Platinacycloalkane complexes containing [P,N] bidentate ligands: synthesis and decomposition studies†

Tebello Mahamo,a,c John R. Moss,†a Selwyn F. Mapolie,b Gregory S. Smith,*a J. Chris Slootwegc and Koop Lammertsmac

A new series of platinacyclopentanes (2a–2f) and platinacycloheptanes (3a–3f) of the type [Pt(N^P)(CH2)n] (n = 4, 6) were obtained by the reaction of [Pt(COD)(CH2)n] with the appropriate imino-phosphine ligand (1a–1f). These complexes were characterised using a variety of spectroscopic and analytical techniques. X-ray structure analysis of complex 2a revealed a slightly distorted square planar geometry around platinum as a consequence of the ring strain imposed by the [P,N] chelate ring formed and the metallocycloalkane. Thermal decomposition analyses of the platinacycloalkanes revealed that the platinacyclopentanes are markedly stable, with the decomposition reaction requiring temperatures higher than 100 °C to occur. The major products obtained from the thermal decomposition reactions were 1-butene (for platinacyclopentanes) and 1-hexene (for platinacycloheptanes).

In these systems, the metallacyclic mechanism has been favoured over the Cossee–Arlman mechanism used to explain the product distribution observed for late transition metal catalysts such as those based on nickel and palladium. However, a Cossee-type mechanism offers no reasonable explanation for C6 or C8 α-olefin selectivity. Production of higher linear α-olefins (up to C10) has also been proposed to proceed via an extended metallacycloalkane mechanism.23 The preparation of tantalum and titanium metallacycles by the reaction of precursor complexes with ethylene and other simple olefins reported by Schrock30 and Whitesides31,32 ultimately paved the way for the construction of a catalytic process for ethylene dimerization and oligomerization. The nature of supporting ligands in these complexes plays an important role in the stability, reactivity and catalytic activity.33,34 For instance, palladium complexes with phosphine ligands have been successfully applied in ethylene oligomerization and polymerization but complexes with N-heterocyclic carbene ligands (NHC’s) have not found such widespread use.35–37 This is likely due to the propensity of metal alkyl complexes of NHC’s to decompose via alkyl-imidazolium reductive elimination.33

The study of metallacyclopentane complexes containing platinum,38–40 palladium41 and nickel42 has been reported. Decomposition studies of a range of platinacycloalkanes by Whitesides and co-workers revealed that the major products in each case are α-olefins. The reaction is believed to occur via β-hydride elimination, to generate a metal-hydride species, followed by reductive elimination (Scheme 1).29 Because the

Introduction

Heterocycles containing a transition metal are an important class of compounds, which have been studied as either catalysts1–3 or key intermediates in catalytic transformations of unsaturated molecules such as olefins4 and acetylenes.5,6 Metallacyclobutanes, for example, are key intermediates in olefin metathesis reactions9,10 while the good selectivity for α-olefins such as 1-hexene and 1-octene displayed by ethylene oligomerization catalysts based on chromium complexes has been attributed to the involvement of metallacyclopentanes, -heptanes and -nonanes as key catalytic intermediates.11–28 As such, metallacycles have achieved a trifecta in terms of selective α-olefin production; all three of the highest value co-monomers (i.e. 1-butene, 1-hexene, and 1-octene) can be made selectively through this route. For these reasons, metallacycles have been proposed as significant intermediates in the trimerisation and tetramerisation of ethylene.29

††Deceased.
Results and discussion

Preparation of platinacyclopentanes 2a–2f and platinacycloheptanes 3a–3f

The reaction of [Pt(COD)Cl2] with the appropriate di-Grignard reagent in THF gave platinacycloalkanes of the type [Pt(COD)-(CH2)n] with n = 4, 6. The iminophosphine-containing platinacycloalkanes were prepared by displacement of 1,5-cyclooctadiene from [Pt(COD)(C6H8)] and [Pt(COD)(C8H12)] with the appropriate iminophosphine ligands to give complexes 2a–2f and 3a–3f, respectively. The products were obtained as yellow or orange solids (2a–2f) or orange oils (3a–3f).

1H NMR spectra of the complexes show an upfield shift of the imine proton signals from 8.98–9.05 ppm in the free ligands to 8.13–8.43 ppm in the metal complexes. The observed upfield shift is attributed to back-bonding from the platinum centre to the imine bond. These signals appear as singlets, in contrast to the doublets observed for free ligands, due to the conformational change of the ligand in order to facilitate coordination.

Similar to other iminophosphine complexes, a downfield shift is observed from 4.64–4.87 ppm for the free ligands to 5.25–5.77 ppm for the platinacyclopentanes for the methylene protons (N–C2R). This is due to the deshielding that occurs upon coordination of the imine nitrogen to platinum. The methyl protons of the platinacycles also show platinum satellites with a HPt = 15.1–17.0 Hz. The alkyl protons of the metallocycles appear as multiplets in the region 0.72–1.91 ppm with the CH3 protons adjacent to the metal centre being assigned to the most upfield resonance.

In the 13C NMR spectra, resonances for the imine carbons shift slightly downfield from between 160.3–161.4 ppm in the free ligands to between 161.6–163.4 ppm in the platinacyclopentanes. These signals appear as doublets, although the magnitude of the coupling constants is smaller compared to those of the free ligands with JHPt = 15.1–17.0 Hz. The alkyl protons of the metallocycles appear as multiplets in the region 0.72–1.91 ppm with the CH3 protons adjacent to the metal centre being assigned to the most upfield resonance.

In the 1H NMR spectra, signals of the imine protons appear as singlets in the range of JHPt = 31.8–37.1 Hz, further support coordination of the imine moiety of the ligands to the metal centre.

Metal-hydride species are short-lived, it is expected that little or no isomerisation of the α-olefin product should occur. Whitesides' studies also showed that metallocyclopentanes are markedly more thermally stable than analogous metallacycloheptanes. This may be a consequence of the constrained geometry of the metallocyclopentanes, which can hinder β-hydride elimination. Similar observations have been made with chromacyclopentanes and chromacycloheptanes. The precise mechanism for the decomposition reaction of metallocyclopentanes has not been conclusively determined. Studies on platinum complexes indicate that although the elimination of a metal hydride is an important step in the thermal decomposition of dialkylplatinum(II) complexes and larger platinacycles, other mechanisms such as 3,5-hydride elimination and intermolecular hydrogen transfer might also be involved. Theoretical studies with titanium complexes suggest that despite the challenges presented by constrained geometry of metallocyclopentanes, the stepwise β-hydride elimination/reductive elimination process is still the most likely decomposition pathway for these complexes.

Due to increased stability of metallocycloalkanes relative to other metallocycloalkanes, their study can offer valuable insights into the nature of transient species in catalytic processes such as ethylene oligomerization, that are proposed to involve metallocycloalkanes as key intermediates. We previously reported a series of iminophosphine ligands 1a–1f (Fig. 1), as well as their palladium dichloride and palladium methyl chloride complexes and the activity of these complexes as pre-catalysts in ethylene oligomerization reactions and Suzuki-Miyaura coupling reactions. With the intent of gaining access to further examples of platinacycloalkanes, their study can offer insights into the nature of transient species in catalytic processes such as ethylene oligomerization, that are proposed to involve metallocycloalkanes as key intermediates. We previously reported a series of iminophosphine ligands 1a–1f (Fig. 1), as well as their palladium dichloride and palladium methyl chloride complexes and the activity of these complexes as pre-catalysts in ethylene oligomerization reactions and Suzuki-Miyaura coupling reactions.

Fig. 1 General structure of iminophosphine ligands 1a–1f.
and C₄ for the platinacycloheptanes 3a–3f. These atoms appear as doublets at 14.9–17.3 ppm with a $^2J_{CP}$ coupling constant between 2.6–3.3 Hz. In contrast, the carbons coordinated trans to the phosphine group (Cₐ) is the most deshielded, appearing as doublets at 32.7–36.1 ppm with coupling constants $^2J_{CP}$ between 4.0–6.2 Hz, almost double the values observed for the carbons cis to the phosphine group.

$^{31}$P NMR spectra of the platinacycloalkanes reveal a downfield shift of the phosphorus resonance from ca. −14 ppm in the free ligands to 25.0–27.1 ppm in the complexes. These signals are accompanied by platinum satellites with coupling constants $^1J_{PPt} = 1843–2066$ Hz, similar to other platinacycloalkane phosphine complexes. In the IR spectra of the platinacycles, the imine stretching band is observed in the region 1630–1635 cm$^{-1}$, a slightly lower frequency compared to the free ligands where the imine absorption band is seen between 1634–1636 cm$^{-1}$. This confirms coordination of the imine nitrogen to platinum. This is in agreement with data reported for other transition metal iminophosphine complexes.

X-ray structural analysis

Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a concentrated solution of complex 2a in DCM. Selected bond lengths and angles for complex 2a are presented in Table 1 and crystal data for the complex is listed in Table 5. The X-ray crystal structure of 2a confirms the bidentate coordination of the iminophosphine ligand to the metal centre. Due to the ring strain imposed by both the chelate ring and N(1)–Pt(1)–P(1)–C(18)–C(13)–C(12) and the metallacycle Pt(1)–C(1)–C(2)–C(3)–C(4), the complex displays a distorted square planar geometry around the metal centre. The iminophosphine ligand forms a puckered chelate ring with platinum, with the benzyl moiety lying above the Pt(P$^*N$(C₄H₈)) plane and a torsion angle Pt(1)–P(1)–C(18)–C(13) being 33.6(4)°. The bite angles, N(1)–Pt(1)–P(1), C(4)–Pt(1)–C(1), C(4)–Pt(1)–P(1) and N(1)–Pt(1)–C(1), around platinum deviate from the expected 90° angles and this can be attributed to the ring strain imposed by the two ring systems around the metal centre (Fig. 2).

A comparison of key bond lengths between complex 2a and other platinacyclic and bisalkenyl complexes with mono- and bidentate phosphine ligands reveals important differences between these complexes and the iminophosphine complex, 2a. Due to the different trans effects of phosphine and imine donor groups, the bond lengths Pt(1)–C(1) and Pt(1)–C(4) are different. As expected, Pt(1)–C(1), which is trans to the

<table>
<thead>
<tr>
<th>Complex</th>
<th>n</th>
<th>R</th>
<th>Complex</th>
<th>n</th>
<th>R</th>
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<tbody>
<tr>
<td>2a</td>
<td>4</td>
<td>Phenyl</td>
<td>3a</td>
<td>6</td>
<td>Phenyl</td>
</tr>
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<td>4</td>
<td>4-Tolyl</td>
<td>3b</td>
<td>6</td>
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<td>2-Furfuryl</td>
<td>3c</td>
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<td>4</td>
<td>2-Thiophenyl</td>
<td>3d</td>
<td>6</td>
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<td>6</td>
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<tr>
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<td>4</td>
<td>Mesityl</td>
<td>3f</td>
<td>6</td>
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Scheme 2 Synthesis of platinacyclopentanes 2a–2f and platinacycloheptanes 3a–3f.

Table 1 Selected bond ligands (Å) and angles (°) for 2a

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Angles</th>
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<tr>
<td>Pt(1)–C(1)</td>
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<tr>
<td>Pt(1)–C(4)</td>
<td>2.052(5)</td>
</tr>
<tr>
<td>Pt(1)–N(1)</td>
<td>2.118(4)</td>
</tr>
<tr>
<td>Pt(1)–P(1)</td>
<td>2.2440(12)</td>
</tr>
<tr>
<td>Pt(1)–C(18)</td>
<td>1.831(5)</td>
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<tr>
<td>C(12)–C(13)</td>
<td>1.469(7)</td>
</tr>
<tr>
<td>N(1)–C(12)</td>
<td>1.281(6)</td>
</tr>
<tr>
<td>N(1)–C(5)</td>
<td>1.487(6)</td>
</tr>
</tbody>
</table>

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phosphine group is slightly longer than Pt(1)–C(4), which is trans to the imine moiety. Pt(1)–C(1) and Pt(1)–C(4) are 2.148(5) Å and 2.052(5) Å, respectively.

Thermal decomposition studies

Effect of temperature on product distribution of 2a. Prior to investigating the thermal decomposition products for all the iminophosphine platinacycloalkanes (2a–2f and 3a–3f), the optimal conditions were determined using complex 2a. The effect of temperature and time as well as the reaction kinetics were studied using complex 2a. The effect of temperature on the decomposition of 2a was studied by monitoring the change in the $^{31}$P NMR spectra of 2a throughout the decomposition process at 100 °C, 120 °C, 140 °C and 170 °C. The results from this study were used to determine the amount of time it takes for complete decomposition of 2a at each temperature. In addition, the NMR study was used to shed light on the nature of the platinum-containing fragment after decomposition. Thus far, this fragment has been referred to as the “Pt(0) species” in the literature.

Fig. 3 shows $^{31}$P NMR spectra of 2a over time at 140 °C. At all temperatures, the spectra show a gradual decrease in the intensity of the resonance at 25.0 ppm ($J_{PPt} = 1917$ Hz). This decrease is accompanied by appearance and gradual increase of a new signal at 26.1 ppm ($J_{PPt} = 2198$ Hz). This result reveals that only one phosphorus-containing compound is formed upon decomposition of 2a and the new phosphorus-containing species is also a platinum complex, as evidenced by the platinum satellites accompanying the new signal. Attempts to isolate this complex for full characterization were unsuccessful due to its instability.

After determining the time required for complete decomposition of 2a at each temperature, the reactions were scaled up (1.5 cm$^3$ solutions) to determine the hydrocarbon product distribution using GC-MS analysis. The results (Table 2) show that the temperature at which the decomposition reaction is carried out has a significant influence on the hydrocarbon distribution. As expected, the rate of reaction is significantly higher at elevated temperatures but isomerisation and hydrogenation to internal olefins and n-alkanes is also prevalent. Decreasing the temperature from 170 °C to 120 °C resulted in an increase in the relative amount of 1-butene from 67% to 91%. At 100 °C, however, no decomposition occurs, reflecting the stability of platinacyclopentanes.

Under solvent free conditions (entry 5, Table 2) and in toluene (entry 4, Table 2) the product distribution obtained is similar. These results indicate that the solvent could act as a hydrogen donor via C–H activation in the formation of saturated hydrocarbons from the decomposition reaction. Formation of n-butane from the decomposition of 2a under...
solvent-free conditions, however, indicates that solvent is not the only available source of hydrogen atoms in this process. It is also possible that the hydrogen atoms could come from the C-H activation of coordinated ligands as has been proposed by Whitesides,43 or platinum hydride species that may form as intermediates or products in the reaction.

**Effect of time on product distribution for 2a.** A time dependence study in which the relative amounts of hydrocarbon products obtained from the decomposition of 2a were compared over time was carried out. The reactions were carried out at 170 °C for two reasons: (1) The rate of decomposition is higher at higher temperatures, therefore appearance of products should be fast. (2) Effect of time on product isomerisation and/or hydrogenation should be detected early. The reaction was followed by analysis of the amounts of 1-butene, 2-butenes and n-butane using GC-MS. The results (Fig. 4) show that the absolute amount of 1-butene obtained decreased. With prolonged heating, the relative amount of 1-butene decreased from 90% after 1 h to 67% after 6 h, and the relative amounts of 2-butenes and n-butane increased. These results further confirm that the primary products in the thermal decomposition of platinacycloalkanes are α-olefins as has been previously reported. Isomerisation and hydrogenation to internal olefins and saturated hydrocarbons are secondary processes. After complete decomposition, the major product was found to be 1-butene, indicating that these secondary reactions occur at a slower rate than the production of 1-butene.

**Kinetic studies of thermal decomposition of 2a and 3a.** Reaction kinetics is an important component in investigating reaction mechanisms. A number of different analytical techniques can be employed to investigate the kinetic behaviour of a reaction. Spectroscopic tools are particularly useful because, in addition to reaction rates, they can provide structural information about the reaction at a molecular level.56

The kinetics of thermal decomposition of complexes 2a and 3a were followed using two procedures. In the first procedure, samples were taken periodically, cooled in liquid nitrogen and GC-MS analysis of the volatiles in solution was performed. Results were obtained by following the total concentration of the hydrocarbon products relative to that of the internal standard (n-decane). In the second procedure, appearance of the new peak at ~26 ppm and the disappearance of the original peak at ~25 ppm in the 31P NMR spectra of the reactions were monitored. The results obtained using these two methods were indistinguishable within experimental error. Kinetic data were collected for the decomposition of 2a and 3a at 140 °C and at 170 °C.

The decomposition reactions were found to follow first-order kinetics for approximately the first 30% to one half-life of the decomposition reaction for both complexes. Beyond this point, the reaction kinetics showed deviations from first order behaviour, indicating increasing involvement of products in the reaction mechanism, most likely the platinum-containing fragment as well as the occurrence of secondary reactions such as isomerisation and hydrogenation. The analysis presented herein is based on the results obtained over the first half life of the decomposition reaction. Rate constants derived from the initial linear regions of the decomposition curves were calculated according to Eqn (1) and are presented in Table 3.

\[
\ln(a_t/a_0) = -kt
\]

where \( a = [\text{Complex } 2a] \) or \( [\text{Complex } 3a] \).

**Table 3** Rate constants for the thermal decomposition of 2a and 3a in toluene

<table>
<thead>
<tr>
<th>Complex</th>
<th>Rate constant (s^{-1})</th>
<th>Rate (M^{-1} s^{-1})</th>
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<tbody>
<tr>
<td></td>
<td>140 °C</td>
<td>170 °C</td>
</tr>
<tr>
<td>2a</td>
<td>2.90 × 10^{-5}</td>
<td>1.50 × 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>(0.104 h^{-1})</td>
<td>(0.525 h^{-1})</td>
</tr>
<tr>
<td>3a</td>
<td>9.00 × 10^{-5}</td>
<td>4.37 × 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>(0.324 h^{-1})</td>
<td>(1.58 h^{-1})</td>
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</tbody>
</table>

\( ^a \) Rate constants in h^{-1} in parenthesis. \( ^b \) Reaction rates in M^{-1} h^{-1} in parenthesis.
Fig. 5 shows the kinetic data plots for the decomposition reaction of $2a$ at 140 °C and 170 °C and Fig. 6 shows data plots for the thermal decomposition of $3a$. As expected, the rate of decomposition at 170 °C is greater than that at 140 °C for both complexes. $^{31}P$ NMR data shows that at 140 °C complete decomposition takes 29 h for $2a$ and 10 h for $3a$. At 170 °C complete decomposition only takes 7 h for $2a$ and 2.5 h for $3a$. The rate constants for decomposition of $2a$ and $3a$ at 140 °C are 0.104 h$^{-1}$ and 0.324 h$^{-1}$, respectively. At 170 °C the rate constant for the decomposition of $2a$ is 0.525 h$^{-1}$, while the rate constant for the decomposition of $3a$ is one order of magnitude higher (1.58 h$^{-1}$). The decomposition of complex $3a$ (a seven-membered ring) was faster than that of $2a$ (a five-membered ring) at both temperatures under investigation.$^{39}$

Thermal decomposition of complexes $2b$–$2f$ and $3a$–$3f$. Decomposition of the rest of the platinacycloalkane complexes in this study was carried out under the following conditions: 140 °C, toluene, 27 h. Results of these reaction are presented in Table 4. These conditions were selected from the temperature study using complex $2a$ and carrying out the reaction in solution does not significantly effect selectively for 1-butene. Finally, doing the reaction under the same conditions would allow for direct comparison of results between complexes.

The thermal decomposition of platinacyclopentanes $2a$–$2f$ (entries 1–6, Table 4) displays similar hydrocarbon product profiles. The nature of the pendant R-group on the imine moiety of the ligand does not seem to have a significant impact on the outcome of the decomposition reaction. A similar observation is made with the platinacycloheptanes $3a$–$3f$. A more noticeable effect is that of the size of the metallacyclic ring. It appears that the larger the ring size, the greater the propensity for isomerisation and hydrogenation. This can be attributed to the fact that, under similar reaction conditions, larger metallacycles will decompose faster than their smaller ring counterparts. This would therefore allow for more secondary reactions to occur for the larger metallacycloalkanes.
Conclusions

A new series of iminophosphine platinacyclopentanes and platinacycloheptanes have been synthesised. Characterisation using several spectroscopic techniques confirmed that the iminophosphine ligands act as [P,N] bidentate donors to platinum. This was further substantiated by the X-ray structure analysis of complex 2a which showed a slightly distorted square planar geometry around platinum as a consequence of the ring strain imposed by the [P,N] bis-chelate ring formed and the metalloycloalkane. Thermal decomposition behaviour of the platinacyclopentanes was studied at different temperatures and under both solvent free conditions and in solution. The results obtained show that: (1) Platinacyclopentanes are markedly more stable than analogous platinacycloheptanes. (2) The platinacycloalkanes decompose to give \( \alpha \)-olefins as the primary, and major products, indicating that formation of a metal hydride intermediate is an important step in the reaction. (3) Reaction temperature and reaction time have a significant effect on the organic product distribution. (4) The decomposition reaction follows first order kinetics over the first half life of the decomposition process, with deviation from first order behaviour thereafter.

Experimental

Materials and equipment

All reactions were carried out under a nitrogen or argon atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques unless otherwise stated. Solvents were dried and purified by distillation under argon using a suitable drying agent and stored under vacuum in a Teflon-valve storage vessel. All commercially available chemicals were purchased from either Sigma-Aldrich or Merck and used without further purification. \( \text{K}_2\text{PtCl}_4 \) and \( \text{PdCl}_2 \) were obtained from Johnson Matthey. The ligands \( \text{1a-1f,47,48 [Pt(COD)(C}_6\text{H}_{12})]_{38,43} \), \( \text{2-Diphenylphosphinobenzaldehyde,57,58 [Pt(COD)(C}_6\text{H}_{12})]_{38,43} \) 2-Diphenylphosphinobenzaldehyde, 57,58 \( \text{Pd(COD)Cl}_2,59 \text{ Pd(COD)MeCl}_2,60 \text{ Pt(COD)Cl}_2 \) were all prepared using literature procedures.

NMR spectra were recorded on a Varian Mercury-300 MHz \(^1\text{H}: 300 \text{ MHz}; \text{13C}: 75.5 \text{ MHz}; \text{31P}: 121 \text{ MHz}\) or Varian Unity-400 MHz \(^1\text{H}: 400 \text{ MHz}; \text{13C}: 100.6 \text{ MHz}; \text{31P}: 161.9 \text{ MHz}\) spectrometer. \(^1\text{H} \text{NMR spectra were referenced internally using the residual protons in deuterated solvents (CDCl}_3; \delta \text{ 7.27; DMSO: } \delta \text{ 2.50 and values reported relative to the internal standard tetramethysilane (} \delta \text{ 0.00). 13C} \text{ NMR spectra were referenced internally to the deuterated solvent resonance (CDCl}_3; \delta \text{ 77.0; DMSO: } \delta \text{ 39.4 and the values are reported relative to tetramethysilane (} \delta \text{ 0.00). All chemical shifts are quoted in } \delta \text{ (ppm) and coupling constants, } J \text{, in Hertz (Hz).}}

Melting points were determined on a Reichert-Jung Thermovar hotstage microscope and are uncorrected. Infrared spectra were recorded on a Thermo Nicolet FT-IR instrument in the 4000–300 cm\(^{-1}\) range using KBr discs or \( \text{CH}_2\text{Cl}_2 \) solutions. Microanalyses were determined using a Fisons EA 1108 CHNO-S instrument. Mass spectra were recorded on a Waters API Quatro Micro triple quadrupole mass spectrometer (ESI,
General procedure for the preparation of complexes 2a–2f and 3a–3f

The metallacycloalkanes were prepared from the reaction of [Pt(COD)]Cl₂ with appropriate di-Grignard reagents to give [Pt(COD)(CH₂)₄Ar-].

Preparation of [Pt(C₂₈H₂₂NPNP)(C₅H₄)] (2a). 2a was prepared by the reaction of [Pt(COD)]Cl₂ (0.18 g, 0.50 mmol) and benzyl-(2-diphenylphosphanyl-benzylidene)-amine (1a) (0.19 g, 0.50 mmol), and the product was obtained as an orange solid (0.26 g, 83%). X-ray quality crystals were obtained from slow diffusion of hexane into a concentrated solution of 2a in dichloromethane. M.p. 164–167 °C (decomp). IR (KBr): 1631 cm⁻¹ (νC=N, imine). ¹H NMR (CDCl₃): 0.79–0.84 (m, 4H; H₁A + H₂A), 1.76–1.79 (m, 4H; H₃A + H₄A), 5.50 (s, 2H, ³JHp-Pt = 16.4 Hz; H₅A), 6.88 (d, 2H, ³JHH = 7.8 Hz; Ar-H), 7.00 (d, 2H, ³JHH = 7.1 Hz; Ar-H), 7.11–7.35 (m, 15H; Ar-H), 8.18 (s, 1H, ³JTHP = 35.1 Hz; H₆A). ¹³C NMR (CDCl₃): 15.8 (d, 2JCP = 2.9 Hz; C₃A), 28.0 (s; C₄A), 29.7 (s; C₅A), 33.9 (d; ³JCP = 5.7 Hz; C₆A), 68.8 (s; C₁A), 127.3 (s; Ar-C₃A), 128.1 (d, ³JCP = 9.0 Hz; Ar-C₄A), 128.4 (s; Ar-C₅A), 128.7 (s; Ar-C₆A), 129.4 (s; Ar-C₇A), 129.8 (s; Ar-C₈A), 130.3 (s; Ar-C₉A), 131.5 (s; Ar-C₁₀A), 131.8 (s; Ar-C₁₁A), 131.9 (d, ³JCP = 4.9 Hz; Ar-C₁₂A), 133.6 (s; Ar-C₁₃A), 133.9 (d, ³JCP = 12.6 Hz; Ar-C₁₄A), 135.3 (d, ³JCP = 8.3 Hz; Ar-C₁₅A), 137.7 (s; Ar-C₁₆A), 138.9 (d, ³JCP = 16.7 Hz; Ar-C₁₇A), 162.0 (d, ³JCP = 5.5 Hz; C₂A). ³¹P NMR (CDCl₃): 25.0 (s, JPPt = 1894 Hz). ESI-MS: m/z 631.18 [M + H⁺], 575.12 [M - C₄H₄⁺]. Anal. Calc. For C₅₇H₄₄N₂P₂Pt: C 73.14; H 5.14; N 2.12; P 2.12. Found: C, 56.91; H, 4.83; N, 2.12.

Preparation of [Pt(C₂₈H₂₂NPNP)(C₅H₄)] (2b). 2b was prepared by the reaction of [Pt(COD)]Cl₂ (0.18 g, 0.50 mmol) and (2-diphenylphosphanyl-benzylidene)-(4-methyl-benzyl)-amine (1b) (0.20 g, 0.50 mmol), and the product was obtained as an orange solid (0.24 g, 76%). M.p. 142–143 °C (decomp). IR (KBr): 1634 cm⁻¹ (νC=N, imine). ¹H NMR (CDCl₃): 0.87–1.01 (m, 4H; H₁A + H₂A), 1.74–1.79 (m, 4H; H₃A + H₄A), 2.31 (s, 3H; H₅A), 5.25 (s, 2H, ³JHH = 15.8 Hz; H₆A), 6.99 (d, 2H, ³JHH = 7.1 Hz; Ar-H), 7.05 (d, 2H, ³JHH = 6.8 Hz; Ar-H), 7.17–7.34 (m, 14H; Ar-H), 8.17 (s, 1H, ³JTHP = 34.8 Hz; H₆B). ¹³C NMR (CDCl₃): 16.1 (d, ³JCP = 3.1 Hz; C₃B), 22.1 (s; C₄B), 28.0 (s; C₅B), 30.3 (s; C₆B), 33.1 (d; ³JCP = 6.0 Hz; C₇B), 67.9 (s; C₈B), 125.5 (s; Ar-C₂B), 127.2 (s; Ar-C₃B), 128.0 (d, ³JCP = 8.8 Hz; Ar-C₄B), 128.5 (s; Ar-C₅B), 128.9 (d, ³JCP = 9.3 Hz; Ar-C₆B), 129.4 (s; Ar-C₇B), 129.6 (s; Ar-C₈B), 129.7 (d, ³JCP = 1.7 Hz; Ar-C₉B), 130.3 (d, ³JCP = 1.2 Hz; Ar-C₁₀B), 131.5 (s; Ar-C₁₁B), 131.8 (s; Ar-C₁₂B), 131.9 (d, ³JCP = 5.1 Hz; Ar-C₁₃B), 132.2 (d, ³JCP = 2.6 Hz; Ar-C₁₄B), 133.6 (s; ³JCP = 5.0 Hz; Ar-C₁₅B), 134.1 (d, ³JCP = 7.9 Hz; Ar-C₁₆B), 135.0 (d, ³JCP = 11.9 Hz; Ar-C₁₇B), 138.1 (s; Ar-C₁₈B), 140.1 (d, ³JCP = 16.9 Hz; Ar-C₁₉B), 162.2 (d, ³JCP = 5.1 Hz; C₂B). ³¹P NMR (CDCl₃): 26.2 (s; JPPt = 1920 Hz). ESI-MS: m/z 645.20 [M + H⁺], 589.44 [M - C₄H₄⁺]. Anal. Calc. For C₅₃H₄₈N₂P₂Pt: 52.82; H, 4.43; N, 2.20; P, 5.04. Found: C, 53.01; H, 4.31; N, 2.17; S, 5.00.
Preparation of [Pt(C25H24NP)(C6H12)] (2c). 2c was prepared by reacting [Pt(COD)(C6H4)] (0.13 g, 0.36 mmol) and (2-diphenylphosphanyl-benzylidene)-pyridin-3-ylmethyl-amine (1e) (0.14 g, 0.36 mmol). The product was obtained as an orange solid (0.17 g, 76%). M.p. 139–142 °C (decom. IR (KBr): 1630 cm⁻¹ (νC=Ν, imine). ¹H NMR (CDCl₃): 0.89–0.93 (m, 4H; H₆ + H₇), 1.41–1.46 (m, 4H; H₈ + H₉), 5.69 (s, 2H, J₂CP = 16.0 Hz, H₁₂), 7.12 (1H, d, JHH = 7.3 Hz; Ar-H), 7.18–7.21 (5H, m; Ar-H), 7.39–7.41 (4H, m; Ar-H), 7.51–7.53 (2H, m; Ar-H), 7.60–7.62 (1H, m; Ar-H), 7.65–7.66 (1H, m; H₃), 8.03 (1H, td, JHH = 2.0 Hz; 7.4 Hz; Ar-H), 8.30 (3H, s; H₂; 8.53 (1H, dd; JHH = 2.1 Hz; H₈), 8.43 (1H, s; JHH = 35.7 Hz; H₇), 8.56 (1H, dd; JHH = 1.4 Hz; 5.0 Hz; H₆). ¹³C NMR (CDCl₃): 16.0 (J₂CP = 2.8 Hz; C₂), 26.3 (s; C₁), 28.5 (s; C₂), 34.1 (d; J₂CP = 5.7 Hz; C₃a), 64.4 (s; C₄), 125.9 (s; C₅), 126.5 (s; C₆), 129.1 (d; J₂CP = 12.3 Hz; Ar-C), 130.4 (d; J₂CP = 1.6 Hz; Ar-C), 131.6 (d; J₂CP = 1.6 Hz; Ar-C), 132.0 (d; J₂CP = 6.7 Hz; Ar-C), 132.8 (s; C₇), 133.1 (d; J₂CP = 12.4 Hz; Ar-C), 134.0 (s; C₈), 134.1 (s; C₉), 134.3 (s; C₁₀), 136.9 (d; J₂CP = 17.4 Hz; Ar-C), 137.2 (s; C₁₁), 139.4 (s; Ar-C), 149.7 (s; C₁₂), 151.0 (s; C₁₃), 162.1 (d; J₂CP = 5.3 Hz; C₁₄). ³¹P NMR (CDCl₃): 25.7 (s; JFP = 1886). ESI-MS: m/z 659.34 [M + H]⁺, 575.20 [M – C₄H₈]⁺.

Preparation of [Pt(C₃₂H₂₈NP)(C₆H₁₂)] (3b). 3b was prepared by the reaction of [Pt(COD)(C₆H₁₂)] (0.25 g, 0.64 mmol) with (2-diphenylphosphanyl-benzylidene)-(4-methyl-benzyl)-amine (1b) (0.25 g, 0.63 mmol). The product was obtained as a brown oil (0.29 g, 68%). IR (KBr): 1635 cm⁻¹ (νC=Ν, imine). ¹H NMR (CDCl₃): 0.76–0.89 (m, 4H; H₄; H₅; H₆), 0.95–1.37 (m, 8H; H₇; H₈; H₉), 2.30 (3s; H₃), 5.45 (2s; JFF = 16.0 Hz; H₂), 7.01 (dd, 1H; JFF = 1.2 Hz; 8.3 Hz; Ar-H), 7.11 (1H; JFF = 1.7 Hz; Ar-H), 7.14 (2d; 2H; JFF = 1.4 Hz; 7.2 Hz; Ar-H), 7.18 (2m; 1H; Ar-H), 7.30–7.44 (m, 12H; Ar-H), 8.13 (s; 1H, JFF = 33.0 Hz; Ar-H). ¹³C NMR (CDCl₃): 17.3 (d; J₂CP = 3.1 Hz; C₇), 21.7 (s; C₈), 25.3 (s; C₉), 27.2 (s; C₁₀), 31.9 (s; C₁₁), 32.0 (s; C₁₂) 34.7 (d; J₂CP = 6.0 Hz; C₁₃), 64.9 (s; C₁₄), 125.5 (s; Ar-C₁₁), 127.2 (s; Ar-C₁₂), 128.0 (d; J₁CP = 9.3 Hz, Ar-C), 129.4 (s; Ar-C₁₃), 129.6 (s; Ar-C₁₄), 129.7 (d; J₁CP = 1.7 Hz; Ar-C), 130.3 (d; J₁CP = 1.2 Hz; Ar-C), 131.5 (s; Ar-C₁₂), 131.8 (s; Ar-C₁₉), 131.9 (d; J₁CP = 5.1 Hz; Ar-C), 132.2 (d; J₂CP = 2.6 Hz; Ar-C), 133.6 (d; J₁CP = 5.0 Hz; Ar-C), 134.1 (d; J₁CP = 7.9 Hz; Ar-C), 135.0 (d; J₁CP = 11.9 Hz; Ar-C), 138.1 (s; Ar-C₁₃), 140.1 (d; J₂CP = 15.9 Hz; Ar-C), 162.2 (d; J₂CP = 5.1 Hz; C₁₃). ³¹P NMR (CDCl₃): 25.9 (s; JFP = 1954 Hz). ESI-MS: m/z 671.63 [M + H]⁺, 589.50 [M – C₄H₈].

Preparation of [Pt(C₂₅H₂₄NP)(C₆H₁₂)] (3c). 3c was prepared by the reaction of [Pt(COD)(C₆H₁₂)] (0.25 g, 0.64 mmol) with (2-diphenylphosphanyl-benzylidene)-furan-2-ylmethyl-amine (1e) (0.24 g, 0.64 mmol). The product was obtained as a dark-orange oil (0.31 g, 77%). IR (KBr): 1632 cm⁻¹ (νC=Ν, imine). ¹H NMR (CDCl₃): 0.72–0.75 (m, 4H; H₄; H₅; H₆), 1.31–1.39 (m, 8H; H₇; H₈; H₉), 5.77 (2s; 2H, JFF = 15.7 Hz; C₇), 6.29 (2H, JFF = 2.0 Hz; 3.1 Hz; H₈), 6.34 (1H, d; JFF = 3.2 Hz; H₉), 7.06 (1H, dd; JFF = 0.9 Hz; 2.0 Hz; H₁₀), 7.24–7.42 (m, 14H; Ar-H), 8.16 (2s; 2H, JFF = 31.8 Hz; H₁₁). ¹³C NMR (CDCl₃): 22.3 (d; J₂CP = 2.8 Hz; C₇), 24.3 (s; C₈), 24.9 (s; C₉), 31.4 (s; C₁₀), 31.5 (s; C₁₁), 33.7 (d; J₂CP = 4.9 Hz; C₁₂), 63.5 (s; C₁₃), 109.6 (s; C₁₄), 110.3 (s; C₁₅), 127.7 (d; J₂CP = 10.0 Hz; Ar-C), 127.9 (d; J₂CP = 11.6 Hz; Ar-C), 128.8 (d; J₂CP = 5.0 Hz; Ar-C), 129.5 (d; J₂CP = 1.4 Hz; Ar-C), 130.7 (d; J₂CP = 1.8 Hz; Ar-C), 131.1 (s; Ar-C), 131.5 (s; Ar-C), 131.7 (s; Ar-C), 131.9 (d; J₂CP = 5.1 Hz; Ar-C), 132.0 (s; Ar-C), 132.8 (d; J₂CP = 2.4 Hz; Ar-C), 134.0 (d; J₂CP = 12.3 Hz; Ar-C), 134.7 (s; Ar-C), 135.6 (d; J₂CP = 8.1 Hz; Ar-C), 138.3 (d; J₂CP = 17.1 Hz; Ar-C), 143.1 (s; C₁₃), 149.7 (s; C₁₄), 162.6 (d; J₂CP = 5.4 Hz; C₁₅). ³¹P NMR (CDCl₃): 26.4 (s; JFP = 1860 Hz). ESI-MS: m/z 649.69 [M + H]⁺, 565.41 [M – C₄H₈].

Preparation of [Pt(C₂₅H₂₄NP)(C₆H₁₂)] (3d). 3d was prepared by the reaction of [Pt(COD)(C₆H₁₂)] (0.25 g, 0.64 mmol)
X-Ray structural analysis

Single-crystal X-ray diffraction data for 2a was collected on a Bruker Kappa APEX II DUO diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection was carried out at 173(2) K. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT.65,66 The data were scaled and absorption corrections were performed using SADABS.65 The structure was solved by direct methods using SHELXS-9764 and refined by full-matrix least-squares methods based on F² using SHELXL-9764 and using the graphics interface program X-Seed.65,66 The programs X-Seed and POV-Ray67 were both used to prepare molecular graphic images. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically with C-H distances ranging from 0.95 Å to 0.98 Å and refined as riding on their parent atoms, with Uiso(H) = 1.2–1.5Ueq(C). The structure was successfully refined to the R factor 0.0238.

Thermal decomposition reactions

Thermal decomposition reactions were carried out in clean, dry, sealed evacuated vertical Schlenk tubes of 1 cm o.d. and 10 cm lengths. Decomposition was accomplished by immersion of the tube in a stirred oil bath set at the desired temperature. Two procedures were used for the thermal decomposition experiments were carried out under solvent free conditions. For solid complexes, a 20 mg sample was added to the tube and dried under vacuum for at least 3 h before the tube was sealed for thermolysis. For the oils, a 20 mg sample was dissolved in dichloromethane and transferred into the tube. The solvent was removed under vacuum, and the sample was dried for at least 3 h before sealing the tube for thermolysis. The decomposition products were extracted by adding cold toluene (0.5 ml) containing n-decane (20 μl) as the internal standard.

For the thermal decompositions in solution, a 0.05 ml aliquot of 0.02 M solution of each sample in toluene was added to the tube by syringe. The tubes were connected to a vacuum line and degassed using three freeze–thaw cycles and then sealed under vacuum. The tubes were then immersed in a heated oil bath held at the desired constant temperature. After the appropriate reaction time, the reaction was quenched by immersion in liquid nitrogen. For the thermolysis in solution, the decomposition solutions were transferred to a liquid nitrogen-cooled sample vial containing n-decane (20 μl) and the sample was made up to a total volume of 0.5 ml.

Decomposition products were analyzed by GC or GC-MS. Products were identified by retention of comparison times to
those of authentic commercial samples. Yields were determined by response relative to an internal standard (n-decane). Response factors were obtained from authentic samples.

**NMR analysis of thermal decomposition**

A 0.02 M solution of complex 2a in toluene-\(d_6\) was prepared and 0.85 ml aliquots of the solution were transferred to NMR tubes fitted with \(J\) Young valves and degassed using three freeze–thaw cycles. The tubes were sealed under vacuum and allowed to warm to room temperature. The NMR tubes were then transferred to oil baths set at the required temperature for each reaction. At appropriate intervals the reaction was quenched by immersion in liquid nitrogen and \(^{31}\)P NMR spectra were measured.

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