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Regiochemical control of a Pt-promoted alkylation of the phenyl ring

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The reactivity of cationic Pt^{II}–phenyl complexes of the type $[PtPh(CH_2{=}CHR)(phen)]^+$ (R = H or Me) has been investigated. In all cases, insertion of the alkene into the Pt–Ph bond has been observed. The fate of the resulting $Pt{-}CH_2CHRPh$ (R = H or Me) derivative depends on the experimental conditions. In the presence of donor ligands (*e.g.* excess olefin, pyridine or triphenylphosphine) the product is stable, while in the absence of them a rapid rearrangement to form $Pt{-}C_6H_4(CHRMe)$-2 occurs.

It has been reported[1] by some of us that cationic Pt^{II}–aryl complexes containing a N,N chelate ligand [*e.g.* $6\text{-}MeC_5H_3N\text{-}2\text{-}CH{=}NR$ (R = Me or Ph)] effectively promote the migratory insertion of alkenes into the $Pt^{II}{-}C_{aryl}$ σ bond. Two different metal-bound hydrocarbyl groups are formed, according to the experimental conditions (Scheme 1). It was observed that the presence of a bidentate N,N ligand with reduced in-plane hindrance,[2] and/or an excess of alkene, promoted the complete formation of **A**. However, no definite conclusion was reached about the mechanistic pattern of the process. In fact, two reaction paths with different transition states could account for the formation of **A** and **B**, or a unique parent precursor could be driven differently by the reaction environment.

In this paper we report an investigation on the mechanism of the above reaction. The studies indicate that the co-ordinating ability of the olefin and of the ancillary ligands as well as the rates of the exchange processes exert a powerful influence in determining the overall reaction pattern and the type of the resulting hydrocarbyl derivative.

Results and Discussion

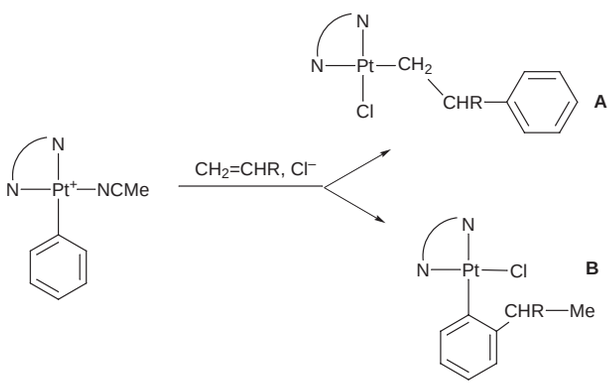
The square-planar [PtPhI(phen)] **1** (phen = 1,10-phenanthroline) complex was used as a starting material to generate the reactive cationic Pt^{II} species by treatment with $AgBF_4$. The iodo derivative was preferred to the chloro homologue because of the faster and quantitative halide removal. By adding at room temperature solid **1** to a nitromethane solution of an equimolar amount of $AgBF_4$ under an olefin (ethene or propene) atmosphere, immediate dissolution of the complex ensued and formation of the *cis*-phenyl–olefin cationic complexes $[PtPh(CH_2{=}CHR)(phen)]BF_4$ (R = H, **2** or R = Me, **3**) was observed [equation (1)]. Within 1 h complete transformation of **2** and **3**

$$[PtPhI(phen)] + AgBF_4 + CH_2{=}CHR \longrightarrow AgI + [PtPh(CH_2{=}CHR)(phen)]BF_4 \quad (1)$$

into the corresponding insertion products $[Pt(CH_2CHRPh)(CH_2{=}CHR)(phen)]BF_4$ [equation (2), R = H, **4** or R = Me, **5**]

$$[PtPh(CH_2{=}CHR)(phen)]BF_4 + CH_2{=}CHR \longrightarrow [Pt(CH_2CHRPh)(CH_2{=}CHR)(phen)]BF_4 \quad (2)$$

was observed in the ^1H NMR monitored experiments. Moreover, while attempts to obtain solid **5** failed, complex **4** and the neutral $[Pt(CH_2CHRPh)I(phen)]$ complexes [obtained by equation (3), R = H, **6** or R = Me, **7**] could be isolated and were fully characterized:



Scheme 1

$$[Pt(CH_2CHRPh)(CH_2{=}CHR)(phen)]BF_4 + KI \longrightarrow [Pt(CH_2CHRPh)I(phen)] + CH_2{=}CHR + KBF_4 \quad (3)$$

The reactive intermediates **2** and **3** were characterized using ^1H NMR spectroscopy with a stoichiometric amount of olefin in order to get sharp signals. The two halves of the phen ligand are not equivalent and the olefin protons couple to ^{195}Pt [*e.g.* for **2**, $\delta(C_2H_4)$ 4.85, $^2J_{Pt-H}$ 69 Hz]. A slight excess of olefin causes broadening of the signals and loss of the satellites, while the unsymmetric pattern is retained for the phen protons. This is consistent with the occurrence of a fast olefin exchange *via* an associative mechanism.[3]

The Markovnikov regiochemistry of propene insertion, *i.e.* formation of the $Pt{-}CH_2CH(Me)Ph$ fragment, is fully consistent with our previous findings.[1] It should be noted that under similar experimental conditions, the analogous palladium(II) complex $[PdPh(MeCN)(bipy)]^+$ showed a different behaviour when treated with propene.[4] In fact, initial formation of the $Pd{-}CH(Me)CH_2Ph$ moiety and its subsequent rearrangement to the Pd–CH(Et)Ph group was observed. The change of regiochemistry on going from Pt to Pd was explained[4] in terms of a stabilizing effect played by the phenyl group on a Pd-bound carbon.

Attempts to isolate the cationic *cis*-phenyl–ethene complex **2** in the solid state were unsuccessful. By adding diethyl ether to a nitromethane solution of the complex immediately after its formation, a yellow solid was obtained. This transformed into a reddish product in spite of careful working up in attempting isolation in the cold. The ^1H NMR spectrum of this material showed only the presence of $Pt{-}C_6H_4Et$-2 and Pt–CHMePh

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groupings. It should be noted that Pt^{II} complexes similar to **2** and **3**, but including alkyl instead of aryl groups, have already been isolated and characterized[3] and are stable towards the insertion migratory process. When a solution of **2** was allowed to stand at room temperature in the absence of free olefin, the signals attributable to the η^2-complex disappeared within 1 h but formation of the Pt–CH_2CH_2Ph fragment was not observed. Instead, a Pt–C_6H_4Et-2 moiety was detected [equation (4)] and [Pt(C_6H_4Et-2)(MeCN)(phen)]BF_4 **8** was

$$[PtPh(CH_2{=}CH_2)(phen)]^+ \longrightarrow \{Pt(C_6H_4Et\text{-}2)(phen)\}^+ \quad (4)$$

isolated in high yield after addition of MeCN [equation (5)]. We

$$\{Pt(C_6H_4Et\text{-}2)(phen)\}^+ + MeCN \longrightarrow [Pt(C_6H_4Et\text{-}2)(MeCN)(phen)]^+ \quad (5)$$

note that if complex **2** is allowed to stand for a longer time in solution in the absence of MeCN a slow decomposition takes place to a brown unidentified material and ethylbenzene. On the other hand, if 1 equivalent of MeCN is immediately added to a freshly prepared solution of **2**, [Pt(CH_2CH_2Ph)(MeCN)(phen)]BF_4 **9** is ultimately obtained [equation (6)]

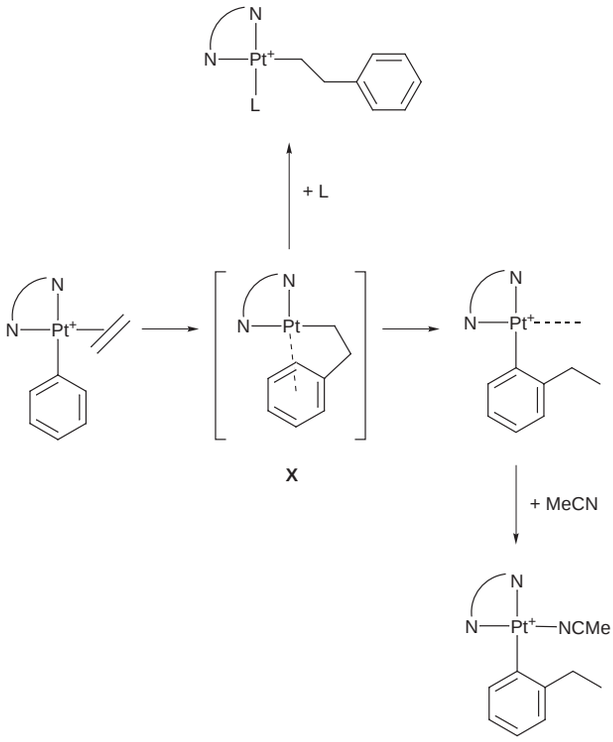
$$[PtPh(CH_2{=}CH_2)(phen)]^+ + MeCN \longrightarrow [Pt(CH_2CH_2Ph)(MeCN)(phen)]^+ \quad (6)$$

as the main reaction product and complex **8** forms only in small amounts.

Similar results were obtained in the case of the propene derivative **3** and the formation of the corresponding Pt–C_6H_4-($CHMe_2$)-2 moiety was clearly observed in the experiments performed in the absence of free MeCN. However, the longer reaction time (*ca.* 2.5 h) required to reduce substantially the amount of the starting η^2 species and a fast decomposition process of the isopropylphenyl derivative to isopropylbenzene prevented the isolation of a definite hydrocarbyl Pt^{II} complex analogous to **8**.

The ensemble of results suggests that the Pt–C_6H_4(CHRMe)-2 group derives from a rearrangement of the Pt–CH_2CHRPh fragment prompted by the absence of ligands able to fill the coordinative unsaturation following the 'usual' migratory insertion process (see species **X** in Scheme 2). Actually, the possibility of such a rearrangement was already presented in a previous work.[1] However, it looked to be only speculative, since the experimental conditions used did not provide clear evidence. In keeping with the above hypothesis, removal of iodine from the neutral [Pt(CH_2CHRPh)I(phen)] complexes (**6** or **7**) in the absence of potential ligands was followed by rapid formation of Pt–C_6H_4(CHRMe)-2 groups. It should be noted that if halogen removal from **6** was performed in the presence of MeCN, a mixture of **8** and **9** was obtained. On the other hand, only [Pt(CH_2CH_2Ph)(L)(phen)]BF_4 species (**4**, **10** or **11**; L = ethene, pyridine or triphenylphosphine) were isolated in the presence of L. Moreover, an analysis of these results discloses some significant differences with those previously obtained[1] by reacting the cationic substrates [PtR′(MeCN)(N,N-chelate)]$^+$ [R′ = C_6H_4-(OMe)-4] with the same olefins used here, *i.e.* ethene and propene. In the former case a markedly longer reaction time (up to 48 h) was necessary to complete the insertion–rearrangement process. Furthermore, only crowded N,N ligands afforded the Pt–C_6H_4(CHRMe)-2 moiety, while ligands similar to phen gave rise only to the corresponding Pt–CH_2-CHRR′ derivatives.

In order to rationalize these results, the reaction of [PtPh-(MeCN)(phen)]BF_4 **12** with ethene was reinvestigated (Scheme 3). A markedly slow reaction was observed and the first detectable product was **4**, irrespective of the C_2H_4–complex ratio. A nearly 50% conversion was evaluated after 5 h, and the reaction was complete after 24 h with quantitative formation of **4**, in the

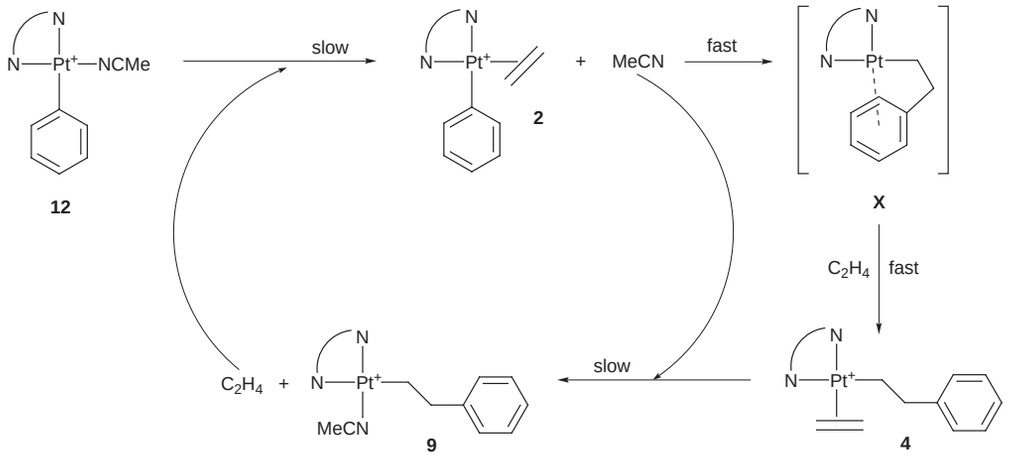


Scheme 2

case of excess ethene being present. Otherwise, besides **4**, an increasing amount of **9** was detected with time. These data suggest the occurrence of a preliminary ligand exchange step, in which acetonitrile is slowly substituted by ethene to form **2**.‡ Since insertion is faster than substitution, formation of species **X** occurs in all cases in the presence of free ethene. Therefore, according to the better ligand ability of ethene relative to MeCN, complex **4** is detected as the first reaction product even though an initial 1 : 1 ethene–Pt ratio is used. However, owing to the presence of free MeCN, an equilibrium process occurs involving **9** (release of ethene) allowing further formation of **4** until the overall reaction to give **4** and **9** is complete. It is noteworthy that the same final result, *i.e.* a mixture of **4** and **9**, was obtained by adding MeCN to a freshly prepared solution of **2** in which no excess ethene was present. In particular, after 30 min only **4** was detected in 50% yield based on Pt.

A suggestion arises by comparing this experiment with that performed in the absence of MeCN [equation (4)]. In the latter case, quantitative formation of Pt–C_6H_4Et-2 ensued. This means that, although (as noted above) acetonitrile does not coordinate to Pt in the early stages of the reaction, it must play an active role in inhibiting the rearrangement [Pt(CH_2CH_2Ph)-(phen)]$^+ \longrightarrow$ [Pt(C_6H_4Et-2)(phen)]$^+$. This inhibition would favor the intervention of unreacted ethene to form **4**, stable towards the rearrangement. Finally, we wish to comment on the observed preference[1] towards the formation of the Pt–C_6H_4Et-2 moiety in the case when the starting substrate contains an N,N-chelate ligand which favors the olefin uptake with formation of a five-coordinate adduct. This preference is largely reduced if the cationic complex [PtR′(C_2H_4)(MeCN)(N,N-chelate)]$^+$ is allowed to stand at a temperature higher than 273 K and/or free olefin is present in solution, and free MeCN also has an inhibitory effect. This behaviour can be rationalized on the basis of the existence of the two equilibria (7). In fact, if the

‡ It should be noted that when [PtR(MeCN)(N,N-chelate)]$^+$ (R = alkyl) species are allowed to stand at room temperature in an ethene-saturated solution, several hours are required to obtain a 50% substitution of MeCN for the olefin with formation of the corresponding species [PtR($CH_2{=}CH_2$)(N,N-chelate)]$^+$.



Scheme 3

$$[PtR'(C_2H_4)(N,N\text{-chelate})]^+ + MeCN \rightleftharpoons$$
II (*e.g.* **2**)
$$[PtR'(C_2H_4)(MeCN)(N,N\text{-chelate})]^+ \rightleftharpoons$$
I
$$[PtR'(MeCN)(N,N\text{-chelate})]^+ + C_2H_4 \quad (7)$$
III (*e.g.* **12**)

steric features of the N,N ligand lead to a fair stabilization of the species **I**, it can be inferred that both the dissociative equilibria are largely displaced towards the five-co-ordinate adduct. Therefore, at low temperature (<273 K) and in the absence of added MeCN and/or olefin, very small concentrations of the dissociation products are present in solution and the migratory insertion on the reactive species **II** can be followed by the intramolecular rearrangement to $Pt(C_6H_4Et\text{-}2)$ prior to the intermolecular addition of released MeCN or C_2H_4 stabilizing the $Pt(CH_2CH_2Ph)$ fragment. On raising the temperature, the increased dissociation of **I** affords a concentration of released ligands sufficient to cause a fair competition between the two processes, so that the preference towards the formation of a final $Pt(C_6H_4Et\text{-}2)$ containing product decreases. The same effect is observed when an excess of C_2H_4 is added to the reaction medium, as it does not disfavor the formation of **II** and its evolution to $Pt(CH_2CH_2Ph)$, but inhibits the subsequent rearrangement to $Pt(C_6H_4Et\text{-}2)$. On the other hand, a large excess of MeCN hinders the whole process shifting the equilibria far from **II**. On this basis, if species **I** contains an N,N ligand with moderate or quite poor five-co-ordination stabilizing properties, dissociation in solution to four-co-ordinate **II** and **III** is largely observed, irrespective of the temperature and of the presence of excess MeCN and/or olefin. As a consequence, only complexes containing the $Pt(CH_2CH_2Ph)$ moiety are obtained.

Conclusion

Two observations stemming from the above study deserve particular comment: (i) the metal-assisted olefin–hydrocarbyl migratory insertion process requires that these two groups are co-ordinated to the same metal center in adjacent positions. However, these intermediates are generally too labile to be detected or too inert to be reactive. The studied reaction system has offered the unique opportunity of identifying a *cis*-Pt^{II}–olefin–phenyl complex whose kinetic stability allows to gain unequivocal evidence both of its presence and of its subsequent transformation. (ii) The conversion of a cationic Pt^{II}–R′ substrate to a cationic Pt^{II}–R′(R)-2 (R′ = aryl, R = alkyl) product by alkene addition is a multi-step process which is affected in two opposite ways by an excess of olefin. The co-ordination of the alkene to the metal and the subsequent migratory-insertion step are clearly favored, while the rearrangement is hindered by a competitive co-ordination to the promoting metal center. The same inhibitory effect is observed if, operating with a stoichiometric amount of olefin, other σ-donor species are present in solution. Actually, the reported results give a further example of the peculiar ability of an unsaturated metal center in promoting unusual reaction paths.[5]

Experimental

Proton NMR spectra were recorded at 250 or 200 MHz on a Bruker AC-250 or a Varian XL-200 spectrometer, respectively. The spectra were recorded at 298 K in deuteriochloroform or deuterionitromethane. Proton NMR chemical shifts are reported in δ (ppm) relative to the solvent ($CDCl_3$, 7.26 ppm; CHD_2NO_2, 4.33 ppm), the abbreviation app defines apparent. The complex [PtPhCl(cod)] (cod = cycloocta-1,5-diene) was prepared according to literature methods.[6] Solvents and reagents were of AnalaR grade and were used without further purification.

Preparations

[PtPhCl(phen)]. A solution of phen (0.18 g, 1.0 mmol) in the minimum amount of methylene chloride was added at room temperature with stirring to a solution of [PtPhCl(cod)] (0.42 g, 1.0 mmol) in methylene chloride (10 ml). After 20 h of stirring the solid was collected and washed with methylene chloride (2 × 3 ml) and dried under vacuum (85–90% yield). The compound was too insoluble in common organic solvents for recording an NMR spectrum (Found: C, 44.28; H, 2.58; N, 5.80. Calc. for $C_{18}H_{13}ClN_2Pt$: C, 44.32; H, 2.69; N, 5.74%).

[PtPh(MeCN)(phen)]BF_4 12. A solution of $AgBF_4$ (0.20 g, 1.0 mmol) in acetonitrile (10 ml) was added at room temperature to a suspension of [PtPhCl(phen)] (0.49 g, 1.0 mmol) in anhydrous methylene chloride (25 ml) under a nitrogen atmosphere. After 24 h of stirring AgCl was removed by filtration and the solvent of the filtrate was evaporated to dryness. The product was obtained as a yellow glassy solid in nearly quantitative yield. ^{1}H NMR (200 MHz, CD_3NO_2): δ 9.25 [1 H, d, ^3J(HH) 5, H^2 of phen], 8.90 (2 H, dd, H^4, H^7 of phen), 8.70 [1 H, d, ^3J(PtH) 60, ^3J(HH) 5, H^9 of phen], 8.20 (1 H, dd, H^3 or H^8 of phen), 8.18 (2 H, s, H^5, H^6 of phen), 7.85 (1 H, dd, H^8 or H^3 of phen), 7.50 [2 H, d, ^3J(PtH) 50, ^3J(HH) 8, H^2, H^6 of Ph], 7.2 (3 H, m, H^3, H^4, H^5 of Ph), 2.73 (3 H, s, MeCN) (Found: C, 41.21; H, 2.84; N, 7.30. Calc. for $C_{20}H_{16}BF_4N_3Pt$: C, 41.40; H, 2.78; N, 7.24%).

[PtPhI(phen)] 1. A saturated solution of KI in water (4 ml) was added to [PtPh(MeCN)(phen)]BF_4 (0.49 g, 1.0 mmol) in nitromethane (4 ml). After 5 min of stirring the precipitated

orange product was collected and washed with acetone (3 × 2 ml), chloroform (2 × 2 mL) and dried under vacuum (85–90% yield). The compound was too insoluble in common organic solvents for recording an NMR spectrum (Found: C, 37.40; H, 2.18; N, 4.91. Calc. for $C_{18}H_{13}IN_2Pt$; C, 37.32; H, 2.26; N, 4.84%).

[Pt(CH$_2$CH$_2$Ph)(phen)(C$_2$H$_4$)]BF$_4$ 4. Solid [PtPhI(phen)] (0.58 g, 1.0 mmol) was added to a solution of $AgBF_4$ (0.20 g, 1.0 mmol) in dry nitromethane (6 ml) under an ethene atmosphere at 273 K. After 5 min of stirring AgI was removed by filtration through Celite under an ethene atmosphere and the solution was allowed to stand at room temperature for 24 h. The volume of the solution was reduced to 2 ml under vacuum. Yellow crystals of product were obtained by careful addition of diethyl ether (70–75% yield). ^{1}H NMR (200 MHz, CD_3NO_2): δ 9.30 [1 H, d, ^3J(PtH) 50, ^3J(HH) 5, H^2 of phen], 9.05 [1 H, d, ^3J(HH) 9, H^4 or H^7 of phen], 8.90 [1 H, d, ^3J(HH) 9, H^7 or H^4 of phen], 8.72 [1 H, d, ^3J(HH) 5, H^9 of phen], 8.30 (1 H, dd, H^3 or H^8 of phen), 8.25 (2 H, s, H^5, H^6 of phen), 8.15 (1 H, dd, H^8 or H^3 of phen), 7.39 [2 H, d, ^3J(HH) 7, H^2, H^6 of Ph], 7.25 (3 H, m, H^3, H^4, H^5 of Ph), 4.55 (4 H, br, C_2H_4), 2.89 [2 H, t, ^3J(HH) 7.5, Pt–CH$_2$C*H*$_2$Ph], 1.62 [2 H, t, ^2J(PtH) 75, Pt–C*H*$_2$CH$_2$Ph] (Found: C, 44.55; H, 3.42; N, 4.60. Calc. for $C_{22}H_{21}BF_4N_2Pt$: C, 44.39; H, 3.56; N, 4.71%).

[Pt(CH$_2$CHRPh)I(phen)] R = H, 6 or R = Me, 7. A saturated solution of KI in water (10 ml) was vigorously shaken with a solution of [Pt(phen)(CH$_2$CHRPh)(ethene)]BF$_4$ (1.0 mmol) in nitromethane (5 ml) and chloroform (10 ml). The organic phase was separated and the water phase was washed with chloroform (2 × 10 ml). The combined organic phases were dried over sodium sulfate and the solvents removed under vacuum to afford the product as an orange solid (80%). ^{1}H NMR (250 MHz, $CDCl_3$): **6** δ 10.30 [1 H, d, ^3J(HH) 6, H^2 of phen], 9.28 [1 H, d, ^3J(PtH) 60, ^3J(HH) 6, H^9 of phen], 8.72 [1 H, d, ^3J(HH) 10, H^4 or H^7 of phen], 8.51 [1 H, d, ^3J(HH) 10, H^7 or H^4 of phen], 7.99 (2 H, s, H^5, H^6 of phen), 7.85 (2 H, m, H^3, H^8 of phen), 7.40 [2 H, d, ^3J(HH) 7, H^2, H^6 of Ph], 7.19 (3 H, m, H^3, H^4, H^5 of Ph), 2.88 [2 H, t, ^3J(HH) 7.5, Pt–CH$_2$-C*H*$_2$Ph], 2.62 [2 H, t, ^2J(PtH) 80, Pt–C*H*$_2$CH$_2$Ph]; **7** δ 10.33 [1 H, d, ^3J(HH) 5, H^2 of phen], 9.17 [1 H, d, ^3J(PtH) 60, ^3J(HH) 5, H^9 of phen], 8.67 [1 H, d, ^3J(HH) 7.5, H^4 or H^7 of phen], 8.52 [1 H, d, ^3J(HH) 7.5, H^7 or H^4 of phen], 7.95 (2 H, s, H^5, H^6 of phen), 7.90 (1 H, m, H^3 or H^8 of phen), 7.73 (1 H, m, H^8 or H^3 of phen), 7.49 [2 H, d, ^3J(HH) 7.5, H^2, H^6 of Ph], 7.20 (3 H, m, H^3, H^4, H^5 of Ph), 3.12 [2 H, m, Pt–CH*HC*H(Me)Ph], 2.26 [1 H, d, ^2J(PtH) 95, ^3J(HH) 5, Pt–C*H*HCH(Me)Ph], 1.55 [3 H, d, ^3J(HH) 7.5, Me] (Found: C, 39.67; H, 2.91; N, 4.40. Calc. for $C_{20}H_{17}IN_2Pt$ **6**: C, 39.55; H, 2.82; N, 4.61. Found: C, 40.57; H, 2.98; N, 4.64. Calc. for $C_{21}H_{19}IN_2Pt$ **7**: C, 40.59; H, 3.08; N, 4.51%).

[Pt(C$_6$H$_4$Et-2)(MeCN)(phen)]BF$_4$ 8. Solid [PtPhI(phen)] (0.58 g, 1.0 mmol) was added to a solution of $AgBF_4$ (0.20 g, 1.0 mmol) in dry nitromethane (6 ml) containing ethene (*ca.* 1 mmol). After 5 min of stirring AgI was removed by filtration through Celite and the solution was stirred at room temperature for 1 h. Acetonitrile (0.041 g, 1.0 mmol) was added to the solution. After 1 h yellow crystals of **8** were obtained by careful addition of diethyl ether (85% yield). ^{1}H NMR (200 MHz, CD_3NO_2): δ 9.33 [1 H, d, ^3J(HH) 5, H^2 of phen], 8.97 [1 H, d, ^3J(HH) 8, H^4 or H^7 of phen], 8.86 [1 H, d, ^3J(HH) 8, H^7 or H^4 of phen], 8.40 [1 H, d, ^3J(HH) 5, H^9 of phen], 8.20 (2 H, m, H^5, H^6 of phen), 8.10 (1 H, dd, H^3 or H^8 of phen), 7.79 (1 H, dd, H^8 or H^3 of phen), 7.49 [1 H, d, ^3J(PtH) 40, ^3J(HH) 7.5, H^6 of Ph], 7.20 (3 H, m, H^3, H^4, H^5 of Ph), 3.02 [2 H, q, ^3J(HH) 8, C*H*$_2$Me], 2.73 (3 H, s, MeCN), 1.22 (3 H, t, CH$_2$*Me*) (Found: C, 43.52; H, 3.26; N, 7.03. Calc. for $C_{22}H_{20}BF_4N_3Pt$: C, 43.44; H, 3.31; N, 6.91%).

Monitoring of the reactions through ^{1}H NMR spectroscopy

A solution of $AgBF_4$ (0.007 g, 0.036 mmol) in deuterionitromethane (*ca.* 1 ml) containing a known amount of the appropriate reagent (acetonitrile, propene, ethene, pyridine or triphenylphosphine) was added to [PtRI(phen)] (R = Ph or CH$_2$CH$_2$Ph) (0.034 mmol). The mixture was filtered through Celite to remove AgI and the clear solution transferred into an NMR tube. Spectra were recorded until no more chemical changes were detected. Selected ^{1}H NMR (200 MHz, CD_3NO_2): **2** δ 9.0 (3 H, m, H^2, H^4, H^7 of phen), 8.81 [1 H, d, ^3J(HH) 5, H^9 of phen], 8.30 (2 H, s, H^5, H^6 of phen), 8.22 (1 H, dd, H^3 or H^8 of phen), 8.10 (1 H, dd, H^8 or H^3 of phen), 7.49 [2 H, d, ^3J(PtH) 40, ^3J(HH) 8, H^2, H^6 of Ph], 7.20 (3 H, m, H^3, H^4, H^5 of Ph), 4.80 [4 H, s, ^2J(PtH) 68, C_2H_4]; **3** δ 9.0 (4 H, m, H^2, H^4, H^7, H^9 of phen), 8.28 (2 H, s, H^5, H^6 of phen), 8.26 (1 H, dd, H^3 or H^8 of phen), 8.00 (1 H, dd, H^8 or H^3 of phen), 7.5 (2 H, m, H^2, H^6 of Ph), 7.20 (3 H, m, H^3, H^4, H^5 of Ph), 5.72 [1 H, app qnt, ^2J(PtH) 76, ^3J(HH) 7, CH$_2$=C*H*Me], 4.92 [1 H, d, ^2J(PtH) 76, ^3J(HH) 7, C*H*H=CHMe], 4.60 [1 H, d, ^2J(PtH) 64, ^3J(HH) 14, CH*H*=CHMe], 1.86 [3 H, d, ^3J(PtH) 60, CH$_2$=CH*Me*]; **5** δ 9.28 [1 H, d, ^3J(PtH) 45, ^3J(HH) 5, H^2 of phen], 9.00 [1 H, d, ^3J(HH) 8, H^4 or H^7 of phen], 8.90 [2 H, m, H^7 or H^4, H^9 of phen], 8.30 (2 H, s, H^5, H^6 of phen), 8.15 (2 H, m, H^3, H^8 of phen), 7.40 [2 H, d, ^3J(HH) 8, H^2, H^6 of Ph], 7.20 (3 H, m, H^3, H^4, H^5 of Ph), 5.80 (1 H, br, CH$_2$=C*H*Me), 4.75 (2 H, br, C*H*$_2$=CHMe), 3.11 [1 H, app sxt, ^3J(HH) 7, Pt–CH$_2$C*H*-(Me)Ph], 1.90–1.60 [2 H, m, Pt–C*H*$_2$CH(Me)Ph], 1.80 [3 H, d, ^3J(HH) 7, Pt–CH$_2$CH(*Me*)Ph], 1.55 [3 H, d, ^3J(PtH) 40, ^3J(HH) 8, CH$_2$=CH*Me*]; **9** δ 9.21 [1 H, d, ^3J(PtH) 48, ^3J(HH) 5, H^2 of phen], 9.05 [1 H, d, ^3J(HH) 5, H^9 of phen], 8.83 (2 H, dd, H^4, H^7 of phen), 8.14 (2 H, s, H^5, H^6 of phen), 8.10 (2 H, m, H^3, H^8 of phen), 7.49 [2 H, d, ^3J(HH) 6, H^2, H^6 of Ph], 7.38 (2 H, t, H^3, H^5 of Ph), 7.21 (1 H, t, H^4 of Ph), 2.84 [2 H, t, ^3J(HH) 5, Pt–CH$_2$C*H*$_2$Ph], 2.77 (3 H, s, MeCN), 2.38 [2 H, t, ^2J(PtH) 80, PtC*H*$_2$CH$_2$]; **10** δ 9.41 [1 H, d, ^3J(HH) 7, H^2 of phen], 2.75 [2 H, t, ^3J(HH) 7, Pt–CH$_2$C*H*$_2$Ph], 2.18 [2 H, t, ^2J(PtH) 65, Pt–C*H*$_2$CH$_2$Ph]; **11** δ 9.52 [1 H, d, ^3J(HH) 7, H^2 of phen], 2.55 [2 H, t, ^3J(HH) 7, Pt–CH$_2$C*H*$_2$Ph], 1.80 [2 H, t, ^2J(PtH) 63, Pt–C*H*$_2$CH$_2$Ph].

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