-C and Pt-P bond lengths are slightly different in **1** when compared to **7**but comparable to the bis(1-heptenyl)platinum(II) analogs and the other literature reports [22,24]. (Pt-C, 2.099(4)-2.101(4) Ǻ for **1**; 2.114(3)-2.118(3) Ǻ for **7** and Pt-P, 2.2811(9)-2.2824(10) Ǻ for **1**; 2.2749(8)-2.2922(8) Ǻ for **7** respectively). The P-Pt-P and C-Pt-C bond angles in **1** and **7** are significantly different and vary from 93.05(4)-93.12(3)° and 85.96(16)-85.15(12)°. The minimum distance between metal and β-hydride is found to be 3.079 and 3.215 (Ǻ) for **1** and **7** respectively.

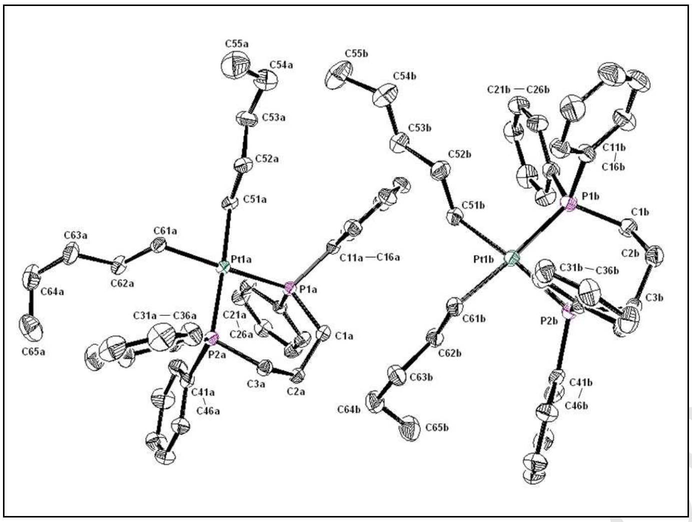


Figure 1. Molecular structure of **1** with bis(diphenylphosphino)propane ligand (dppp), showing the atom numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Selected bond lengths (Ǻ) and Bond angles (°): Pt(1)-C(61) 2.099(4); Pt(1)-C(51) 2.101(4); Pt(1A)-P(1A) 2.2811(9); Pt(1)-P(2) 2.2824(10); C(61)-Pt(1)-C(51) 85.96(16); C(61)-Pt(1)-P(1) 174.67(11); C(51)-Pt(1)-P(1) 90.46(11); P(1)-Pt(1)-P(2) 93.05(4).

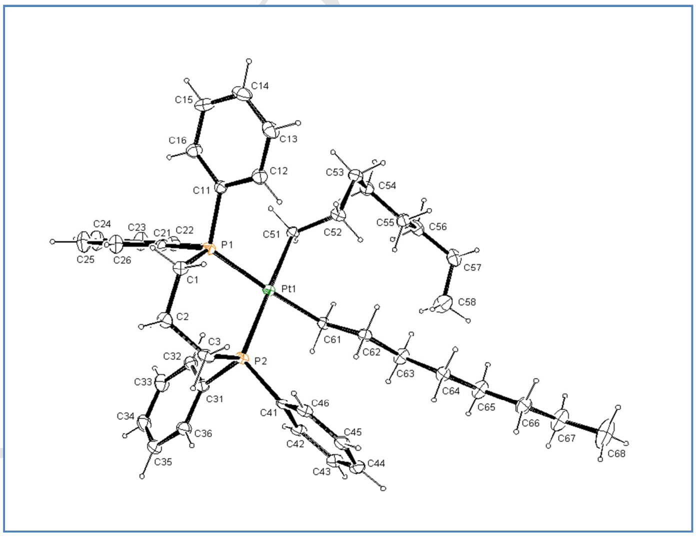


Figure 2. Molecular structure of **7** with bis(diphenylphosphino)propane ligand (dppp), showing the atom numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Selected bond lengths (Ǻ) and Bond angles (°): Pt(1)-C(61) 2.114(3); Pt(1)-C(51) 2.118(3); Pt(1)-P(1) 2.2749(8); Pt(1)-P(2)

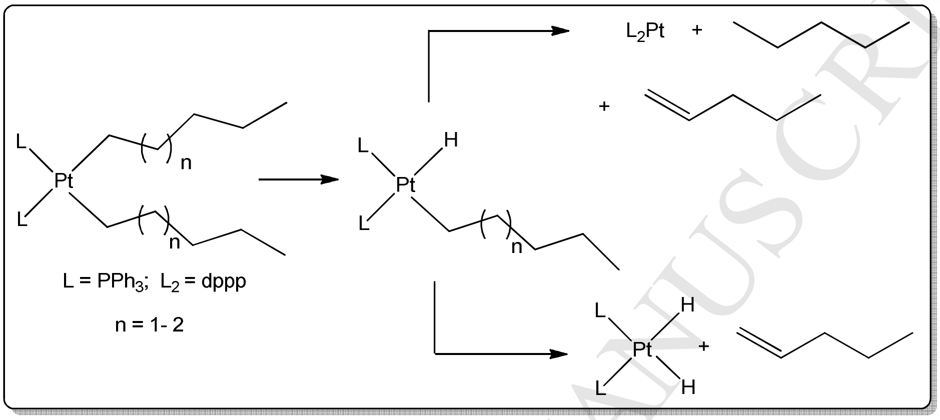
2.2922(8); C(61)-Pt(1)-C(51) 85.15(12); C(61)-Pt(1)-P(1) 174.83(8); C(51)-Pt(1)-P(1) 89.89(9); C(61)-Pt(1)-P(2) 91.71(9); C(51)-Pt(1)-P(2) 174.67(9); P(1)-Pt(1)-P(2) 93.12(3).

Thermolysis Studies.

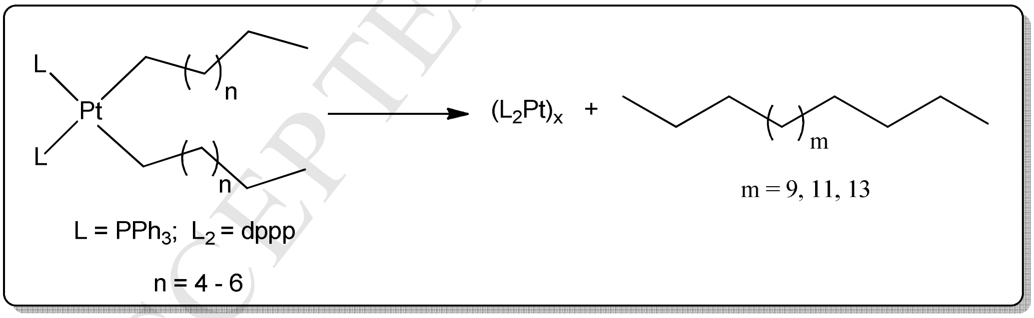
β-Hydride elimination is the most important mechanism for metal alkyl decomposition through the agostic interaction [25, 26] and metal-catalyzed isomerization with involvement of *d*-orbitals of the metal in the reaction pathway and this is a lower energy process than many others, such as α-elimination, γ-elimination, reductive elimination, and transmetalation [27]. It is very important to suppress the *β*-hydride elimination for the success of many transition metal mediated reactions achieving the efficiency [28].

In the present work, thermolysis of shorter chain (< C_7) platinum(II)-dialkyl compounds showed the formation of a mixture of 1-alkenes and 2-alkenes through β-hydride elimination (Scheme 3 and Table 1), which is consistent with the literature data for small chain compounds [5, 25]. It is significant to note that the nature of the ligand does not influence the decomposition pathway, though PPh_3 complexes decompose at relative low temperatures (< 100 ºC) than the diphosphine analogues. Surprisingly, the reductive elimination reaction dominated over β-hydride elimination when the chain length was increased (Eq.1). It seems that this reaction pathway is governed by the distance between metal and β-hydrogen. In the case of **1** with relatively shorter alkyl chains (C_5), the β-hydride elimination is more predominant as the metal- β-hydrogen distance is shorter ((3.079 Ǻ) whereas **7** with longer alkyl chains (C_8) exhibits reductive elimination due to the significantly longer distance *i.e.* 3.215 (Ǻ) (Fig.3 and Table 1).

This phenomenon can be explained with the co-planar conformation of M-C-C-H unit in an organometallic complex to accommodate the 4-centered concerted planar transition state to lead to β-hydride elimination. As the length of alkyl chains increases, it is less feasible for the M-C-C-H unit to adopt a planar conformation to favour β-hydride elimination [29]. On the other hand, strongly bound or unlabile ligands [29], reduced electron density on the metal and strong π-acceptor ligands attached to the metal [30] retard β-hydride elimination in organoplatinum(II) complexes. Further, the large bite angle of bidentate phosphine ligands accelerates reductive elimination by forcing the two alkyl groups closer together about the metal center [31]**.** The bidentate bis(diphenylphosphino)ferrocene ligand also favors reductive elimination by enforcing a cis geometry for the vinyl and alkyl ligands on square planar Pd(II) [32]. If a slight increase in chain length prefers the reductive elimination due to the steric bulk, it should have happened in the decomposition of *cis*-bis(alkenyl)-platinum(II) complexes [33]. But no such reductive elimination was observed in the latter complexes as the presence of unsaturated olefinic double bond shows a different chemistry.

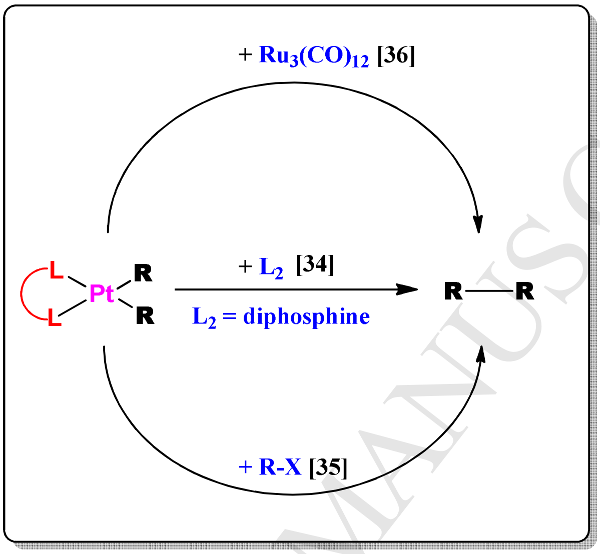


Scheme.3 β-hydride elimination shown by dialkyl-platinum(II) complexes with shorter alkyl chains (C_3-C_6)



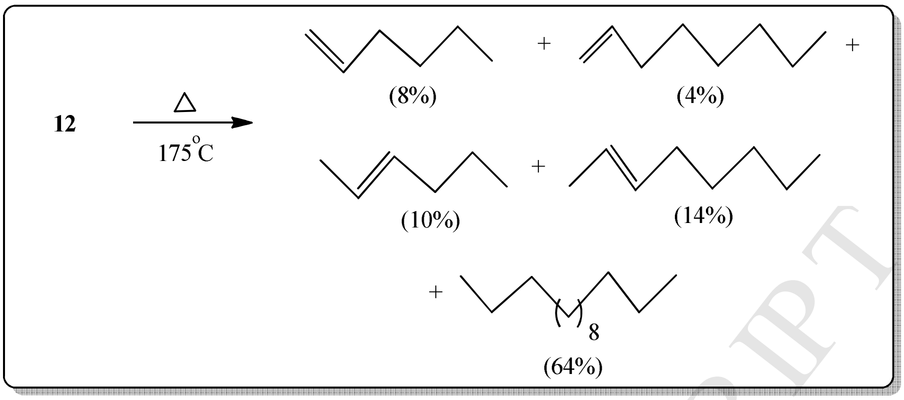
Eq.1. Reductive elimination shown by dialkyl-platinum(II) complexes with longer alkyl chains (C_7-C_9)

There are two other instances where the reductive elimination was preferred over β-hydride elimination as given in Scheme 4. *Firstly,* the addition of free dppp ligand was tested *i.e.* on heating, the interaction of dppp with [L_2PtR_2] yielded the products [$(dppp)_2Pt$] and R-R quantitatively by reductive elimination reaction as reported earlier [29,34]. *Secondly*, reductive elimination was favoured in the presence of either alkyl halides (MeI) [35] or $Ru_3(CO)_{12}$[36] through the oxidative addition reaction with $[L_2PtR_2]$ complexes and subsequent formation of hexacoordinate tetravalent platinum species. A similar trend was obtained for the $[(dppp)NiR_2]$ complexes *i.e.* when R = *n*-pentyl, β-hydride elimination is more predominant and only the reductive elimination product was observed when R = *n*-decyl [37].



Scheme.4. Other routes for reductive elimination reactions

On thermolysis, **12** yielded the organic product distribution as shown in Eq.2. As expected, the major product was the reductively eliminated *n*-butadecane in 64% yield. The selective formation of products through either β-hydride elimination or reductive elimination was more difficult to envision, as the formation of these products requires completely different conditions. In the case of complex **7** with octyl chains, the rate of C-C bond forming reductive elimination would need to be faster than the competing β-hydride elimination. We show here that it is feasible to achieve selectivity for complex **7** by employing same chelating ligands to minimize the rate of β-hydride elimination. The dihedral angles of the M-dialkyl complexes might be different in solution as well as the solid state during the decomposition at high temperatures.



Eq.2: Organic product distribution of **12** upon thermolysis

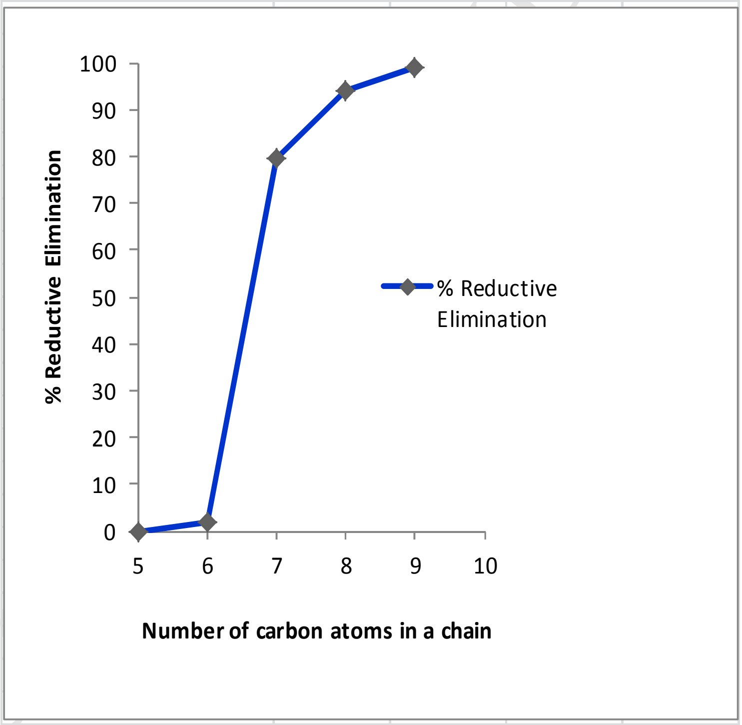


Fig.3: Reductive elimination of dialkyl complexes (where L_2 = dppp ligand) as a function of length of carbon chains.

Table 1: Thermal decomposition products of *n*-dialkyl-platinum(II) complexes (**1-11**)

		Organic products identified*, %**				
Compound	Ligand	1-pentene	2-pentene	*n*-pentane	*n*-decane	
1	dppp	38	33	29	0	
2	PPh_3	59	0	41	0	
		1-hexene	2-hexene	*n*-hexane	*n*-dodecane	
3	dppp	37	26	35	2	
4	PPh_3	35	22	38	5	
		1-heptene	2-heptene	*n*-heptane	*n*-tetradecane	
5	dppp	14	5	13	68	
6	PPh_3	4	1	4	91	
		1-octene	2-octene	*n*-octane	*n*-hexadecane	
7	dppp	0	2	0	98	
8	PPh_3	9	4	6	81	
		1-nonene	2-nonene	*n*-nonane	*n*-octadecane	
9	dppp	0	1	0	99	
10	PPh_3	0	1	0	99	
		1-pentene	2-pentene	1-octene	2-octene	*n*-tetradecane
12	dppp	8	10	4	14	64

*determined by GC-MS analysis; **average of three determinations each

Theoretical Aspects: In Pt-complexes (**1** and **7**) the co-ordination environment of the central metal atom displays a slightly distorted square planar geometry with minute deviations from experimental numbers. The bonding parameters from the X-ray crystal structure are compared with the optimized geometrical parameters (supporting information). The difference in calculated and observed bonding parameters is negligible and does not provide any useful additional outcome. The comparison of some DFT computed key geometrical parameters between **1** and **7** is highly essential. Focussing on the distance parameters only, it is indispensable to target the β-hydrogens as they are highly involved in the reaction mechanism of the complexes. The important geometrical parameters related to β- hydrogens are summarised in Table 2. The Pt(1) –

H(62) and Pt(1) – H(63) distances in **1** are 3.380Å and 3.329 Å respectively though both on the same atom C(58) while as the distance between Pt(1) and Hs on C(70) is almost same. Similarly in **7**, the distance between Pt(1) and hydrogens on C(58) is almost the same but different between the Pt(1) and hydrogens on C(70). It is clear that Pt(1)- H(β) distances are smaller in **1** in comparison to **7** and the complexes show varying distances between the Pt centre and β-hydrogens within a single complex which may have a significant effect on the reaction mechanism. The optimized geometries of **1** and **7** are traced out in Fig. 4 and 5 respectively.

Table 2: Theoretically calculated distances between the Pt(1)-Hs(β)of **1** and **7**.

Molecule	Centers involved	Theoretical distances [a]
1	Pt(1) – H(62) Pt(1) – H(63) Pt(1) – H(74) Pt(1) – H(75)	3.380 3.329 3.281 3.281
7	Pt(1) – H(62) Pt(1) – H(63) Pt(1) – H(74) Pt(1) – H(75)	3.374 3.378 3.310 3.298

[a] Distances are in angstroms (Å) and numbering of atoms is given as in optimized geometries at DFT level.

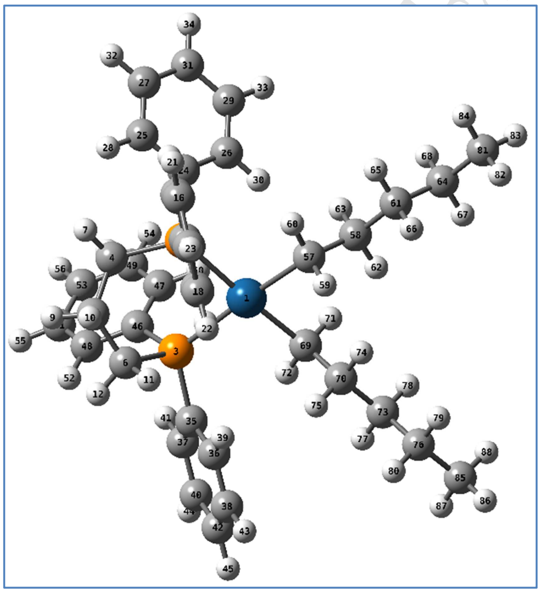


Fig. 4. Optimized structure of **1**.

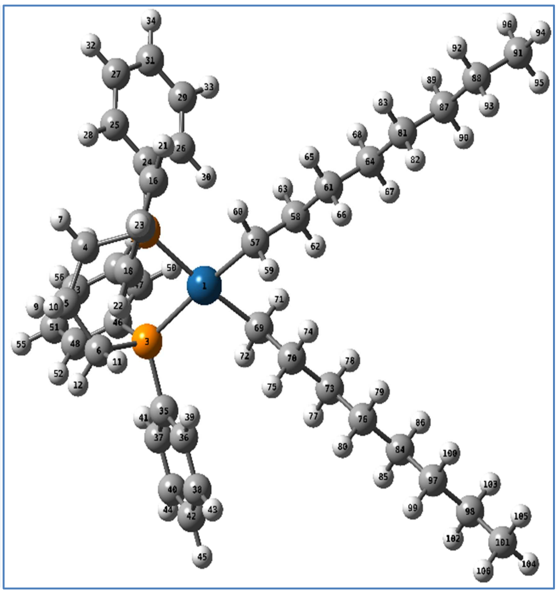


Fig 5. Optimized structure of **7**.

To extract more meaningful and comprehensible understanding of Pt-complexes regarding the nature of bonding, the electronic structure was evaluated (supporting information). Natural population analysis (NPA) revealed a partial charge on the Pt atom while a positive charge on the bonded phosphorous (P2, P3) atoms and a negative charge on the bonded carbon (C57, C69) atoms were observed respectively (supporting information). The significant covalent interactions between the central metal atom and ligands have been obtained from quantum chemistry wave function-based Wiberg bond index analysis (supporting information). The polar nature of these covalent bonds and resonance stabilization of the Pt-complex was obtained from the natural bond orbital (NBO) analysis. Perturbation theory energy analysis revealed that the strongest delocalizations in both complexes involve the interaction of Pt–C bond pair electron density with the trans positioned Pt–P antibonding orbital and vice-versa. These geminal interactions stabilize the complexes (supporting information). The electron density plots for the complexes of interest are given in Fig.6 and Fig.7.

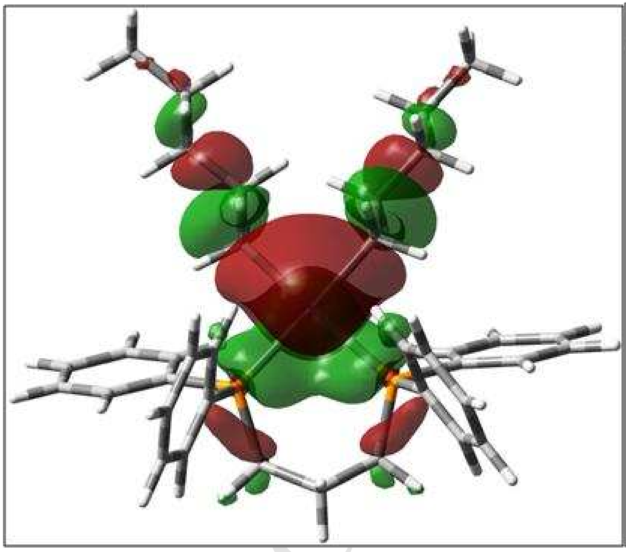


Fig. 6 HOMO of **1**

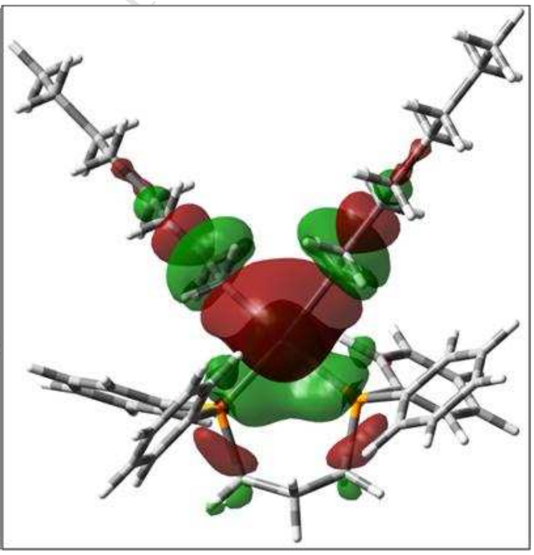


Fig. 7: HOMO of **7**

Conclusions

We report the synthesis, spectroscopic characterization, X-ray single crystal structures, and thermolysis studies of platinum-dialkyl complexes of the type [Pt(L_2)R_2], (where L_2 = dppp (1,3-bis(diphenylphosphino)propane or L = PPh_3; R = *n*-butyl to *n*-nonyl). Thermal decomposition studies of these complexes provided interesting patterns; the longer chain dialkyls *i.e.* C_7-C_9

complexes undergo reductive elimination whereas the shorter chain dialkyl complexes and C_3-C_6 prefer only the β-hydride elimination reaction. Theoretical calculations reveal that Pt(1)- H(β) distances are smaller in **1** in comparison to **7** and the complexes show varying distances between the Pt centre and β-Hs within a single complex which may have a significant effect on the reaction mechanism. It is also clear that strongest delocalizations in both complexes involve the interaction of Pt–C bond pair electron density with the trans positioned Pt–P antibonding orbital and vice-versa.

Acknowledgements

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[23]. a) Structure determination and crystallographic data for 1: crystals were obtained by slow diffusion of *n*-hexane into a solution of 1 in dichoromethane. $C_{43}H_{60}P_2Pt$, Mr =

833.94 gmol^{-}1, triclinic, space group P-1, a = 12.5422(2), b = 12.5954(2), c = 14.9657(3) Ǻ, α = 109.0670(10), β = 90.8960(10), γ = 115.2990(10), V = 1986.56(6) Ǻ^3, Z = 2, ρ_{calcd} = 1.394 gcm^{-3}, T = 113(2) K, m = 3.640 mm^{-1}, F(000)= 852, 4.44°<2θ<25.65°, λ-(MoKα)=0.71073 Ǻ, crystal size 0.13 X 0.17 X 0.21 mm^3. Intensity data were collected with a Nonius Kappa CCD diffractometer. 56406 reflections, 7458 independent (R_{int}=0.0349), empirical absorption correction (SADABS), structure solution using direct methods (SHELXS-97), structure refinement on F^2 using full-matrix least-squares procedures (SHELXL-97), R_1= 0.0257 [I>2σ(I)], wR_2=0.0536 (all data), GOF=1.041; b) Structure determination and crystallographic data for 7: crystals were obtained by slow diffusion of *n*-hexane into a solution of 7 in dichoromethane. $C_{37}H_{48}P_2Pt$, Mr = 749.78 gmol^{-1}, triclinic, space group P-1, a = 13.3720(10), b = 14.1812(10), c = 18.4824(2) Ǻ, α = 88.7040(10), β = 75.0170(10), γ = 89.2170(10), V = 3384.70(5) Ǻ^3, Z = 4, ρ_{calcd}= 1.471 gcm^{-3}, T = 223(2) K, m = 4.263 mm^{-1}, F(000) = 1512, 1.14°<2θ<26.11°, λ-(MoKα) = 0.71073 Ǻ, crystal size 0.06 X 0.09 X 0.11 mm^3. Intensity data were collected with a Nonius Kappa CCD diffractometer. 87254 reflections, 10362 independent (R_{int}= 0.0670), empirical absorption correction (SADABS), structure solution using direct methods (SHELXS-97), structure refinement on F^2 using full-matrix least-squares procedures (SHELXL-97), R_1 = 0.0301 [I>2σ(I)], wR_2 = 0.0575 (all data), GOF = 1.055. CCDC-1403607 (**1**) and CCDC-1403608 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

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Highlights

- Platinum(II)-dialkyl complexes were synthesized and structurally characterized.
- On heating, the shorter chain dialkyl complexes prefer to undergo only the β-hydride elimination pathway.
- On contrary, the longer chain dialkyls *i.e.* C_7-C_9 complexes undergo selectively reductive elimination.
- DFT calculations reveal the shorter Pt(1)-H(β) distances in shorter chain dialkyl complexes in comparison to longer chain dialkyls.