



Synthesis and reactivity of platinacycloalkanes

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ABSTRACT

Novel large platinacycloalkane compounds containing 19- and 21- membered rings of the type $L_2Pt(CH_2)_n$ ($L_2 = dppp$ and $n = 18, 20$) are synthesized through the ring closing metathesis (RCM) reaction of bis(1-alkenyl)platinum(II) complexes using Grubbs' catalysts. These compounds are characterized by various spectroscopic and analytical techniques. The cross metathesis reactions with different dienes and substituted alkynes yielded interesting *inter-* and *intra-* molecular metathesis reaction products. Various factors such as concentration, solvent, phosphine ligand and length of the alkenyl chains affect the RCM reaction significantly to yield different products such as monomeric, dimeric and polymeric species. The novel chemical reactivity aspects of these title compounds with elemental sulfur, carbon monoxide and methyl iodide are discussed.

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1. Introduction

Catalytic olefin metathesis has emerged as a significant synthetic tool for the synthesis of a wide range of organic and polymeric materials, through the construction of carbon–carbon bonds [1]. The scope of metal containing olefin metathesis in the synthesis of coordination and organometallic compounds remains relatively limited [2]. Various metallocene-containing species including dendrimers, polymers, and *ansa*-metallocenes have been prepared using either RCM, cross metathesis, or ring opening metathesis polymerization (ROMP) reactions [3]. Polymers containing main group elements such as Sn and Si have also been prepared using the acyclic diene metathesis reaction (ADMET) [4]. The most noteworthy are the creative efforts from the laboratory of Gladysz in applying RCM to a variety of metal compounds with phosphine ligands bearing terminal alkenes, which resulted in novel compounds including sterically shielded linear gyroscope-like molecules [5,6].

Very recently, we have reported a synthetic route for the preparation of medium to large metallacycloalkanes using the RCM route with Grubbs' catalysts [7,8]. These metallacycloalkanes are an important class of organometallic compounds which have been known for many years to be key intermediates in useful catalytic

reactions [9–17]. In spite of the importance of medium to large metallacycloalkanes as intermediates, very little is known about such compounds. Noteworthy, up to now, few higher metallacycloalkanes have been prepared and characterized [18a].

In the present paper, we report the synthesis of new medium to large ring platinacycles of the type $L_2M(CH_2)_n$ (where $n = 8, 18, 20$; $L_2 = dppp$ or $dppe$) from their bis(1-alkenyl) precursors, [19] i.e. with up to a 21- membered ring compound by this route (Scheme 1). This RCM method can also be extended to even number metallacycloalkane compounds [20] as well as other metals with a variety of ligand systems [21]. We also report the syntheses and spectroscopic characterization of interesting platinacycles through *inter-* and *intra-* molecular ring closing metathesis reactions and also describe the reactivity of these compounds.

2. Results & discussion

Platinacycloalkane compounds are relatively stable to moderate temperatures i.e. ca. 80 °C, but quite unstable above 100 °C. The stability of these compounds strongly depends on the nature of ligand as shown in the following trend: diphosphine $\gg \gg PPh_3 > SMe_2 \gg COD > 1,10$ -phenanthroline $> CH_3CN=CO$. It can be seen that the chelating nature of diphosphine ligands gives much stability than the other ligands. The stability of metallacycloalkanes containing no substituents on the β -carbons follows the trend: Pt \gg Pd $>$ Ni [21].

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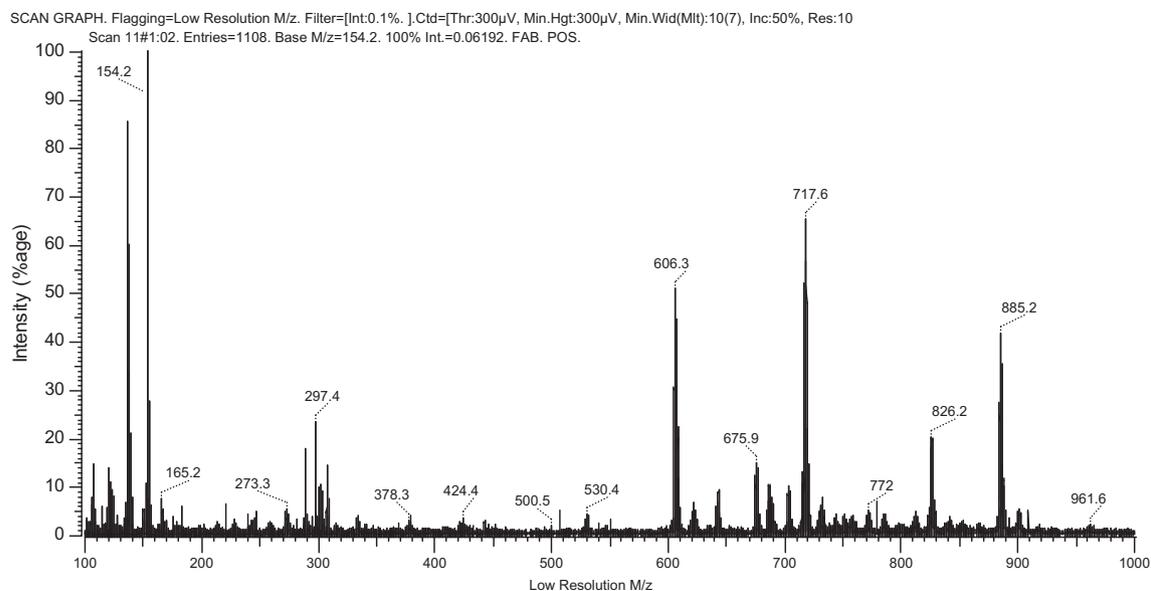


Fig. 1. Mass spectrum of mixture of compounds **3a** and **6**.

isomeric forms of **3a** and **6**. As expected, thermal decomposition of these products indicated the formation of 1-octene, 1,7-octadiene and *n*-octane by GC-MS, as well as diphenylacetylene derivative **8** ($m/z = 290$) (Scheme 2).

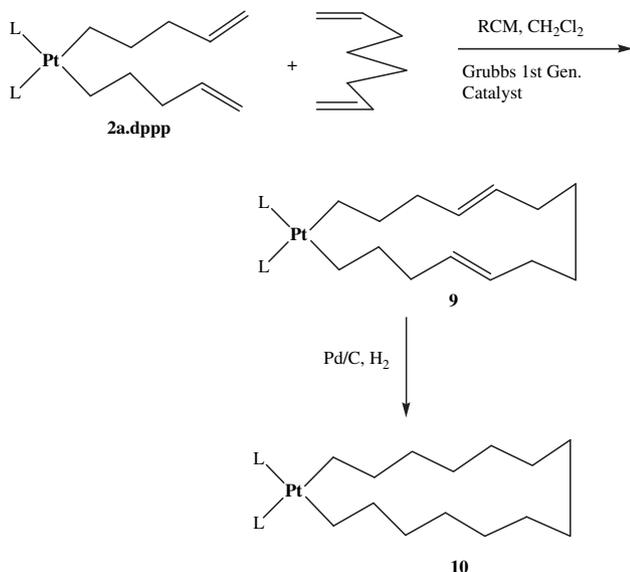
2.1.3. Cross metathesis

Studies on the influence of various dienes during the RCM reaction of bis(1-alkenyl)platinum(II) complexes clearly indicated the formation of a variety of products, depending on the experimental conditions.

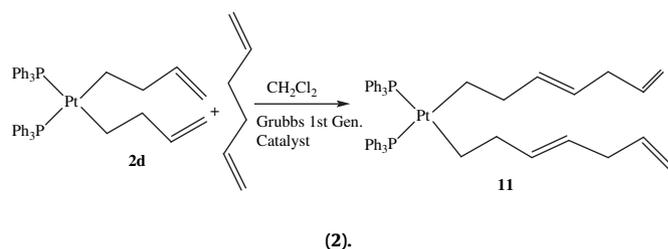
Reaction of **2a(dppp)** complex with 1,7-octadiene in the presence of 5 mol % of Grubbs' catalyst showed the formation of new broad internal alkene signals and the reaction was complete within 12 h at 45 °C (Scheme 3). The broad multiplet signals in the ^1H NMR spectrum (in a range of δ 4.2–4.4 and δ 5.2–5.8) are due to the formation of various products through, intermolecular and

intramolecular metathesis reactions. The ^{31}P NMR spectrum also showed the appearance of very close singlets and a multiplet at δ 46.8 ($J_{\text{Pt-P}} = 1617$ Hz) indicating that these cross metathesis products contain similar species as their precursors. A similar trend was observed with **2a(dppe)** complex. The mass spectrum of the isolated compound **9**, showed mass fragments corresponding to: Pt (dppp) $^+$ ($m/z = 607.4$), 9-membered ring ($m/z = 718.6$), 10-membered diene-ring ($m/z = 733.8$), 12-membered diene- ($m/z = 761.2$), 15-membered ring ($m/z = 799.6$), 22-membered ring ($m/z = 900.6$), 23-membered ring ($m/z = 912.4$) and other species containing lower as well as higher mass values. Products from self metathesis of 1,7-octadiene were not found. Hydrogenation of **9** yielded the known compound **10** [8] in good yields and the ^{31}P NMR spectrum of **10** showed a singlet at δ 3.45 with similar $J_{\text{Pt-P}}$ values as the precursors (Scheme 3).

When the RCM reaction was carried out with **2d** in the presence of 1,5-hexadiene, the terminal alkene protons in ^1H NMR spectrum were unchanged even after refluxing the reaction mixture for several days in the presence of Grubbs' catalyst added batch-wise (Eq. (2)). The formation of **11** with internal alkene protons was significant in ^1H NMR spectrum. This could be due to the cross metathesis reaction of 1,5-hexadiene molecules with each alkenyl chain of the precursor without closing the ring. Mass spectrum indicated the molecular ion ($m/z = 911.5$) and evidence of other mass fragments as expected.



Scheme 3. Ring closing metathesis reaction of **2a(dppp)** in the presence of 1,7-octadiene.



2.2. Reactivity

The interest in reactions of metallacycloalkanes resides in the scope they offer for functionalising hydrocarbons to give valuable

organic compounds, such as alkenes, aldehydes, acids, ethers and thiolates [22–27]. Thermal decomposition studies of metallacycloalkanes have been investigated due to their importance as key intermediates in ethylene oligomerization reactions [7,8,28]. We report herein the results of some CO and S₈ insertion reactions with platinacycles, to give interesting new compounds as shown in Scheme 4.

2.2.1. Insertion of CO

Extensive work has been published on the insertion of CO into transition metal–carbon bonds. Generally all the metals have been shown to undergo CO insertion, except for Nb, Ta, Tc, Cu, Ag, and Au [22–27]. Only a small number of investigations of CO insertion into Pt–alkyl complexes have been undertaken [27]. Insertion of some neutral and cationic complexes of platinum into Pt–C bonds has been demonstrated [29]. The carbonylation reaction was followed by IR spectroscopy. This reaction proved to be relatively slow, and this could principally be due to the strong metal–carbon bond seen in most 5d transition metal complexes [27]. The di-acyl compound **12** (Scheme 4) was obtained in a reasonable yield and its formulation was confirmed by the appearance of bridging carbonyl bands in its IR spectrum as well as a peak in the region of δ 203 in the ¹³C NMR spectrum. These formulations agree well with our previous reports [30]. A mechanism leading to this product may proceed via an intermediate 5-coordinate platinum species [31].

Attempts to insert oxygen into the Pt–C bonds of **4a** failed as the reaction mixtures decomposed completely in the presence of either oxygen or hydrogen peroxide. The expected product **13** (Scheme 4) could not be identified. This could be due to the radical reaction of nascent oxygen in solution.

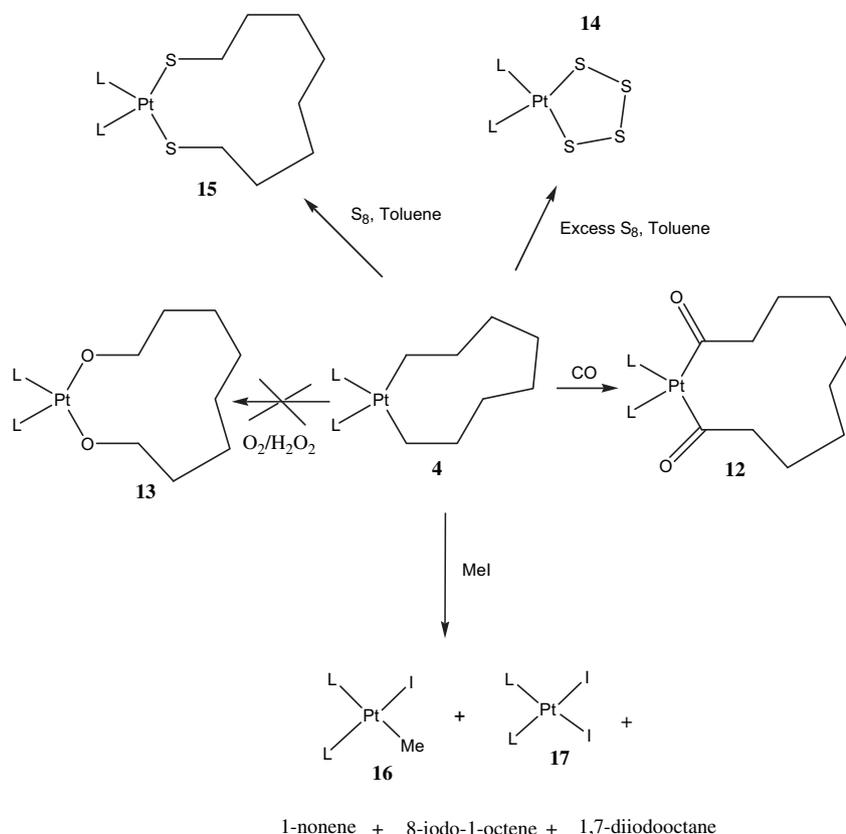
2.2.2. Reaction of elemental sulfur

Very little work has been reported in the literature on the insertion of elemental sulfur (S₈) into transition metal–carbon bonds [32]. Some nickel(II)-thiolate complexes obtained from insertion of sulfur have been reported [33]. Our studies indicated from mass spectrometry, the formation of the sulfur di-inserted product (Scheme 4) and some traces of metallacyclosulfides. The latter products are presumed to be due to the presence of S₄, S₆ and other fragments in polar solvents, according to literature [34]. The ring size of the platinacyclosulfides strongly depends on the reaction conditions, especially temperature.

The reaction of the platinacyclononane **4a** with S₈ resulted in a mixture of products including a platinacyclosulphide (**14** in traces) and **15** which is formed by the insertion of two sulfur atoms from S₈ into the two Pt–C bonds. A peak assigned to the dppp ligand in an environment containing Pt–S bonds was observed in the region of δ –3.23 ppm in the ³¹P NMR spectrum of the product. Similar products have also been seen in the reaction of S₈ with platinum bis(1-alkenyl) complexes and the mechanism leading to these platinacyclosulphides is still not understood [35]. The di-insertion of sulfur into the Pt–C bonds may proceed through a mechanism similar to that reported by Legzdins and co-workers [36].

2.2.3. Oxidative addition of **4a**(dppp) with methyl iodide

The reaction of methyl iodide with **4a**(dppp) yielded known products **16** and **17** [37] (Scheme 4) at 175 °C through the formation of a hexacoordinate platinum(IV) complex. This oxidative addition reaction strongly depends on the nature of ligands. Surprisingly, the formation of cyclooctane was not observed in contrast to the



Scheme 4. Reactivity studies of platinacyclononane.

smaller platinacycloalkenes [18b]. The other organic products such as 1-nonene and 8-iodo-octene were formed by cross reductive elimination.

2.2.4. UV-irradiation studies

The UV-irradiation studies of **4a(dppp)** and **4b(dppe)** yielded a very complex mixture of products and the reaction solutions changed from colourless to yellow brown and finally to reddish brown and these products could not be isolated and characterized. However, the distribution of organic products was very similar to the thermal decomposition results reported previously [21a,b].

3. Conclusions

In conclusion, we have prepared medium to large ring metalacycloalkanes in high yield through a ring closing metathesis reaction, and that such compounds are quite thermally stable. It is noteworthy that platinacycloalkane compounds can undergo a variety of reactions with various substrates depending on the experimental conditions. We are currently exploring the mechanistic pathways for these interesting reactions. We are also investigating the reactivity of similar compounds with other metals as well as even membered ring metallacycloalkanes and cross ring closing metathesis reactions to prepare novel organometallic complexes.

4. Experimental section

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 residual proton resonance in the deuterated solvents. Mass spectral data was obtained using VG70SE with 8 kV acceleration and the FAB gun is an Iontech Saddlefield, using xenon gas and operating at 8 Kv. All matrices were made with 3-nba. Microanalyses were conducted with a Thermo Flash 1112 Series CHNS-O Analyzer instrument. $\text{PtCl}_2(\text{COD})$ [38], 1-alkenyl Grignard reagents ($\text{BrMgCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$; $n = 1, 3, 4, 6$) were prepared according to literature procedures [39]. Compounds **2a(dppp)**, **2a(dppe)** and **2d** were prepared as described earlier.[8] $\text{PPh}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dppp) and $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dppe) were purchased from Aldrich Chemical Co. and used without further purification. Grubbs' catalyst ($\text{Ru}(\text{=CHPh})\text{PCy}_3)_2(\text{Cl})_2$ and Palladium, 10 wt. % on activated carbon used as received from Aldrich.

4.1. Preparation of compound 2b

A Schlenk flask was charged with $\text{PtCl}_2(\text{COD})$ (455 mg, 1.217 mmol) and diethyl ether (25 mL). The mixture was cooled to $T = -78^\circ\text{C}$ and 1-decenyl Grignard reagent (3.4 mL, 1.08 M, 3.65 mmol) was added. The solution was brought to around 0°C and then stirred until the solution became clear. To this, dppe (485 mg, 1.217 mmol) was added and stirred for 1h until a clear solution was formed. The excess Grignard reagent was removed by hydrolyzing the reaction mixture with 5 mL of saturated aqueous NH_4Cl at -78°C . The aqueous layer was washed with 2×5 mL of *n*-hexane and the organic layer was separated using a separating funnel. The solvent was removed from the organic layer under reduced pressure and the residue was purified from a $\text{CH}_2\text{Cl}_2/\text{hexane}$ mixture (1:5) at -10°C for 48 h. The colourless oily mass was separated by decanting the mother liquor and dried under vacuum for several hours. For **2b**; yield 92%; ^1H NMR: δ 7.22–7.60

(m, 20H, Ph); 5.48–5.62 (m, 2H, =CH); 4.67–4.77 (m, 4H, =CH₂); 2.43–2.56 (m, 4H, P–CH₂); 0.86–2.08 (m, 32H, –CH₂); $^{13}\text{C}\{^1\text{H}\}$ NMR: 139.3, 133.2 (d, CH=), 127.7–133.4 (m, Ph), 113.8, 114.1 (d, =CH₂), 36.1, 33.9, 33.7, 23.7, 23.4, 22.6, 22.1; $^{31}\text{P}\{^1\text{H}\}$: δ 45.5 (s) ($J_{\text{Pt-P}} = 1617$ Hz). Anal. Calcd for $\text{C}_{46}\text{H}_{62}\text{P}_2\text{Pt}$: C, 63.36; H, 7.17. Found: C, 63.96; H, 7.76.

4.2. Preparation of compound 2c

$\text{PtCl}_2(\text{COD})$ (326 mg, 0.871 mmol) in diethyl ether (20 mL) was cooled down to $T = -78^\circ\text{C}$ and 2.7 mL of 1-undecenyl Grignard reagent (0.98 M, 2.61 mmol) was added. The solution was brought to around 0°C and then stirred until the solution became clear. To this, dppp (359 mg, 0.871 mmol) was added and stirred for 36 h until a clear solution was formed. The reaction mixture was worked up as described above. The obtained viscous colourless oily mass was dried under high vacuum for several hours. For **2c**; yield 82%; ^1H NMR δ 6.98–7.91 (m, 20H, Ph); 5.69–5.90 (m, 2H, =CH); 4.91–5.11 (m, 4H, =CH₂); 1.86–2.19 (m, 6H, P–CH₂); 0.82–1.68 (m, 36H, –CH₂); $^{31}\text{P}\{^1\text{H}\}$ 3.84 (s) ($J_{\text{Pt-P}} = 1619$ Hz). Anal. Calcd for $\text{C}_{49}\text{H}_{68}\text{P}_2\text{Pt}$: C, 64.38; H, 7.50. Found: C, 64.76; H, 8.23.

4.3. Preparation of compound 3b

Compound **2b** (225 mg, 0.258 mmol) and Grubbs 1st generation catalyst (ca. half of 16 mg, 0.0194 mmol, 5 mol%) were added to 30 mL of dichloromethane. The solution was refluxed at 50°C . After 3 h, the remaining catalyst was added. After another 4 h, the solvent was removed using a vacuum pump. The residue was purified from a $\text{CH}_2\text{Cl}_2/\text{hexane}$ mixture (3 mL: 10 mL) to give **3b** as an oily mass. Yield 88%; ^1H NMR: δ 7.31–7.93 (m, 20H, Ph); 5.28–5.46 (m, 2H, =CH); 1.88–2.24 (m, 4H, P–CH₂); 0.84–1.62 (m, 32H, –CH₂); $^{31}\text{P}\{^1\text{H}\}$: 45.47, 45.05, 45.29, 44.98 (isomers) ($J_{\text{Pt-P}} = 1617$ Hz). Anal. Calcd. for $\text{C}_{44}\text{H}_{58}\text{P}_2\text{Pt}$: C, 62.62; H, 6.93. Found: C, 62.96; H, 7.15.

4.4. Preparation of compound 3c

Compound **2c** (206 mg, 0.2254 mmol) and Grubbs 1st generation catalyst (ca. half of 16 mg, 0.0194 mmol, 5 mol%) were added to 30 mL of dichloromethane. The solution was refluxed at 50°C . After 4 h, the remaining catalyst was added. After another 4 h, the solvent was removed using a vacuum pump. The residue was purified from a $\text{CH}_2\text{Cl}_2/\text{hexane}$ mixture (1:5) to give **3c** as an oily mass. Yield 81%; ^1H NMR: δ 7.26–7.81 (m, 20H, Ph); 5.30–5.44 (m, 2H, =CH); 1.87–2.21 (m, 6H, P–CH₂); 0.78–1.82 (m, 32H, –CH₂); $^{31}\text{P}\{^1\text{H}\}$: 3.23, 3.41, 3.49, 3.57 (isomers) ($J_{\text{Pt-P}} = 1632$ Hz). Anal. Calcd. for $\text{C}_{47}\text{H}_{64}\text{P}_2\text{Pt}$: C, 63.71; H, 7.28. Found: C, 64.96; H, 8.15.

4.5. Preparation of compound 4b

Compound **3b** (125 mg, 0.148 mmol) and 10 mg of Pd/C (10%) catalyst were added to 25 mL of toluene. After bubbling the contents of the flask with H_2 gas for 2–3 min, the solution was stirred at 50°C under ambient pressure of hydrogen (balloon). After 72 h, the solvent was removed under the reduced pressure. The residue was filtered and purified from a $\text{CH}_2\text{Cl}_2/\text{hexane}$ mixture (1:8 v/v) to get a colourless oily mass; Yield 72%; ^1H NMR δ 6.90–7.95 (m, 20H, Ph); 1.85–2.22 (m, 4H, P–CH₂); 0.51–1.79 (m, 42H, –CH₂ and CH₃); $^{31}\text{P}\{^1\text{H}\}$ NMR: 45.6 (s) ($J_{\text{Pt-P}} = 1617$ Hz). MS (FAB, m/z) = 844.3 (M^+), 593.1 [(dppe)Pt⁺].

4.6. Preparation of compound 4c

Compound **3c** (142 mg, 0.160 mmol) and 10 mg of Pd/C (10%) catalyst were added to 25 mL of toluene. A similar procedure was

used as described above for the hydrogenation reaction. The residue was filtered and purified from a CH_2Cl_2 /hexane mixture (1:8 v/v); Yield 82%; ^1H NMR: δ 6.99–7.44 (m, 20H, Ph); 1.97–2.23 (m, 6H, P– CH_2); 0.55–1.85 (m, 20H, – CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR: 2.91 (s) ($J_{\text{Pt-P}} = 1623$ Hz). MS (FAB, m/z) = 890.3 (M^+), 606.3 [(dppp)Pt $^+$].

4.7. Preparation of polymer **5** from RCM reaction of **2a(dppe)**

2a(dppe) (192 mg, 0.2627 mmol) and Grubbs 1st generation catalyst (ca. half of 12 mg, 5 mol%) were taken in a John-Young NMR tube. To this, 0.4 mL of C_6D_6 was added. Then the solution was heated at 50 °C. After 6 h, the remaining catalyst was added. After another 6 h, the solvent was removed by the vacuum pump which gave an oily mass. Attempts to isolate the impurities from the residue were not successful as the products were sensitive to preparative TLC and silica gel. Crude yield 68%; ^1H NMR: δ 6.38–8.46 (m, Ph); 4.24–5.87 (m, =CH); 0.62–2.90 (m, P– CH_2 and – CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR: 45.4–47.5 (broad) ($J_{\text{Pt-P}} = 1675$ Hz). MS (FAB, m/z) = 703.2 [monomer, 9-membered platinacycloalkene], 815.9 [(dimer)-(dppePt)] and 582.8 [(dppe)Pt $^+$].

4.8. RCM reaction of **3a(dppp)** in the presence of diphenylacetylene

2a(dppp) (202 mg, 0.271 mmol), diphenylacetylene (97 mg, 0.542 mmol) and Grubbs 1st generation catalyst (ca. half of 14 mg, 5 mol%) were added to 30 mL of dichloromethane. The solution was refluxed at 50 °C. After 5 h, the remaining catalyst was added. After another 6 h, the solvent was removed using a vacuum pump. The residue was purified from a CH_2Cl_2 /hexane mixture (2:5) to give a mixture of products **3a** and **6** as a colourless solid. Attempts to isolate these products from the reaction mixture were not successful. The reaction mixture as such was used for the hydrogenation reaction. Yield 82% (mixture of products); ^1H NMR: δ 7.03–7.81 (m, Ph); 4.90, 5.13, 5.50 (t, =CH); 2.24–2.72 (m, P– CH_2); 0.597–2.0 (m, – CH_2); $^{31}\text{P}\{^1\text{H}\}$: δ 3.45 (m, $J_{\text{Pt-P}} = 1624$ Hz) and δ 5.17 (s, $J_{\text{Pt-P}} = 1516$ Hz) (isomers). MS (FAB, m/z) = 891.3 (M^+ for **6**) and 717.6 (M^+ for **3a(dppp)**), 606.3 [(dppp)Pt $^+$].

4.9. Hydrogenation of the reaction mixture from **6**

126 mg of the product mixture (**3a.dppp** + **6**) and 10 mg of Pd/C (10%) catalyst were added to 25 mL of toluene. A similar procedure was used as described above in **4b** for the hydrogenation reaction. The residue was filtered and purified from a CH_2Cl_2 /hexane mixture (1:2 v/v); Yield 62%; ^1H NMR: δ 7.04–7.86 (m, 20H, Ph); 2.29–2.59 (m, 6H, P– CH_2); 0.51–1.93 (m, 20H, – CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 3.49 and 3.53 ($J_{\text{Pt-P}} = 1597$ Hz).

4.10. RCM reaction of **2a(dppp)** in the presence of 1,7-octadiene

2a(dppp) (214 mg, 0.287 mmol), 1,7-octadiene (32 mg, 0.0181 mmol) and Grubbs 1st generation catalyst (ca. half of 12 mg, 5 mol%) were added to 15 mL of dichloromethane. The solution was refluxed at 50 °C. After 5 h, the remaining catalyst was added. After another 6 h, the solvent was removed using a vacuum pump. The residue was purified from a CH_2Cl_2 /hexane mixture (2:5) to give a product **9** as colourless oil. Yield 58% (mixture of products); ^1H NMR: δ 7.16–7.75 (m, 20H, Ph); 5.06–5.56 (m, 4H, =CH); 0.60–2.58 (m, 26H, P– CH_2 and – CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 5.32 (m, $J_{\text{Pt-P}} = 1617$ Hz). MS (FAB, m/z) = 799.6 (M^+ for **9**) and 606.3 [(dppp)Pt $^+$].

4.11. RCM of **2d** in the presence of 1,5-hexadiene

2d (360 mg, 0.434 mmol), 1,5-hexadiene (180 mg, 2.19 mmol) and Grubbs 1st generation catalyst (ca. half of 14 mg, 5 mol%) were added to 30 mL of dichloromethane. The solution was refluxed at 50 °C. After 5 h, the remaining catalyst was added. After another 30 h, the solvent was removed using a vacuum pump. The residue was purified from a CH_2Cl_2 /hexane mixture (2:5) to give a product **11** as a colourless solid. Yield 82%, m.p. 144–176 °C; ^1H NMR: δ 7.05–7.79 (m, 30, Ph); 5.68–5.88 (m, 2H, $\text{CH}_2=\text{CH}$), 5.33–5.48 (m, 4H, =CH), 4.91–5.07 (m, 4H, = CH_2), 0.83–2.49 (m, 12H, – CH_2); $^{31}\text{P}\{^1\text{H}\}$: δ 27.3 (s, $J_{\text{Pt-P}} = 1864$ Hz). MS (FAB, m/z) = 911.5 [M^+ for **11**] and 719.3 [(PPh_3) $_2$ Pt $^+$].

4.12. Carbonylation of **4a(dppp)**

4a (242 mg, 336 mmol) was transferred into a 100 mL round bottom flask and dissolved in dry THF (25 mL). The flask was then closed with a stopper containing a tap, which was in turn equipped with a CO gas filled balloon. The tap was opened allowing the gas to enter the flask while stirring at room temperature for 21 days, during which the progress of the reaction was monitored by IR spectroscopy. After 21 days the solvent was removed from the now pale pink solution to give a light red oil. The oil was recrystallized from benzene (15 mL) to yield colourless crystals of the product **12**. Yield 77%; m.p. 123–125 °C; ^1H NMR (300 MHz, C_6D_6): δ 6.93–7–75 (m, 20H Ph); 2.03–2.27 (m, 4H P– CH_2); 0.99–1.90 (m, 18H CH_2); ^{13}C NMR (100 MHz, C_6D_6): δ 203.68 (s, 2C); 133.56–133.81 (m, 12C); 129.65 (s, 8C); 127.68 (s, 4C); 32.47 (s, 2C); 30.02 (s, 2C); 29.36 (s, 2C); 27.25 (s, 2C); 22.72 (s, 2C); 20.82 (s, 1C); ^{31}P NMR (121 MHz, C_6D_6): δ 45.43 (s), $J(^{195}\text{Pt-P}) = 2322.13$ Hz; Elemental analysis calculated for $\text{C}_{37}\text{H}_{42}\text{O}_2\text{P}_2\text{Pt}$: C, 57.29; H, 5.46; Found: C, 57.38; H, 5.64; $\nu_{\text{max}}/\text{cm}^{-1}$ (DCM): 1606, m, 1673, s (C=O), LRMS (FAB) $\text{C}_{37}\text{H}_{42}\text{O}_2\text{P}_2\text{Pt}$: m/z = [775.1] $^+$

4.13. Preparation of compounds **14** and **15**

4a (292 mg, 0.406 mmol) was transferred into a 100 mL round bottom flask and dissolved in dry toluene (30 mL). Elemental sulfur (S_8) (25 mg, 0.812 mmol) was added to the solution and it was stirred at room temperature for 21 days, during which the solution had turned from colourless to orange–yellow. The solvent was removed by rotary evaporation to give a semi-solid crude product, which was passed through an alumina column eluting with a 50:50 mixture of dichloromethane and hexane. A light yellow band was collected and after removal of the volatiles a yellow solid was obtained. This yellow solid was found to contain a mixture of products **14** and **15** and attempts to separate these products were unsuccessful. Yield (110 mg); m.p. 112–121 °C (mixture); ^{31}P NMR: (121 MHz, CDCl_3): δ –3.23 (s), $J(^{195}\text{Pt-P}) = 2688.59$ Hz; LRMS (FAB) $\text{C}_{35}\text{H}_{42}\text{S}_2\text{P}_2\text{Pt}$: m/z = [783.19] $^+$. $\text{C}_{27}\text{H}_{26}\text{S}_4\text{P}_2\text{Pt}$: m/z = [767.11] $^+$.

4.14. Oxidative addition of **4a.dppp** with methyl iodide

3 mL of methyl iodide was added to **4a.dppp** (156 mg, 0.217 mmol). The mixture was stirred for 72 h at room temperature. After removing all the volatiles under reduced pressure, the obtained colourless product was heated in an oil bath at 175 °C for 8 h. The pyrolysis products were found to be [(dppp)PtMeI], [(dppp)PtI $_2$] and 1-nonenone as major species. The other minor products were 1,7-diiodooctane and iodooctane. The organic products were analyzed by GC-MS and the complexes [(dppp)PtMeI] and [(dppp)PtI $_2$] were identified by NMR spectroscopy [40].

4.15. UV-irradiation studies

Irradiations were carried out with a Englehard Hanovia Lamp (125 W) at a distance of 16 cm from the reaction vessel. **4a.dppp** (24 mg, 0.033 mmol) or **4b.dppe** (28 mg, 0.04 mmol) was transferred to a J. Young NMR tube and toluene- d^8 (0.9 mL) was added. The resulting solution was subjected to three freeze–thaw cycles, and then allowed to warm to room temperature. The colourless solution was then irradiated for 9 h.

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