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

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A new series of platinacyclopentanes (**2a–2f**) and platinacycloheptanes (**3a–3f**) of the type [Pt(N^P)$(CH_2)_n$] (n = 4, 6) were obtained by the reaction of [Pt(COD)$(CH_2)_n$] with the appropriate iminophosphine 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).

Introduction

Heterocycles containing a transition metal are an important class of compounds, which have been studied as either catalysts[1–5] or key intermediates in catalytic transformations of unsaturated molecules such as olefins[6] and acetylenes.[7,8] Metallacyclobutanes, for example, are key intermediates in olefin metathesis reactions[9,10] while the good selectivity for high-value 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 volume and 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]

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 C_6 or C_8 α-olefin selectivity. Production of higher linear α-olefins (up to C_{30}) 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 Schrock[30] and Whitesides[31,32] 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* alkylimidazolium reductive elimination.[33]

The study of metallacyclopentane complexes containing platinum,[38–40] palladium[41] and nickel[42] 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

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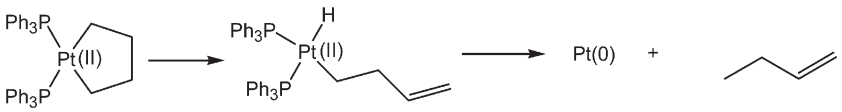


Scheme 1 Decomposition platinacyclopentanes.[29]

metal-hydride species is short-lived, it is expected that little or no isomerisation of the α-olefin product should occur.[30] Whitesides' studies also showed that metallacyclopentanes are markedly more thermally stable than analogous metallacycloheptanes.[31,32,38–40] This may be as a consequence of the constrained geometry of the metallacyclopentanes, which can hinder β-hydride elimination. Similar observations have been made with chromacyclopentanes and chromacycloheptanes.[26] The precise mechanism for the decomposition reaction of metallacyclopentanes 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-hydrogen transfer[29] and intermolecular hydrogen transfer[43] might also be involved. Theoretical studies with titanium complexes suggest that despite the challenges presented by constrained geometry of metallacyclopentanes, the stepwise β-hydride elimination/reductive elimination process is still the most likely decomposition pathway for these complexes.[44–46]

Due to increased stability of platinacycloalkanes relative to other metallacycloalkanes, their study can offer valuable insights into the nature of transient species in catalytic processes such as ethylene oligomerization, that are proposed to involve metallacycloalkanes 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[47] and Suzuki–Miyaura coupling reactions.[48] With the intent of gaining access to further examples of platinacycloalkane complexes, and to gain insight into the possible role played by supporting ligands in the reactivity of such compounds, we have now prepared a series of platinacycloalkanes of the general formula [Pt(P^N)$(CH_2)_n$] (n = 4, 6), based on these iminophosphine ligands. An investigation of the thermal decomposition behaviour of these metallacycloalkanes was also carried out.

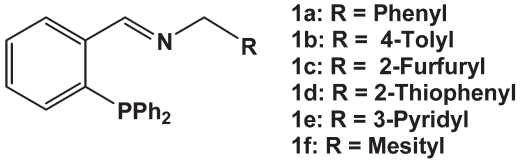


Fig. 1 General structure of iminophosphine ligands **1a–1f**.

Results and discussion

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

The reaction of [Pt(COD)Cl_2] with the appropriate di-Grignard reagent in THF gave platinacycloalkanes of the type [Pt(COD)-$(CH_2)_n$], n = 4, 6.[38,43] The iminophosphine-containing platinacycloalkanes were prepared by displacement of 1,5-cyclooctadiene from [Pt(COD)(C_4H_8)] and [Pt(COD)(C_6H_{12})] (Scheme 2) by 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**).

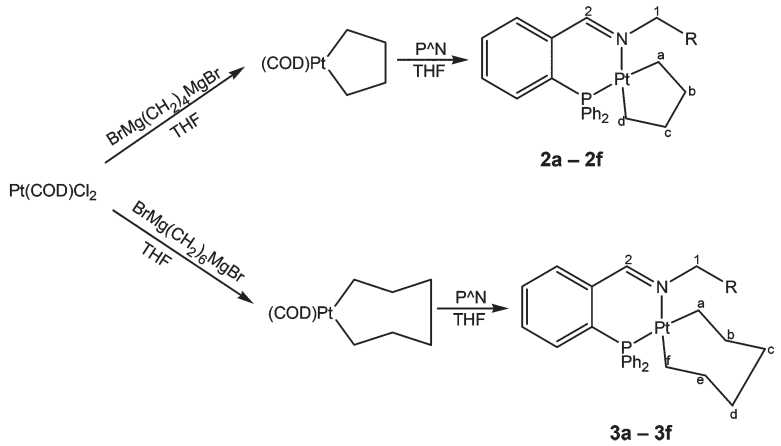
^{1}H NMR spectra of the complexes show an upfield shift of the imine proton signals from 8.98–9.05 ppm in the free ligands to 8.13–8.43 ppm in the metal complexes. The observed upfield shift is attributed to back-bonding from the platinum centre to the imine bond. These signals appear as singlets, in contrast to the doublets observed for free ligands,[47] due to the conformational change of the ligand in order to facilitate coordination.[49] Platinum satellites, with coupling constants in the range of $^3J_{HPt}$ = 31.8–37.1 Hz, further support coordination of imine moiety of the ligands to the metal centre.

Similar to other iminophosphine complexes, a downfield shift is observed from 4.64–4.87 ppm for the free ligands[47] to 5.25–5.77 ppm for the platinacycles for the methylene protons (N-C$\boldsymbol{H}_2$-R). This is due to the deshielding that occurs upon coordination of the imine nitrogen to platinum. The methylene protons (N-C$\boldsymbol{H}_2$-R) also show platinum satellites with a $^3J_{HPt}$ = 15.1–17.0 Hz. The alkyl protons of the metallacycles appear as multiplets in the region 0.72–1.91 ppm with the CH_2 protons adjacent to the metal centre being assigned to the most upfield resonance.

In the ^{13}C 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 platinacycles. These signals appear as doublets, although the magnitude of the coupling constants is smaller compared to those of the free ligands with a $^3J_{CP}$ in the range of 4.3–6.0 Hz for the platinacycles compared to 21.1–23.4 Hz for the free ligands. A downfield shift of up to 9.1 ppm is observed for the methylene carbon atoms (N-$\boldsymbol{C}H_2$-R) upon coordination. Resonances for the carbon atoms of the carbocyclic fragment of the platinacycloalkanes are observed between 14.9 and 36.1 ppm. The carbon atoms bonded to the metal centre (Pt-$\boldsymbol{C}H_2$–) resonate as doublets as a result of coupling to the phosphorus nucleus of the iminophosphine ligand.

The most shielded carbon atoms are those that are *cis* to the phosphine group, C_d for the platinacyclopentanes **2a–2f**

Complex	n	R	Complex	n	R
2a	4	Phenyl	**3a**	6	Phenyl
2b	4	4-Tolyl	**3b**	6	4-Tolyl
2c	4	2-Furfuryl	**3c**	6	2-Furfuryl
2d	4	2-Thiophenyl	**3d**	6	2-Thiophenyl
2e	4	3-Pyridyl	**3e**	6	3-Pyridyl
2f	4	Mesityl	**3f**	6	Mesityl



Scheme 2 Synthesis of platinacyclopentanes **2a–2f** and platinacycloheptanes **3a–3f**.

and C_f 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 (C_a) 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 in the range $^1J_{PPt}$ = 1843–2066 Hz, similar to other platinacycloalkane phosphine complexes.[50–54] 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.[6]

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

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

Bond Lengths		Bond Angles	
Pt(1)–C(1)	2.148(5)	C(4)–Pt(1)–N(1)	176.77(18)
Pt(1)–C(4)	2.052(5)	N(1)–Pt(1)–C(1)	92.2(2)
Pt(1)–N(1)	2.118(4)	C(4)–Pt(1)–C(1)	84.6(2)
Pt(1)–P(1)	2.2440(12)	C(4)–Pt(1)–P(1)	94.98(15)
P(1)–C(18)	1.831(5)	C(1)–Pt(1)–P(1)	176.78(14)
C(12)–C(13)	1.469(7)	N(1)–Pt(1)–P(1)	88.18(11)
N(1)–C(12)	1.281(6)		
N(1)–C(5)	1.487(6)		

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)(C_4H_8) 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[50–55] 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

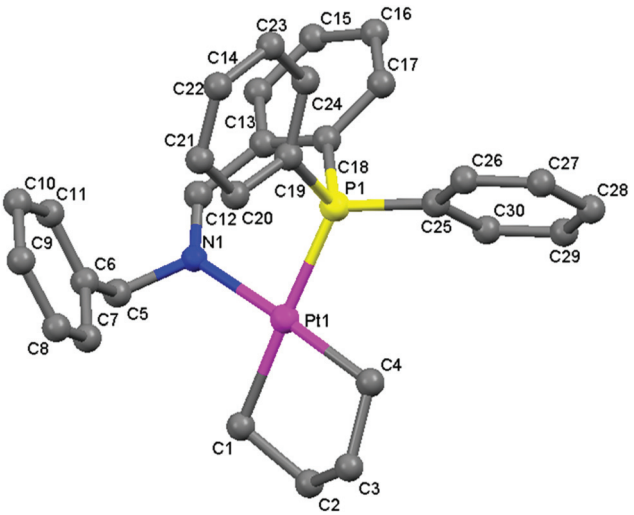


Fig. 2 The ORTEP plot of the molecular structure of **2a** showing numbering scheme. All non-hydrogen atoms are shown as ellipsoids with probability level of 30%.

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"[39] 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 ($^{1}J_{PPt}$ = 1917 Hz). This decrease is accompanied by appearance and gradual increase of a new signal at 26.1 ppm ($^{1}J_{PPt}$ = 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

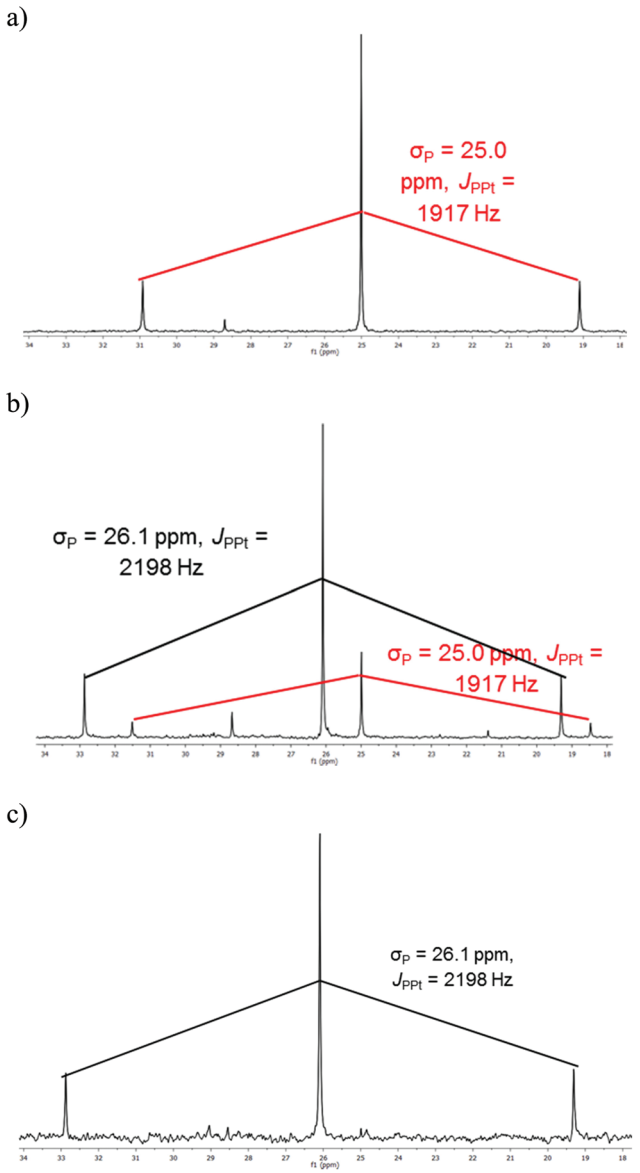


Fig. 3 ^{31}P NMR spectra of complex **2a** during heating at 140 °C, (a) $t_{0\ h}$, (b) $t_{11\ h}$, (c) $t_{27\ h}$.

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.[38]

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

Table 2 Thermal decomposition of complex **2a**[a]

Entry	Temp. (°C)	Solvent	Time (h)	1-Butene[b]	2-Butenes[b]	Butane[b]
1	100	Toluene	120	0	0	0
2	120	Toluene	90	91	8	1
3	140	Toluene	27	81	17	2
4	170	Toluene	6	67	22	11
5	170	—	6	67	26	7

[a] Reactions done in triplicate. Error: ±1%. [b] Amounts given as percentages.

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-butene 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 ^{31}P 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.

$$\ln(a_t/a_0) = -kt \quad (1)$$

where a = [Complex **2a**] or [Complex **3a**].

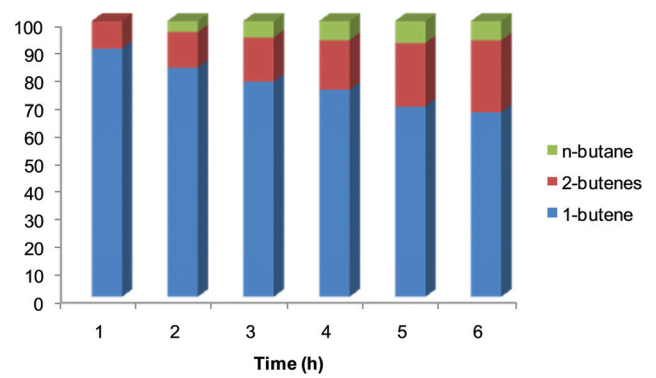


Fig. 4 Product composition (%) for the thermal decomposition of 5.1 over time.

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

	Rate constant[a] (s^{-1})		Rate[b] (M^{-1} s^{-1})	
Complex	140 °C	170 °C	140 °C	170 °C
2a	2.90×10^{-5} (0.104 h^{-1})	1.50×10^{-4} (0.525 h^{-1})	4.31×10^{-7} (1.55×10^{-3})	2.02×10^{-6} (7.27×10^{-3})
3a	9.00×10^{-5} (0.324 h^{-1})	4.37×10^{-4} (1.58 h^{-1})	1.23×10^{-6} (4.44×10^{-3})	6.06×10^{-6} (2.18×10^{-2})

[a] Rate constants in h^{-1} in parenthesis. [b] Reaction rates in M^{-1} h^{-1} in parenthesis.

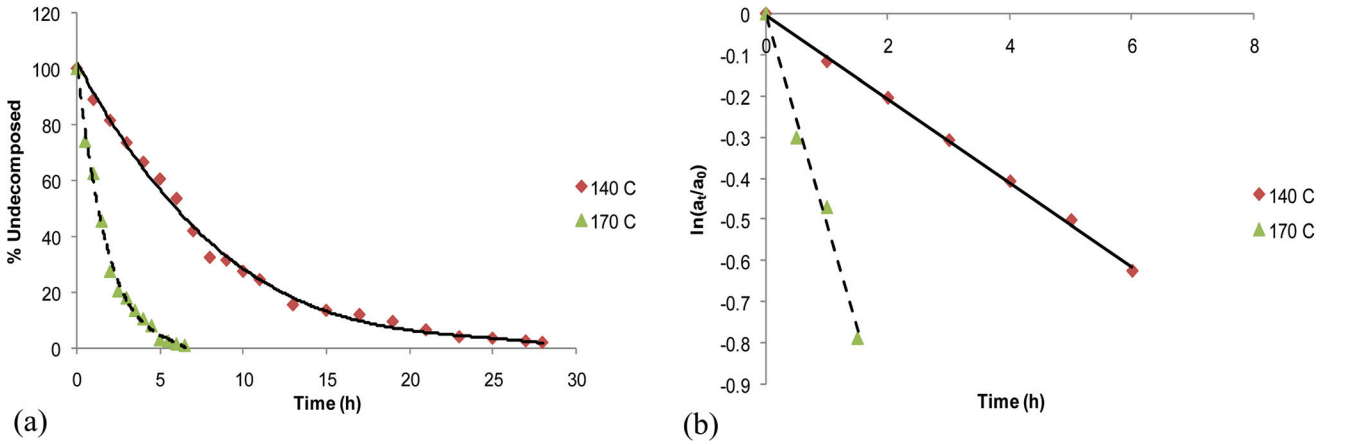


Fig. 5 Representative speciation (a) and first order (b) plots for the thermal decomposition of complex **2a** at 140 °C and 170 °C.

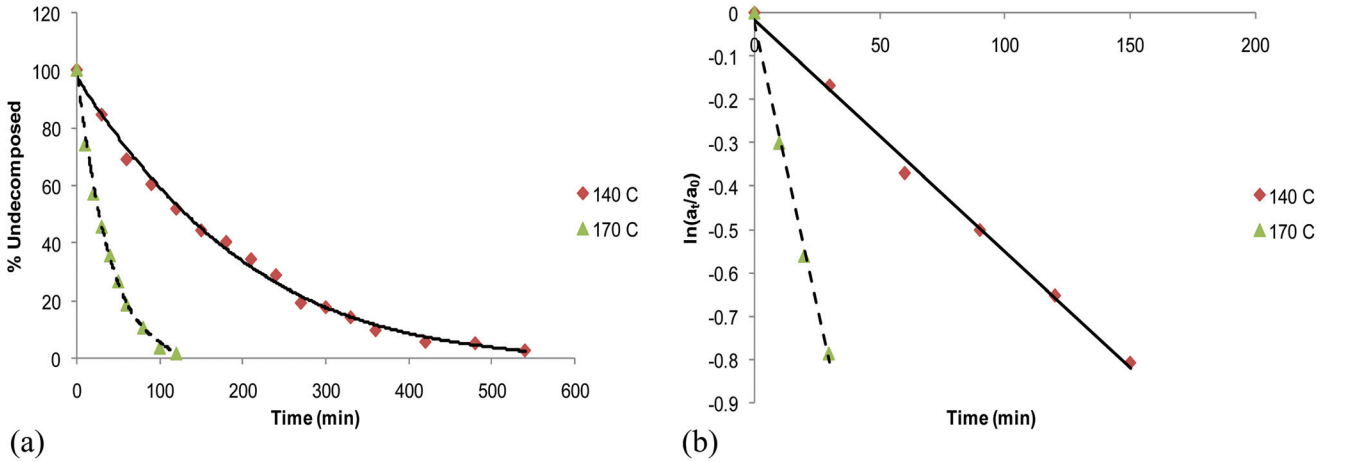


Fig. 6 Representative speciation (a) and first order (b) plots for the thermal decomposition of complex **3a** at 140 °C and 170 °C.

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.

Table 4 Thermal decomposition of complexes **2a–2f** and **3a–3f**[a]

Entry	Complex	*n*	R	α-Olefin[b]	Internal olefins[b,c]	*n*-Alkanes[b]
1	**2a**	4	Phenyl	81	17	2
2	**2b**	4	4-Tolyl	85	11	4
3	**2c**	4	2-Furfuryl	71	20	9
4	**2d**	4	2-Thiophenyl	76	13	11
5	**2e**	4	3-Pyridyl	80	13	7
6	**2f**	4	Mesityl	84	11	5
7	**3a**	6	Phenyl	50	33	17
8	**3b**	6	4-Tolyl	63	27	10
9	**3c**	6	2-Furfuryl	56	29	15
10	**3d**	6	2-Thiophenyl	54	35	11
11	**3e**	6	3-Pyridyl	52	28	20
12	**3f**	6	Mesityl	58	20	22

[a] Reaction conditions: 0.02 M in toluene, 140 °C, 27 h. [b] Amounts given as percentages. [c] Mixture of *cis* and *trans* internal olefins.

Table 5 Crystal data for **2a**

Formula	$C_{30}H_{30}NPPt$
Formula weight	630.61
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.7744(13)
b (Å)	11.3517(15)
c (Å)	12.6780(16)
α (°)	72.898(3)
β (°)	67.960(3)
γ (°)	82.749(3)
V (Å^3)	1246.0(3)
Z	2
D_c (g cm^{-3})	1.681
μ (mm^{-1})	5.713
θ Range for data collection (°)	1.80–28.34
Limiting indices	$-13 \le h \le 13$ $-15 \le k \le 15$ $-16 \le l \le 16$
No. of reflns collected	27 034
No. of reflns unique (R_{int})	6180 (0.0549)
No. of params	298
R_1	0.0448
wR_2	0.0786
Goodness of fit on F^2	1.043

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 metallocycloalkane. 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 α-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. K_2PtCl_4 and $PdCl_2$ were obtained from Johnson Matthey. The ligands **1a–1f**,[47,48] [Pt(COD)(C_4H_8)],[38,43] [Pt(COD)(C_6H_{12})],[38,43] 2-Diphenylphosphinobenzaldehyde,[57,58] Pd(COD)Cl_2,[59] Pd(COD)MeCl,[60] Pt(COD)Cl_2 [39,61] were all prepared using literature procedures.

NMR spectra were recorded on a Varian Mercury-300 MHz (^{1}H: 300 MHz; ^{13}C: 75.5 MHz; ^{31}P: 121 MHz) or Varian Unity-400 MHz (^{1}H: 400 MHz; ^{13}C: 100.6 MHz; ^{31}P: 161.9 MHz) spectrometer. ^{1}H NMR spectra were referenced internally using the residual protons in deuterated solvents ($CDCl_3$: δ 7.27; DMSO: δ 2.50) and values reported relative to the internal standard tetramethylsilane (δ 0.00). ^{13}C NMR spectra were referenced internally to the deuterated solvent resonance ($CDCl_3$: δ 77.0; DMSO: δ 39.4) and the values are reported relative to tetramethylsilane (δ 0.00). All chemical shifts are quoted in δ (ppm) and coupling constants, J, in Hertz (Hz).

Melting points were determined on a Reichert-Jung Thermovar hotstage microscope and are uncorrected. Infrared spectra were recorded on a Thermo Nicolete FT-IR instrument in the 4000–300 cm^{-1} range using KBr discs or CH_2Cl_2 solutions. Microanalyses were determined using a Fisons EA 1108 CHNO-S instrument. Mass spectra were recorded on a Waters API Quatro Micro triple quadruple mass spectrometer (ESI,

70 eV) at the University of Stellenbosch. GC analyses were performed using a Varian 3900 gas chromatograph equipped with an FID and a 50 m × 0.20 mm HP-PONA column (0.50 μm film thickness). The carrier gas was helium at 40 psi. The oven was programmed to hold the temperature at 32 °C for 4 min and then to ramp to 200 °C at 10° min^{-1} and hold for 5 min and then ramp to 250 °C at 10° min^{-1} and hold for 5 min. GC-MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60 m × 0.25 mm Rtx-1 column (0.5 μm film thicknesses). The carrier gas was helium at 0.9 ml min^{-1}. The oven was programmed to hold at 50 °C for 2 min and then ramp to 250 °C at 10° min^{-1} and hold for 8 min.

General procedure for the preparation of complexes 2a–2f and 3a–3f

The metallacycloalkanes were prepared from the reaction of $[Pt(COD)Cl_2]$ with appropriate di-Grignard reagents to give $[Pt(COD)(CH_2)_n]$, where n = 4 or 6. After work-up, the 1,5-cyclooctadiene was displaced by the iminophosphine ligands in a 1 : 1 reaction.

Preparation of $[Pt(C_{26}H_{22}NP)(C_4H_8)]$ (2a). **2a** was prepared by the reaction of $[Pt(COD)(C_4H_8)]$ (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} ($\nu_{C=N}$, imine). ^{1}H NMR ($CDCl_3$): 0.79–0.84 (m, 4H; H_a + H_d), 1.76–1.79 (m, 4H; H_b + H_c), 5.50 (s, 2H, $^3J_{H-Pt}$ = 16.4 Hz; H_1), 6.88 (d, 2H, $^3J_{HH}$ = 7.8 Hz; Ar-*H*), 7.00 (d, 2H, $^3J_{HH}$ = 7.1 Hz; Ar-*H*), 7.11–7.35 (m, 15H; Ar-*H*), 8.18 (s, 1H, $^3J_{HPt}$ = 35.1 Hz; H_2). ^{13}C NMR ($CDCl_3$): 15.8 (d, $^2J_{CP}$ = 2.9 Hz; C_d), 28.0 (s; C_c), 29.7 (s; C_b), 33.9 (d; $^2J_{CP}$ = 5.7 Hz; C_a), 68.8 (s; C_1), 127.3 (s; Ar-*C*), 128.1 (d, $^1J_{CP}$ = 9.0 Hz; Ar-*C*), 128.4 (s; Ar-*C*), 128.7 (s; Ar-*C*), 129.4 (s; Ar-*C*), 129.8 (s; Ar-*C*), 130.3 (s; Ar-*C*), 131.5 (s; Ar-*C*), 131.8 (s; Ar-*C*), 131.9 (d, $^3J_{CP}$ = 4.9 Hz; Ar-*C*), 133.6 (s; Ar-*C*), 133.9 (d, $^1J_{CP}$ = 12.6 Hz; Ar-*C*), 135.3 (d, $^1J_{CP}$ = 8.3 Hz; Ar-*C*), 137.7 (s; Ar-*C*), 138.9 (d, $^2J_{CP}$ = 16.7 Hz; Ar-*C*), 162.0 (d, $^3J_{CP}$ = 5.5 Hz; C_2). ^{31}P NMR ($CDCl_3$): 25.0 (s, J_{PPt} = 1894 Hz). ESI-MS: m/z 631.18 $[M + H]^+$, 575.12 $[M - C_4H_8]^+$. Anal. Calc. For $C_{30}H_{30}NPPt$ (630.62): C, 57.14; H, 4.80; N, 2.22. Found: C, 56.91; H, 4.83; N, 2.12.

Preparation of $[Pt(C_{27}H_{24}NP)(C_4H_8)]$ (2b). **2b** was prepared by the reaction of $[Pt(COD)(C_4H_8)]$ (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} ($\nu_{C=N}$, imine). ^{1}H NMR ($CDCl_3$): 0.87–1.01 (m, 4H; H_a + H_d), 1.74–1.79 (m, 4H; H_b + H_c), 2.31 (s, 3H; H_1), 5.25 (s, 2H, $^3J_{HPt}$ = 15.8 Hz; H_2), 6.99 (d, 2H, $^3J_{HH}$ = 7.1 Hz; Ar-*H*), 7.05 (d, 2H, $^3J_{HH}$ = 6.8 Hz; Ar-*H*), 7.17–7.34 (m, 14H; Ar-*H*), 8.17 (s, 1H, $^3J_{HPt}$ = 34.8 Hz; H_3). ^{13}C NMR ($CDCl_3$): 16.1 (d, $^2J_{CP}$ = 3.1 Hz; C_d), 22.1 (s; C_1), 28.0 (s; C_c), 30.3 (s; C_d), 33.1 (d; $^2J_{CP}$ = 6.0 Hz; C_a), 67.9 (s; C_2), 125.5 (s; Ar-*C*), 127.2 (s; Ar-*C*), 128.0 (d, $^1J_{CP}$ = 8.8 Hz; Ar-*C*), 128.5 (s; Ar-*C*), 128.9 (d, $^1J_{CP}$ = 9.3 Hz; Ar-*C*), 129.4 (s; Ar-*C*), 129.6 (s; Ar-C), 129.7 (d, $^3J_{CP}$ = 1.7 Hz; Ar-*C*), 130.3 (d, $^3J_{CP}$ = 1.2 Hz; Ar-*C*), 131.5 (s; Ar-*C*), 131.8 (s; Ar-*C*), 131.9 (d, $^2J_{CP}$ = 5.1 Hz; Ar-*C*), 132.2 (d, $^3J_{CP}$ = 2.6 Hz; Ar-C), 133.6 (d, $^2J_{CP}$ = 5.0 Hz; Ar-*C*), 134.1 (d, $^2J_{CP}$ = 7.9 Hz; Ar-*C*), 135.0 (d, $^1J_{CP}$ = 11.9 Hz; Ar-*C*), 138.1 (s; Ar-*C*), 140.1 (d, $^2J_{CP}$ = 16.9 Hz; Ar-*C*), 162.2 (d, $^3J_{CP}$ = 5.1 Hz; C_3). ^{31}P NMR ($CDCl_3$): 26.2 (s, J_{PPt} = 1920 Hz). ESI-MS: m/z 645.20 $[M + H]^+$, 589.44 $[M - C_4H_8]^+$. Anal. Calc. For $C_{31}H_{32}NPPt$ (644.64): C, 57.76; H, 5.00; N, 2.17. Found: C, 57.79; H, 5.03; N, 2.15.

Preparation of $[Pt(C_{24}H_{20}NOP)(C_4H_8)]$ (2c). **2c** was prepared by the reaction of $[Pt(COD)(C_4H_8)]$ (0.14 g, 0.40 mmol) and (2-diphenylphosphanyl-benzylidene)-furan-2-ylmethyl-amine (**1c**) (0.15 g, 0.40 mmol). The product was obtained as an orange solid. (0.22 g, 87%). M.p. 146–148 °C (decomp). IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$, imine). ^{1}H NMR ($CDCl_3$): 0.86–0.88 (m, 4H; H_a + H_d), 1.45–148 (m, 4H; H_b + H_c), 5.49 (s, 2H, $^3J_{H-Pt}$ = 15.1 Hz; H_5), 6.22 (dd, 1H, $^3J_{HH}$ = 1.9 Hz, 3.2 Hz; H_3), 6.27 (d, 1H, $^3J_{HH}$ = 3.2 Hz; H_2), 7.08 (dd, 1H, $^3J_{HH}$ = 0.8 Hz, 1.8 Hz; *H*1), 7.24–7.41 (m, 14H; Ar-*H*), 8.15 (s, 1H, J_{H-Pt} = 35.0 Hz; H_6). ^{13}C NMR ($CDCl_3$): 15.8 (d, $^2J_{CP}$ = 2.8 Hz; C_d), 26.3 (s; C_c), 28.0 (s; C_b), 33.9 (d, $^2J_{CP}$ = 5.8 Hz; C_a), 60.9 (s; C_5), 110.2 (s; C_3), 111.7 (s; C_2), 128.1 (d, $^1J_{C-P}$ = 9.7 Hz; Ar-*C*), 128.3 (d, $^1J_{CP}$ = 11.0 Hz; Ar-*C*), 128.6 (d, $^2J_{CP}$ = 5.4 Hz; Ar-*C*), 129.7 (d, $^3J_{CP}$ = 1.8 Hz; Ar-*C*), 130.2 (d, $^3J_{CP}$ = 1.4 Hz; Ar-*C*), 131.4 (s; Ar-*C*), 131.7 (s; Ar-*C*), 131.9 (d, $^3J_{CP}$ = 4.9 Hz; Ar-*C*), 132.0 (s; Ar-*C*), 132.3 (d, $^3J_{CP}$ = 2.7 Hz, Ar-*C*), 133.9 (d, $^1J_{CP}$ = 12.6 Hz; Ar-*C*), 134.1 (s; Ar-*C*), 135.2 (d, $^2J_{CP}$ = 8.3 Hz; Ar-*C*), 138.7 (d, $^2J_{CP}$ = 16.4 Hz, Ar-*C*), 142.7 (s; *C*1), 150.4 (s; C_4), 161.6 (d, $^3J_{CP}$ = 5.2 Hz; C_6). ^{31}P NMR ($CDCl_3$): 25.3 (s, J_{PPt} = 1904 Hz). ESI-MS: m/z 621.17 $[M + H]^+$, 564.50 $[M - C_4H_8]^+$. Anal. Calc. For $C_{28}H_{28}NOPPt$ (620.58): C, 54.19; H, 4.55; N, 2.26. Found: C, 54.41; H, 4.82; N, 2.36.

Preparation of $[Pt(C_{24}H_{20}NPS)(C_4H_8)]$ (2d). **2d** was prepared by the reaction of $[Pt(COD)(C_4H_8)]$ (0.13 g, 0.36 mmol) and (2-diphenylphosphanyl-benzylidene)-thiophen-2-ylmethyl-amine (**1d**) (0.14 g, 0.36 mmol). The product was obtained as an orange solid (0.19 g, 81%). M.p. 127–129 °C (decomp). IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$, imine). ^{1}H NMR ($CDCl_3$): 0.80–0.83 (m, 4H; H_a + H_d), 1.69–1.72 (m, 4H; H_b + H_c), 5.70 (s, 2H, $^3J_{HPt}$ = 16.4 Hz; H_5), 6.38 (dd, 1H, $^3J_{HH}$ = 1.8 Hz, 3.0 Hz; H_3), 6.45 (d, 1H, $^3J_{HH}$ = 3.2 Hz; H_2), 7.14 (dd, 1H, $^3J_{HH}$ = 1.0 Hz, 1.8 Hz; H_1), 7.28–7.47 (m, 14H; Ar-*H*), 8.21 (s, 1H, $^3J_{HPt}$ = 36.4 Hz; H_6). ^{13}C NMR ($CDCl_3$): 15.9 (d, $^2J_{CP}$ = 3.0 Hz; C_d), 25.9 (s; C_c), 27.8 (s; C_b), 36.1 (d, $^2J_{CP}$ = 5.9 Hz; C_a), 61.4 (s; C_5), 123.5 (s; C_3), 125.0 (s; C_2), 128.0 (d, $^1J_{CP}$ = 10.1 Hz; Ar-*C*), 128.5 (d, $^1J_{CP}$ = 11.4 Hz; Ar-*C*), 128.9 (d, $^2J_{CP}$ = 4.8 Hz; Ar-*C*), 129.5 (d, $^3J_{CP}$ = 2.0 Hz; Ar-*C*), 130.9 (d, $^3J_{CP}$ = 1.8 Hz; Ar-*C*), 131.5 (s; Ar-*C*), 131.6 (s; Ar-*C*), 131.8 (d, $^3J_{CP}$ = 5.1 Hz; Ar-*C*), 132.1 (s; Ar-*C*), 132.5 (d, $^3J_{CP}$ = 2.9 Hz, Ar-*C*), 134.2 (d, $^1J_{CP}$ = 11.6 Hz; Ar-*C*), 134.4 (s; Ar-*C*), 135.5 (d, $^2J_{CP}$ = 8.8 Hz; Ar-*C*), 137.9 (d, $^2J_{CP}$ = 16.0 Hz, Ar-*C*), 143.3 (s; C_1), 151.6 (s; *C*4), 162.4 (d, $^3J_{CP}$ = 4.3 Hz; C_6). ^{31}P NMR ($CDCl_3$): 25.7 (s, J_{PPt} = 2066 Hz). ESI-MS: m/z 637.13 $[M + H]^+$, 581.08 $[M - C_4H_8]^+$. Anal. Calc. For $C_{28}H_{28}NPSPt$ (636.65): C, 52.82; H, 4.43; N, 2.20; S, 5.04. Found: C, 53.01; H, 4.31; N, 2.17; S, 5.00.

Preparation of [Pt($C_{25}H_{21}N_2P$)(C_4H_8)] (2e). **2e** was prepared by reacting [Pt(COD)(C_4H_8)] (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 (decomp). IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$, imine). ^1H NMR ($CDCl_3$): 0.89–0.93 (m, 4H; H_a + H_d), 1.41–146 (m, 4H; H_b + H_c), 5.69 (s, 2H, $^3J_{H-Pt}$ = 16.0 Hz; H_6), 7.12 (1H, d, $^3J_{HH}$ = 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; *H*3), 8.03 (1H, td, $^3J_{HH}$ = 2.0 Hz; 7.4 Hz, Ar-*H*), 8.30 (s, 1H; H_4) 8.35 (1H, d, $^4J_{HH}$ = 2.1, Hz; H_2), 8.43 (1H, s, $^3J_{HPt}$ = 35.7 Hz; H_7), 8.56 (1H, dd, $^3J_{HH}$ = 1.4 Hz, 5.0 Hz; H_1). ^{13}C NMR ($CDCl_3$): 16.0 (d, $^2J_{CP}$ = 2.8 Hz; C_d), 26.3 (s; C_c), 28.5 (s; C_b), 34.1 (d, $^2J_{CP}$ = 5.7 Hz; C_a), 64.4 (s; C_6), 125.9 (s; C_3), 126.5 (s; *C*), 129.1 (d, $^1J_{CP}$ = 12.3 Hz; Ar-*C*), 130.4 (d, $^3J_{CP}$ = 1.6 Hz; Ar-*C*), 131.6 (d, $^3J_{CP}$ = 1.6 Hz; Ar-*C*), 132.0 (d, $^2J_{CP}$ = 6.7 Hz; Ar-*C*), 132.8 (s; C_5), 133.1 (d, $^1J_{CP}$ = 12.4 Hz; Ar-*C*), 134.0 (s; Ar-*C*), 134.1 (s; Ar-*C*), 134.3 (s; C_4), 136.9 (d, $^2J_{CP}$ = 17.4 Hz; Ar-*C*), 137.2 (s; Ar-*C*), 139.4 (s; Ar-*C*), 149.7 (s; C_2), 151.0 (s; C_1), 162.1 (d, $^3J_{CP}$ = 5.3 Hz; C_7). ^{31}P NMR ($CDCl_3$): 25.7 (s, J_{PPt} = 1886). ESI-MS: *m*/*z* 632.27 $[M + H]^+$, 575.36 [M − C_4H_8]. Anal. Calc. for $C_{29}H_{29}N_2PPd$ (631.61): C, 55.15; H, 4.63; N, 4.44. Found: C, 55.20; H, 4.77; N, 4.39.

Preparation of [Pt($C_{29}H_{28}NP$)(C_4H_8)] (2f). **2f** was prepared using [Pt(COD)(C_4H_8)] (0.17 g, 0.48 mmol) and (2-diphenylphosphanyl-benzylidene)-(2,4,6-trimethyl-benzyl)-amine (**1f**) (0.17 g, 0.40 mmol). The product was obtained as an orange solid (0.27 g, 85%). M.p. 172–175 °C (decomp). IR (KBr): 1635 cm^{-1} ($\nu_{C=N}$, imine). ^1H NMR ($CDCl_3$): 0.81–0.92 (m, 4H, H_a + H_d), 1.76–1.80 (m, 4H, H_b + H_c), 2.21 (s, 6H; H_2 + $H_{2'}$), 2.40 (s, 3H; H_1), 5.27 (2H, s, $^3J_{H-Pt}$ = 17.0 Hz; H_3), 7.01 (d, 2H, $^3J_{HH}$ = 7.6 Hz; Ar-*H*), 7.10 (d, 2H, $^3J_{HH}$ = 7.0 Hz; Ar-*H*), 7.21–7.30 (m, 12H, Ar-*H*), 8.20 (s, 1H, $^3J_{H-Pt}$ = 35.4 Hz; H_4). ^{13}C NMR ($CDCl_3$): 15.8 (d, $^2J_{CP}$ = 3.0 Hz; C_d), 22.1 (s; C_2 + $C_{2'}$), 24.0 (s; C_1), 27.6 (s; C_c), 29.9 (s; C_b), 32.7 (d; $^2J_{CP}$ = 5.9 Hz; C_a), 66.7 (s; *C*3), 126.3 (s; Ar-*C*), 128.0 (s; Ar-*C*), 128.8 (d, $^1J_{CP}$ = 9.0 Hz; Ar-*C*), 129.0 (s; Ar-*C*), 129.5 (d, $^1J_{CP}$ = 9.1 Hz; Ar-*C*), 129.6 (s; Ar-*C*), 129.9 (s; Ar-C), 130.0 (d, $^3J_{CP}$ = 1.4 Hz; Ar-*C*), 130.3 (d, $^3J_{CP}$ = 1.5 Hz; Ar-*C*), 131.7 (s; Ar-*C*), 131.8 (s; Ar-*C*), 132.0 (d, $^2J_{CP}$ = 5.3 Hz; Ar-*C*), 132.9 (d, $^3J_{CP}$ = 2.4 Hz; Ar-C), 133.8 (d, $^2J_{CP}$ = 5.4 Hz; Ar-*C*), 134.4 (d, $^2J_{CP}$ = 9.3 Hz; Ar-*C*), 134.8 (d, $^1J_{CP}$ = 12.1 Hz; Ar-*C*), 137.9 (s; Ar-*C*), 139.4 (s, Ar-C), 142.2 (d, $^2J_{CP}$ = 16.5 Hz; Ar-*C*), 161.9 (d, $^3J_{CP}$ = 5.3 Hz; C_4). ^{31}P NMR ($CDCl_3$): 26.7 (s, J_{PPt} = 1843 Hz). ESI-MS: *m*/*z* 672.23 $[M + H]^+$, 617.16 [M − C_4H_8]$^+$. Anal. Calc. For $C_{31}H_{32}NPPt$ (672.70): C, 58.92; H, 5.39; N, 2.08. Found: C, 58.97; H, 5.00; N, 2.01.

Preparation of [Pt($C_{26}H_{22}NP$)(C_6H_{12})] (3a). **3a** was prepared by the reaction of [Pt(COD)(C_6H_{12})] (0.25 g, 0.64 mmol) with benzyl-(2-diphenylphosphanyl-benzylidene)-amine (**1a**) (0.24 g, 0.64 mmol). The product was obtained as a brown oil. (0.32 g, 73%). IR (KBr): 1635 cm^{-1} ($\nu_{C=N}$, imine). ^1H NMR ($CDCl_3$): 0.74–0.76 (m, 4H; H_a + H_f), 1.42–1.45 (8H, m; (H_b − H_e), 5.38 (2H, s, $^3J_{HPt}$ = 16.8 Hz; H_1), 7.08 (dd, 1H, $^3J_{HH}$ = 1.2 H, 8.3 Hz; Ar-*H*), 7.11 (d, 1H, $^4J_{HH}$ = 1.8 Hz; Ar-*H*), 7.13 (dd, 2H, $^5J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 7.8 Hz; Ar-*H*), 7.21 (m, 1H; Ar-*H*), 7.39–7.51 (m, 14H; Ar-*H*), 8.33 (s, 1H, $^3J_{HPt}$ = 34.7 Hz; H_2). ^{13}C NMR ($CDCl_3$): 14.9 (d, $^2J_{CP}$ = 3.0 Hz; C_f), 26.2 (s; C_e), 28.1 (s; C_b), 32.3 (s; C_d), 32.4 (s; C_c), 34.2 (d; $^2J_{CP}$ = 5.0 Hz; C_a), 65.4 (s; C_1), 125.9 (s; Ar-*C*), 127.6 (d, $^1J_{CP}$ = 9.3 Hz; Ar-*C*), 127.9 (s; Ar-*C*), 128.4 (s; Ar-*C*), 128.6 (s; Ar-*C*), 129.0 (s; Ar-*C*), 129.4 (s; Ar-*C*), 129.9 (s; Ar-*C*), 130.7 (s; Ar-*C*), 131.3 (s; Ar-*C*), 132.0 (d, $^2J_{CP}$ = 5.1 Hz; Ar-*C*), 133.6 (s; Ar-*C*), 134.6 (d, $^1J_{CP}$ = 12.2 Hz; Ar-*C*), 135.5 (d, $^1J_{CP}$ = 9.1 Hz; Ar-*C*), 137.9 (s; Ar-*C*), 138.6 (d, $^2J_{CP}$ = 17.0 Hz; Ar-*C*), 162.7 (d, $^3J_{CP}$ = 5.5 Hz; C_2). ^{31}P NMR ($CDCl_3$): 26.8 (s, J_{PPt} = 1802 Hz). ESI-MS: *m*/*z* 659.34 $[M + H]^+$, 575.20 [M − C_4H_8]$^+$.

Preparation of [Pt($C_{27}H_{24}NP$)(C_6H_{12})] (3b). **3b** was prepared by the reaction of [Pt(COD)(C_6H_{12})] (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} ($\nu_{C=N}$, imine). ^1H NMR ($CDCl_3$): 0.76–0.89 (m, 4H; H_a + H_f), 0.95–1.37 (m, 8H; H_b − H_e), 2.30 (s, 3H; H_1), 5.45 (s, 2H, $^3J_{HPt}$ = 16.0 Hz; H_2), 7.01 (dd, 1H, $^3J_{HH}$ = 1.2 H, 8.3 Hz; Ar-*H*), 7.11 (d, 1H; $^4J_{HH}$ = 1.7 Hz, Ar-*H*), 7.14 (dd, 2H, $^3J_{HH}$ = 1.4 Hz, 7.2 Hz; Ar-*H*), 7.18 (m, 2H; Ar-*H*), 7.30–7.44 (m, 12H; Ar-*H*), 8.13 (s, 1H, $^3J_{PtH}$ = 33.0 Hz; H_3). ^{13}C NMR ($CDCl_3$): 17.3 (d, $^2J_{CP}$ = 3.1 Hz; C_f), 21.7 (s; C_1), 25.3, (s; C_e), 27.2 (s; C_b), 31.9 (s; C_d), 32.0 (s; C_c) 34.7 (d, $^2J_{CP}$ = 6.0 Hz; C_a), 64.9 (s; C_2), 125.5 (s; Ar-*C*), 127.2 (s; Ar-*C*), 128.0 (d, $^1J_{CP}$ = 8.8 Hz; Ar-*C*), 128.5 (s; Ar-*C*), 128.9 (d, $^1J_{CP}$ = 9.3 Hz; Ar-*C*), 129.4 (s; Ar-*C*), 129.6 (s; Ar-C), 129.7 (d, $^3J_{CP}$ = 1.7 Hz; Ar-*C*), 130.3 (d, $^3J_{CP}$ = 1.2 Hz; Ar-*C*), 131.5 (s; Ar-*C*), 131.8 (s; Ar-*C*), 131.9 (d, $^2J_{CP}$ = 5.1 Hz; Ar-*C*), 132.2 (d, $^3J_{CP}$ = 2.6 Hz; Ar-C), 133.6 (d, $^2J_{CP}$ = 5.0 Hz; Ar-*C*), 134.1 (d, $^2J_{CP}$ = 7.9 Hz; Ar-*C*), 135.0 (d, $^1J_{CP}$ = 11.9 Hz; Ar-*C*), 138.1 (s; Ar-*C*), 140.1 (d, $^2J_{CP}$ = 15.9 Hz; Ar-*C*), 162.2 (d, $^3J_{CP}$ = 5.1 Hz; C_3). ^{31}P NMR ($CDCl_3$): 25.9 (s, J_{PPt} = 1954 Hz). ESI-MS: *m*/*z* 671.63 $[M + H]^+$, 589.50 [M − C_4H_8].

Preparation of [Pt($C_{24}H_{20}NOP$)(C_6H_{12})] (3c). **3c** was prepared by the reaction of [Pt(COD)(C_6H_{12})] (0.25 g, 0.64 mmol) with (2-diphenylphosphanyl-benzylidene)-furan-2-ylmethyl-amine (**1c**) (0.24 g, 0.64 mmol). The product was obtained as a dark-orange oil (0.31 g, 77%). IR (KBr): 1632 cm^{-1} ($\nu_{C=N}$, imine). ^1H NMR ($CDCl_3$): 0.72–0.75 (m, 4H; H_a + H_f), 1.31–1.39 (m, 8H; H_b − H_e), 5.77 (s, 2H, $^3J_{HPt}$ = 15.7 Hz; C_5), 6.29 (dd, 1H, $^3J_{HH}$ = 2.0 Hz, 3.1 Hz; H_3), 6.34 (1H, d, $^3J_{HH}$ = 3.2 Hz; H_2), 7.06 (1H, dd, $^3J_{HH}$ = 0.9 Hz, 2.0 Hz; H_1), 7.24–7.42 (m, 14H; Ar-*H*), 8.16 (s, 2H, $^3J_{HPt}$ = 31.8 Hz; H_6). ^{13}C NMR ($CDCl_3$): 15.1 (d, $^2J_{CP}$ = 2.8 Hz; C_f), 24.3 (s; C_e), 24.9 (s; C_b), 31.4 (s; C_d), 31.5 (s; C_c), 33.7 (d, $^2J_{CP}$ = 4.9 Hz; C_a), 63.5 (s; C_5), 109.6 (s; C_3), 110.3 (s; C_2), 127.7 (d, $^1J_{CP}$ = 10.0 Hz; Ar-*C*), 127.9 (d, $^1J_{CP}$ = 11.6 Hz; Ar-*C*), 128.8 (d, $^2J_{CP}$ = 5.0 Hz; Ar-*C*), 129.5 (d, $^3J_{CP}$ = 1.4 Hz; Ar-*C*), 130.7 (d, $^3J_{CP}$ = 1.8 Hz; Ar-*C*), 131.1 (s; Ar-*C*), 131.5 (s; Ar-C), 131.7 (s; Ar-*C*), 131.9 (d, $^3J_{CP}$ = 5.1 Hz; Ar-*C*), 132.0 (s; Ar-*C*), 132.8 (d, $^3J_{CP}$ = 2.4 Hz, Ar-*C*), 134.0 (d, $^1J_{CP}$ = 12.3 Hz; Ar-*C*), 134.7 (s; Ar-*C*), 135.6 (d, $^2J_{CP}$ = 8.1 Hz; Ar-*C*), 138.3 (d, $^2J_{CP}$ = 17.1 Hz, Ar-*C*), 143.1 (s; C_1), 149.7 (s; *C*4), 162.6 (d, $^3J_{CP}$ = 5.4 Hz; C_6). ^{31}P NMR ($CDCl_3$): 26.4 (s, J_{PPt} = 1860 Hz). ESI-MS: *m*/*z* 649.69 $[M + H]^+$, 565.41 [M − C_4H_8].

Preparation of [Pt($C_{24}H_{20}NPS$)(C_6H_{12})] (3d). **3d** was prepared by the reaction of [Pt(COD)(C_6H_{12})] (0.25 g, 0.64 mmol)

with (2-diphenylphosphanyl-benzylidene)-thiophen-2-ylmethyl-amine (**1d**) (0.25 g, 0.64 mmol). The product was obtained as a dark-orange oil (0.30 g, 71%). IR (KBr): 1631 cm^{-1} ($\nu_{C=N}$, imine). ^1H NMR ($CDCl_3$): 0.76–0.80 (m, 4H; $H_a + H_f$), 1.26–1.43 (8H, m; $H_b - H_e$), 5.50 (2H, s, $^3J_{HPt}$ = 16.1 Hz; C_5), 6.17 (1H, dd, $^4J_{HH}$ = 2.0 Hz, $^3J_{HH}$ 3.2 Hz, H_3), 6.23 (1H, d, $^3J_{HH}$ = 3.0 Hz, H_2), 7.11 (1H, dd, $^4J_{HH}$ = 0.8 Hz, $^3J_{HH}$ = 1.8 Hz; H_1), 7.30–7.39 (m, 14H; Ar-*H*), 8.17 (1H, s, $^3J_{HPt}$ = 33.8 Hz; H_6). ^{13}C NMR ($CDCl_3$): 17.1 (d, $^2J_{CP}$ = 2.9 Hz; C_f), 22.9 (s; C_e), 23.3 (s; C_b), 30.4 (s; C_d), 30.7 (*C*c), 34.1 (d, $^2J_{CP}$ = 6.0 Hz; C_a), 63.9 (s; C_5), 122.7 (s; C_3), 124.0 (s; C_2), 128.3 (d, $^1J_{CP}$ = 10.7 Hz; Ar-*C*), 128.6 (d, $^1J_{CP}$ = 11.7 Hz; Ar-*C*), 129.1 (d, $^2J_{CP}$ = 4.8 Hz; Ar-*C*), 129.5 (d, $^3J_{CP}$ = 1.8 Hz; Ar-*C*), 130.7 (d, $^3J_{CP}$ = 1.8 Hz; Ar-*C*), 131.3 (s; Ar-*C*), 131.6 (s; Ar-*C*), 131.8 (d, $^3J_{CP}$ = 5.4 Hz; Ar-*C*), 132.3 (s; Ar-*C*), 132.9 (d, $^3J_{CP}$ = 3.1 Hz, Ar-*C*), 134.2 (d, $^1J_{CP}$ = 12.1 Hz; Ar-*C*), 134.1 (s; Ar-*C*), 135.5 (d, $^2J_{CP}$ = 9.7 Hz; Ar-*C*), 137.9 (d, $^2J_{CP}$ = 15.8 Hz, Ar-*C*), 142.3 (s; C_1), 151.1 (s; C_4), 163.0 (d, $^3J_{CP}$ = 5.1 Hz; C_6). ^{31}P NMR ($CDCl_3$): 27.1 (s, J_{PPt} = 1830 Hz). ESI-MS: *m*/*z* 665.59 $[M + H]^+$, 581.45 $[M - C_4H_8]$.

Preparation of $[Pt(C_{25}H_{21}N_2P)(C_6H_{12})]$ (3e). **3e** was prepared by the reaction of $[Pt(COD)(C_6H_{12})]$ (0.25 g, 0.64 mmol) with (2-diphenylphosphanyl-benzylidene)-pyridin-3-ylmethyl-amine (**1e**) (0.24 g, 0.64 mmol). The product was obtained as a brown oil (0.27 g, 65%). IR (KBr): 1634 cm^{-1} ($\nu_{C=N}$, imine). ^1H NMR ($CDCl_3$): 0.76–0.81 (m, 4H; $H_a + H_f$), 1.37–1.63 (m, 8H; $H_b - H_e$), 5.38 (s, 2H, $^3J_{HPt}$ = 15.9 Hz; H_6), 7.09 (1H, dd, $^3J_{HH}$ = 7.8 Hz, 9.3 Hz; Ar-*H*), 7.15–7.24 (4H, m; Ar-*H*), 7.36–7.40 (4H, m; Ar-*H*), 7.53–7.57 (3H, m; Ar-*H*), 7.64–7.64 (1H, m; Ar-*H*), 7.70–7.72 (1H, m; H_3), 8.09 (1H, td, $^3J_{HH}$ = 2.3 Hz; 7.8 Hz, Ar-*H*), 8.32–8.33 (m, 1H; H_4), 8.36 (1H, $^4J_{HH}$ = 1.6 Hz, 5.4 Hz; H_2), 8.41 (1H, s, $^3J_{HPt}$ = 37.1 Hz; H_7), 8.60 (1H, dd, d, $^4J_{HH}$ = 2.0, Hz; H_1). ^{13}C NMR ($CDCl_3$): 16.8 (d, $^2J_{CP}$ = 3.3 Hz; C_f), 24.7 (s; C_e), 25.4 (s; C_b), 31.4 (s; C_d), 31.7 (*C*c), 33.5 (d, $^2J_{CP}$ = 5.6 Hz; C_a), 67.2 (s; C_6), 126.1 (s; C_3), 126.4 (s; Ar-*C*), 129.7 (d, $^1J_{CP}$ = 12.2 Hz; Ar-*C*), 130.9 (d, $^3J_{CP}$ = 1.8 Hz; Ar-*C*), 131.6 (d, $^3J_{CP}$ = 1.6 Hz; Ar-*C*), 132.3 (d, $^2J_{CP}$ = 7.0 Hz; Ar-*C*), 132.6 (s; Ar-*C*), 133.5 (d, $^1J_{CP}$ = 12.4 Hz; Ar-*C*), 133.9 (s; *C*4), 134.1 (s; Ar-*C*), 134.8 (s; *C*5), 136.7 (d, $^2J_{CP}$ = 16.9 Hz; Ar-*C*), 137.5 (s; Ar-*C*), 140.1 (s; Ar-*C*), 148.9 (s; C_2), 150.8 (s; C_1), 161.9 (d, $^3J_{CP}$ = 6.0 Hz; C_7). ^{31}P NMR ($CDCl_3$): 26.6 (s, J_{PPt} = 1835 Hz). ESI-MS: *m*/*z* 660.61 $[M + H]^+$, 576.47 $[M - C_4H_8]$.

Preparation of $[Pt(C_{29}H_{28}NP)(C_6H_{12})]$ (3f). **3f** was prepared by reaction of $[Pt(COD)(C_6H_{12})]$ (0.21 g, 0.54 mmol) with (2-diphenylphosphanyl-benzylidene)-(2,4,6-trimethyl-benzyl)-amine (**1f**) (0.23 g, 0.54 mmol). The product was obtained as a brown oil (0.23 g, 60%). IR (KBr): 1634 cm^{-1} ($\nu_{C=N}$, imine). ^1H NMR ($CDCl_3$): 0.79–0.93 (m, 4H; $H_a + H_f$), 1.80–1.91 (m, 8H; $H_b - H_e$), 2.26 (s, 6H; $H_2 + H_{2'}$), 2.43 (s, 3H; H_1), 5.53 (2H, s, $^3J_{HPt}$ = 16.4 Hz; H_3), 7.07 (d, 2H, $^3J_{HH}$ = 7.8 Hz; Ar-*H*), 7.13 (d, 2H, $^3J_{HH}$ = 7.3 Hz; Ar-*H*), 7.33–7.42 (m, 12H; Ar-*H*), 8.17 (s, 1H, $^3J_{HPt}$ = 35.0 Hz; H_4). ^{13}C NMR ($CDCl_3$): 16.7 (d, $^2J_{CP}$ = 2.6 Hz; C_f), 24.3 (s; $C_2 + C_{2'}$), 24.9 (s; C_1), 26.2 (s; C_e), 26.9 (s; C_b), 29.1 (s; C_d), 29.4 (s; C_c), 33.3 (d, $^2J_{CP}$ = 6.2 Hz; C_a), 65.9 (s; C_3), 127.3 (s; Ar-*C*), 128.2 (s; Ar-*C*), 128.4 (d, $^1J_{CP}$ = 9.3 Hz; Ar-*C*), 129.2 (s; Ar-*C*), 129.5 (d, $^1J_{CP}$ = 9.1 Hz; Ar-*C*), 129.7 (s; Ar-*C*), 129.9 (s; Ar-*C*), 130.1 (d, $^3J_{CP}$ = 1.8 Hz; Ar-*C*), 130.5 (d, $^3J_{CP}$ = 1.8 Hz; Ar-*C*), 131.7 (s; Ar-*C*), 131.8 (s; Ar-*C*), 131.9 (d, $^2J_{CP}$ = 5.0 Hz; Ar-*C*), 133.1 (d, $^3J_{CP}$ = 2.6 Hz; Ar-*C*), 134.0 (d, $^2J_{CP}$ = 5.1 Hz; Ar-*C*), 134.3 (d, $^2J_{CP}$ = 10.0 Hz; Ar-*C*), 134.6 (d, $^1J_{CP}$ = 11.9 Hz; Ar-*C*), 138.3 (s; Ar-*C*), 139.6 (s, Ar-C), 141.9 (d, $^2J_{CP}$ = 17.7 Hz; Ar-*C*), 163.4 (d, $^3J_{CP}$ = 5.1 Hz; C_4). ^{31}P NMR ($CDCl_3$): 26.7 (s, J_{PPt} = 1863 Hz). ESI-MS: *m*/*z* 701.53 $[M + H]^+$, 617.49 $[M - C_4H_8]$.

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 (χ = 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.[62] The data were scaled and absorption corrections were performed using SADABS.[63] The structure was solved by direct methods using SHELXS-97[64] and refined by full-matrix least-squares methods based on F^2 using SHELXL-97[64] and using the graphics interface program X-Seed.[65,66] The programs X-Seed and POV-Ray[67] 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 $U_{iso}(H)$ = 1.2–1.5U_{eq}(C). The structure was successfully refined to the *R* factor 0.0238

Thermal decomposition reactions

Thermolysis 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 comparison of retention 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_8 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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