

# Preparation and Fluxional Behaviour of $\eta^3$ -Methylbenzyl Platinum and Palladium Complexes

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Protonation of the complexes  $[M(\eta^2\text{-CH}_2\text{=CHPh})(\text{L-L})]$  [ $M = \text{Pt}$ ,  $\text{L-L} = (\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_{11})_2$ ,  $n = 2$  or  $3$  (**1a** or **1c**),  $\text{Bu}^t_2\text{P}(\text{CH}_2)_n\text{PBu}^t_2$ ,  $n = 2$  or  $3$  (**1b** or **1d**), and  $\text{Bu}^t_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}^t_2$  (**1e**);  $M = \text{Pd}$ ,  $\text{L-L} = \text{Bu}^t_2\text{P}(\text{CH}_2)_n\text{PBu}^t_2$ ,  $n = 2$  or  $3$  (**1f** or **1g**) and  $\text{Bu}^t_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}^t_2$  (**1h**)] with  $\text{HBF}_4$  in diethyl ether affords a series of complexes,  $[M(\eta^3\text{-MeCHPh})(\text{L-L})][\text{BF}_4]$  (**2a-2h**), which contain an  $\eta^3$ -methylbenzyl ligand. The complexes **2a-2h** were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy and all except **2a** and **2f** were found to undergo intramolecular rearrangement in solution at or below room temperature. A mechanism is proposed, on the basis of variable-temperature NMR studies, that involves an  $\eta^3 \rightleftharpoons \sigma$  conversion coupled with single-bond rotation and  $\beta$ -elimination/hydride migration processes. For **2a-2e**, the influence of the chelating diphosphine on the nature of the  $\eta^3$ -benzyl interaction was investigated by  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopy and it was found that the largest diphosphines induce the most asymmetric  $\eta^3$  interaction. Similarly, it was found that the activation barriers to intramolecular rearrangement are lowest for the complexes with the largest diphosphine ligands.

The desire to understand more fully reactions in which C-H bonds form or are broken at transition-metal centres is a continuing challenge to chemists. Such reactions are known to be fundamental steps in a variety of catalytic reactions of industrial importance, *e.g.* hydrogenation, hydroformylation and alkene oligomerization. Many homogeneous reactions of hydrocarbons, catalysed by transition metals, are proposed to proceed *via* a mechanism that involves a co-ordinatively unsaturated intermediate,<sup>1</sup> *i.e.* a complex with a vacant co-ordination site. Such intermediates are very difficult to isolate or even identify because of the inherent reactivity which is associated with the co-ordinative unsaturation. However, a co-ordinatively unsaturated complex can gain stability through a secondary metal-ligand interaction. Many ligands can fill an adjacent vacant co-ordination site by co-ordinating another atom or atoms of the ligand to the metal, resulting in the formation of chelated complexes or the adoption of an alternative ligand bonding mode. For example, an organic ligand that usually forms a  $\sigma$  bond may change its bonding mode to  $\eta^n$  ( $n > 1$ ) in order to accommodate the unsaturation at the metal centre. Such switches in bonding have been reported for a variety of ligand types.<sup>2</sup> An example which is relevant to this paper is the benzyl ligand  $\text{CH}_2\text{Ph}$  which is capable of adopting a variety of metal-benzyl linkages and to date five different types have been reported.<sup>3</sup> A number of organometallic complexes have been synthesised containing a benzyl ligand in the  $\eta^3$  co-ordination mode and a variety of preparative routes have been developed.<sup>4-8</sup> Recently, our research has been concerned with the chemistry of platinum, palladium and nickel diphosphine complexes, lightly stabilized by a secondary interaction with the  $\beta$ -C-H bond of a co-ordinated alkyl group.<sup>9-12</sup> These compounds are generated by the protonation of platinum(0),<sup>9,11</sup> palladium(0)<sup>10,12</sup> or nickel(0)<sup>12</sup> alkene complexes, by the protonation of platinum(II) dialkyl complexes and by other methods.<sup>11,13</sup> Although considerable progress had been made in assessing the influence of the chelating diphosphine ligands on the bonding in these complexes, the effect of changing the substituents on the alkene group had not been explored. In order to investigate the effect of substituents on the alkyl group, a series of platinum(0) and palladium(0) diphosphine complexes were prepared with styrene as the co-ordinating alkene. However, the cationic species formed on protonation of the styrene complexes were

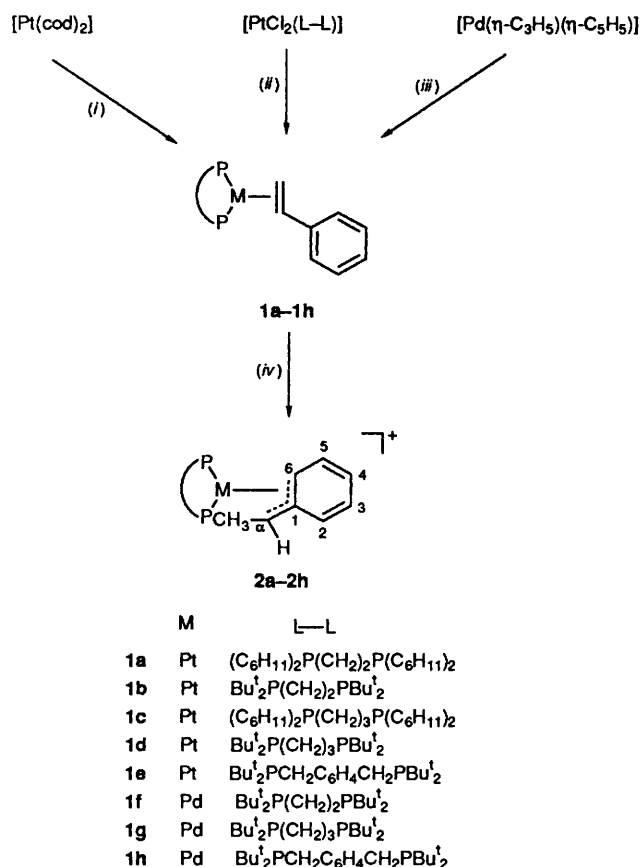
found to be stabilized by an  $\eta^3$ -methylbenzyl linkage rather than a  $\beta$ -agostic interaction. The influence of the diphosphine ligand on the metal-benzyl bond and on the dynamic processes that occur in these  $\eta^3$ -methylbenzyl complexes are discussed in this paper. Part of this work has been reported in preliminary form.<sup>14</sup>

## Results and Discussion

The complexes  $[\text{Pt}(\eta^2\text{-CH}_2\text{=CHPh})(\text{L-L})]$  **1a-1e** can, in general, be prepared by two methods (Scheme 1). First, the reaction of  $[\text{Pt}(\text{cod})_2]$  ( $\text{cod} = \text{cycloocta-1,5-diene}$ ) with the appropriate chelating diphosphine and excess of styrene, and secondly, by the reduction of  $[\text{Pt}(\text{L-L})\text{Cl}_2]$ , with Na/Hg amalgam in the presence of an excess of the appropriate styrene. The first method is applicable to the synthesis of all complexes except **1c**. In the latter case the styrene does not displace completely the second  $\text{cod}$  molecule and thus  $[\text{Pt}(\text{cod})(\text{L-L})]$  is produced as the major product.

The characterization of **1a-1e** is based on multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ ) spectroscopy (Tables 1-3). There are two multiplets in a 2:1 intensity ratio for the alkene protons and both signals are coupled to platinum-195. In principle there should be three signals as the three alkene protons are not equivalent, and indeed the analogous palladium complexes (**1f-1h**) show three distinct signals. Attempts to simplify the 2H multiplet by homonuclear decoupling thereby resolving the two chemical shifts have not been successful at 300 MHz. However, there is no doubt that there is a genuine coincidence of two inequivalent signals as the integrals are unambiguous and there are no other signals in the spectrum which are unaccounted for. Furthermore, we have also examined the spectra of the  $\text{Pt}^0$  complexes of various substituted styrenes<sup>15</sup> and these are very similar to those of **1a-1e** except that in some cases two separate resonances are just resolved for the  $\text{CH}_2$  protons.

The two non-equivalent protons with coincident signals have  $^1J(\text{PtH})$  values of approximately 62 Hz, whilst the other proton resonates at a higher frequency and with slightly smaller  $^1J(\text{PtH})$  values of  $54 \pm 1$  Hz. By analogy with free styrene and  $[\text{PtCl}_2(\text{CH}_2\text{=CHPh})_2]$ <sup>16</sup> the high frequency signal is assigned to the proton bonded to the phenyl-substituted alkene carbon



**Scheme 1** (i) Diphosphine, L-L, styrene, hexane, 273 K; (ii) 1% Na/Hg amalgam, styrene, thf, 298 K; (iii) L-L, styrene, hexane, 298 K; (iv) HBF<sub>4</sub>·OMe<sub>2</sub>, diethyl ether, 273 K

atom. Another interesting and characteristic feature of the <sup>1</sup>H NMR spectra of **1a–1e** is the shift to lower frequency of approximately 0.4 ppm of one of the tertiary butyl or cyclohexyl groups. This can be explained on the basis that one of the alkyl groups on the phosphine lies above the aromatic ring of styrene, which induces a low-frequency shift in the <sup>1</sup>H NMR resonance.

The <sup>13</sup>C-<sup>1</sup>H NMR spectra of **1a–1e** are also consistent with η<sup>2</sup> co-ordination of styrene. Signals for the chelating diphosphines are observed in the expected regions and although some of the phenyl resonances are obscured by solvent, the spectra show characteristic signals for the contact carbon atoms of the co-ordinated alkene. The <sup>31</sup>P-<sup>1</sup>H NMR spectra of **1a–1e** all show two resonances with <sup>195</sup>Pt satellites, as expected. However, complex **1e** and the palladium analogue **1h**, which have the bulky Bu'<sub>2</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PBu'<sub>2</sub> ligand, have broad <sup>31</sup>P NMR signals suggesting slow <sup>31</sup>P exchange at room temperature. A possible mechanism for the exchange would be rotation of styrene about the metal-alkene bond. Table 2 also illustrates how the <sup>1</sup>J(PtP) coupling constants increase with increasing bite angle of the bidentate diphosphine ligand.

The most suitable route to the complexes **1f–1h** was the reaction of [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(η<sup>3</sup>-C<sub>5</sub>H<sub>5</sub>)] with the appropriate diphosphine in the presence of an excess of styrene (Scheme 1). Multinuclear NMR studies of complexes **1f–1h** show similar features to those of the platinum analogues (Tables 1 and 2). In the <sup>1</sup>H NMR spectra of **1f–1h** there are four different Bu' signals with one of the resonances shifted to low frequency due to the proximity of a Bu' group to the phenyl ring of the co-ordinated styrene. Phenyl and diphosphine bridge protons are in the expected regions and there are three multiplets for the alkene protons. In the <sup>31</sup>P-<sup>1</sup>H NMR spectra, two phosphorus environments are observed indicating, as expected, the absence of fast rotation about the metal-alkene bond on the NMR time-scale (Table 2).

Protonation of [Pt(η<sup>2</sup>-CH<sub>2</sub>=CHPh)(L-L)] **1a–1e** with HBF<sub>4</sub>·OMe<sub>2</sub> at 273 K affords the complexes [Pt(η<sup>3</sup>-MeCHPh)(L-L)]-[BF<sub>4</sub>]<sup>-</sup> **2a–2e** in ca. 85% yield (Scheme 1). Whilst the complexes **2a–2c** are stable in CH<sub>2</sub>Cl<sub>2</sub> solution and can be recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O, **2d** undergoes partial dissociation at ambient temperature to form the dinuclear species [Pt<sub>2</sub>(μ-H)<sub>2</sub>{Bu'<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PBu'<sub>2</sub>}]<sub>2</sub>[BF<sub>4</sub>]<sub>2</sub>,<sup>17</sup> in equilibrium with the η<sup>3</sup>-methylbenzyl complex. However, **2e** decomposes in CH<sub>2</sub>Cl<sub>2</sub> above 250 K to form uncharacterized species, and therefore was not isolated. The palladium complexes [Pd(η<sup>3</sup>-MeCHPh)(L-L)]-[BF<sub>4</sub>]<sup>-</sup> (**2f–2h**) are similarly obtained by protonation of [Pd(η<sup>2</sup>-CH<sub>2</sub>=CHPh)(L-L)] (**1f–1h**).

Complexes **2a–2h** did not readily form crystals suitable for X-ray diffraction studies. However, suitable crystals were obtained for the 4-bromo analogue of **2d**, [Pt(η<sup>3</sup>-MeCHC<sub>6</sub>H<sub>4</sub>Br-4){Bu'<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PBu'<sub>2</sub>}] [BF<sub>4</sub>]<sup>-</sup> **3**. The solid-state structure of **3** has been reported previously<sup>14</sup> and revealed an η<sup>3</sup>-bonding mode for the MeCHC<sub>6</sub>H<sub>4</sub>Br-4 group. Furthermore, the methyl group was shown to occupy an *anti* position which is in contrast to the more normal *syn* orientation for substituents on η<sup>3</sup>-benzyl and -allyl ligands. The NMR spectroscopic data for complex **3** are entirely analogous to those of the unsubstituted compound **2d**, from which **3** differs only in the 4-bromo group on the phenyl ring.

The cations **2** are fluxional in solution at room temperature except for **2a** and **2f**. The static <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H NMR spectra of **2** are consistent with an η<sup>3</sup>-benzyl linkage and separate signals are observed for each of the phenyl carbon atoms and the attached protons. The carbon atoms C<sup>6</sup> can be assigned on the basis of the low frequency chemical shift (δ 106.0, **2a**; 97.4, **2b**; 107.0, **2c**; 103.1, **2d**; 104.4, **2f**), and C<sup>1</sup> by the low intensity of the signal due to long relaxation times and the reduced nuclear Overhauser effect (NOE). The <sup>1</sup>H and <sup>13</sup>C NMR spectra show signals for inequivalent tertiary butyl or cyclohexyl groups. As with the M<sup>0</sup> styrene complexes **1a–1h**, the <sup>1</sup>H NMR spectra show one of these resonances shifted to low frequency by approximately 0.4 ppm due to the proximity of the phenyl group. A signal characteristic of a benzyl proton is also observed (δ 3.31, **2a**; 4.42, **2b**; 3.49, **2c**; 4.55, **2d**; 4.21, **2e**; 4.98, **2f**; 5.24, **2g**; 5.25, **2h**). The <sup>31</sup>P-<sup>1</sup>H NMR spectra of **2a–2e** show two resonances for the inequivalent phosphorus nuclei, one of which has a large value of <sup>1</sup>J(PtP) consistent with a phosphorus atom lying *trans* to a weakly co-ordinating phenyl group, whereas the other displays smaller values of <sup>1</sup>J(PtP) and may be assigned to a phosphorus *trans* to the strongly bonded C<sub>α</sub>. The large differences observed in <sup>1</sup>J(PtP) are mirrored in the crystallographic results for **3** which give a large difference in the two Pt-P bond lengths.<sup>14</sup> The <sup>31</sup>P-<sup>1</sup>H NMR spectra for **2g** and **2h** also show, as expected, two inequivalent phosphorus nuclei (Table 2).

Although the X-ray results establish that an *anti* configuration of the methylbenzyl ligand is possible, it cannot be assumed that the same structure is necessarily adopted in solution. Nevertheless, the <sup>1</sup>H NMR chemical shift of the benzyl proton in complexes **2b** and **2d–2h** all strongly suggest that this proton must occupy the *syn* position. The cases of **2a** and **2c** are less clear as both these complexes have benzyl proton shifts 1 ppm lower than the other complexes. Furthermore, the chemical shift of the phenyl carbon atoms C<sup>2</sup> (**2a**, δ 112.5 and **2c**, 114.6) are lower than expected and rather different to the values observed for **2b** and **2d** (δ 127.9 and 128.8 respectively).

It has been established that η<sup>3</sup>-benzyl complexes can undergo rapid [1,5] shifts<sup>6</sup> and it could be argued that **2a** and **2c** are present in solution as a mixture of *syn* and *anti* isomers which are interconverting rapidly on the NMR time-scale. However, the proton NMR spectrum of **2a** shows very little sensitivity to temperature and in particular the benzyl proton signal moves only very slightly from δ 3.31 at 293 K to 3.20 at 193 K. Unfortunately, as discussed below, the signal for the methyl group is obscured by the Bu' signals and no useful information was obtained from that source. There is also little change

**Table 1** Proton and  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR data for the complexes  $[\text{M}(\eta^2\text{-CH}_2=\text{CHPh})(\text{L-L})]$  [ $\text{M} = \text{Pt}$  (1a–1e) or  $\text{Pd}$  (1f–1h)] and  $[\text{M}(\eta^3\text{-MeC}_6\text{H}_4\text{Ph})(\text{L-L})][\text{BF}_4]$  [ $\text{M} = \text{Pt}$  (2a–2c and 2e) or  $\text{Pd}$  (2f–2h)]<sup>a</sup>

Complex	$^1\text{H}$ ( $\delta$ )	$^{13}\text{C}$ - $\{^1\text{H}\}$ ( $\delta$ )
<b>1a</b>	0.9–1.3 (br, 22 H, $\text{C}_6\text{H}_{11}$ ), 1.5–1.8 (br, 22 H, $\text{C}_6\text{H}_{11}$ ), 1.98 (br, 4 H, $\text{PCH}_2\text{CH}_2\text{P}$ ), 2.75 [m, 2 H, $J(\text{PtH})$ 54, $\text{CH}_2=\text{CH}$ ], 4.10 [m, 1 H, $J(\text{PtH})$ 63, $\text{CH}_2=\text{CH}$ ], 6.8–6.9 (br m, 1 H, Ph), 7.17 (m, 2 H, Ph) 7.18 [t, 2 H, $J(\text{HH})$ 7.6, Ph]	24.5 [dd, $^1J(\text{PC})$ 60, $^2J(\text{PC})$ 25, $\text{PCH}_2\text{CH}_2\text{P}$ ], 24.5 [dd, $^1J(\text{PC})$ 53, $^2J(\text{PC})$ 27, $\text{PCH}_2\text{CH}_2\text{P}$ ], 26.3–30.2 (m, $\text{C}_6\text{H}_{11}$ ), 35.1 [dd, partially obscured, $J(\text{P}_{\text{trans}}\text{C})$ 24, $J(\text{P}_{\text{cis}}\text{C})$ 4, alkene], 35.1–35.2 (br, m, $\text{C}_6\text{H}_{11}$ ), 44.7 [dd, $J(\text{PtC})$ 214, $J(\text{P}_{\text{trans}}\text{C})$ 35, $J(\text{P}_{\text{cis}}\text{C})$ 6, alkene], 121.5 (s, Ph), 125.3 [d, $J(\text{PtC})$ 18, $J(\text{PC})$ 3, Ph], 127.6 (s, Ph), 151.8 [d, $J(\text{PtC})$ 49, $J(\text{PC})$ , <i>ipso</i> -Ph]
<b>1b</b>	0.75 [d, 9 H, $J(\text{PH})$ 12.5, $\text{C}(\text{CH}_3)_3$ ], 1.11 [d, 9 H, $J(\text{PH})$ 12.2, $\text{C}(\text{CH}_3)_3$ ], 1.11 [d, 9 H, $J(\text{PH})$ 11.0, $\text{C}(\text{CH}_3)_3$ ], 1.15 [d, 9 H, $J(\text{PH})$ 12.4, $\text{C}(\text{CH}_3)_3$ ], 1.2–1.4 (br, m, 4 H, $\text{PCH}_2\text{CH}_2\text{P}$ ), 2.69 [m, 2 H, $J(\text{PtH})$ 54, $\text{CH}_2=\text{CH}$ ], 3.79 [m, 1 H, $J(\text{PtH})$ 64, $\text{CH}_2=\text{CH}$ ], 6.83 (m, 1 H, Ph), 7.18 (s, 4 H, Ph)	26.0 (m, $\text{PCH}_2\text{CH}_2\text{P}$ ), 29.6 [dd, partially obscured, $J(\text{PtC})$ 226, $J(\text{P}_{\text{trans}}\text{C})$ 38, $J(\text{P}_{\text{cis}}\text{C})$ 6, alkene], 29.7 [d, $J(\text{PC})$ 6, $\text{C}(\text{CH}_3)_3$ ], 30.1 [d, $J(\text{PC})$ 6, $\text{C}(\text{CH}_3)_3$ ], 30.3 [d, $J(\text{PC})$ 7, $\text{C}(\text{CH}_3)_3$ ], 30.5 [d, $J(\text{PC})$ 7, $\text{C}(\text{CH}_3)_3$ ], 35.0 [br m, $\text{C}(\text{CH}_3)_3$ ], 45.2 [dd, $J(\text{PtC})$ 223, $J(\text{P}_{\text{trans}}\text{C})$ 36, $J(\text{P}_{\text{cis}}\text{C})$ 5, alkene], 121.6 (s, Ph), 125.4 [d, $J(\text{PtC})$ 20, $J(\text{PC})$ 3, Ph], 127.6 (s, Ph), 152.0 [d, $J(\text{PtC})$ 53, $J(\text{PC})$ 7, <i>ipso</i> -Ph]
<b>1c</b>	0.8–2.1 (br, 44 H, $\text{C}_6\text{H}_{11}$ ), 2.2–3.0 (br m, 8 H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ , $\text{CH}_2=\text{CH}$ ), 3.86 [m, 1 H, $J(\text{PtH})$ 62, $\text{CH}_2=\text{CH}$ ], 6.88 [t, 1 H, $J(\text{HH})$ 6.8, Ph], 7.00–7.28 (m, 4 H, Ph)	21.5 [dd, $^1J(\text{PC})$ 19, $^2J(\text{PC})$ 7, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 25.1–30.0 (m, $\text{C}_6\text{H}_{11}$ , $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ , alkene), 35.3 (m, $\text{C}_6\text{H}_{11}$ ), 38.0 (m, $\text{C}_6\text{H}_{11}$ ), 44.6 [dd, $J(\text{PtC})$ 210, $J(\text{P}_{\text{trans}}\text{C})$ 33, $J(\text{P}_{\text{cis}}\text{C})$ 7, alkene], 121.7 (s, Ph), 125.4 [d, $J(\text{PtC})$ 19, $J(\text{PC})$ 4, Ph], 151.5 [d, $J(\text{PtC})$ 46, $J(\text{PC})$ 6, <i>ipso</i> -Ph]
<b>1d</b>	0.73 [d, 9 H, $J(\text{PH})$ 12.3, $\text{C}(\text{CH}_3)_3$ ], 1.13 [d, 9 H, $J(\text{PH})$ 12.0, $\text{C}(\text{CH}_3)_3$ ], 1.16 [d, 9 H, $J(\text{PH})$ 11.7, $\text{C}(\text{CH}_3)_3$ ], 1.20 [d, 9 H, $J(\text{PH})$ 12.0, $\text{C}(\text{CH}_3)_3$ ], 1.3–1.5 (br m, 4 H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 1.6–1.9 (br m, 2 H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 2.62 [m, 2 H, $J(\text{PtH})$ 55, $\text{CH}_2=\text{CH}$ ], 3.53 [m, 1 H, $J(\text{PtH})$ 60, $\text{CH}_2=\text{CH}$ ], 6.86 (m, 1 H, Ph), 7.17 (s, 2 H, Ph), 7.19 (s, 2 H, Ph)	21.0 [d, $J(\text{PC})$ 13, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 21.5 [d, $J(\text{PC})$ 16, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 26.0 [s, $J(\text{PtC})$ 35, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 29.7 [d, $J(\text{PC})$ 7, $\text{C}(\text{CH}_3)_3$ ], 29.8 [d, $J(\text{PC})$ 6, $\text{C}(\text{CH}_3)_3$ ], 30.0 [d, $J(\text{PC})$ 6, $\text{C}(\text{CH}_3)_3$ ], 32.9 [dd, $J(\text{PtC})$ 220, $J(\text{P}_{\text{trans}}\text{C})$ 39, $J(\text{P}_{\text{cis}}\text{C})$ 6, $\text{CH}_2=\text{CH}$ ], 35.0–35.2 [br m, $\text{C}(\text{CH}_3)_3$ ], 45.6 [dd, $J(\text{PtC})$ 228, $J(\text{P}_{\text{trans}}\text{C})$ 35, $J(\text{P}_{\text{cis}}\text{C})$ 6, $\text{CH}_2=\text{CH}$ ], 122.2 (s, Ph), 125.9 [d, $J(\text{PtC})$ 21, $J(\text{PC})$ 3, Ph], 127.6 (s, Ph), 152.1 [d, $J(\text{PtC})$ 49, $J(\text{PC})$ 6, <i>ipso</i> -Ph]
<b>1e</b>	0.86 [vt, 9 H $ J(\text{PH}) + J(\text{P'H}) $ 12.6, $\text{C}(\text{CH}_3)_3$ ], 1.21 [vt, 9 H, $ J(\text{PH}) + J(\text{P'H}) $ 12.6, $\text{C}(\text{CH}_3)_3$ ], 1.26 [vt, 9 H, $ J(\text{PH}) + J(\text{P'H}) $ 12.2, $\text{C}(\text{CH}_3)_3$ ], 1.30 [vt, 9 H, $ J(\text{PH}) + J(\text{P'H}) $ 12.1, $\text{C}(\text{CH}_3)_3$ ], 2.62 [br m, 2 H, $J(\text{PtH})$ 54, $\text{CH}_2=\text{CH}$ ], 3.3–3.6 (br m, 5 H, $\text{CH}_2=\text{CH}$ , $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 6.94 (m, 3 H, Ph), 7.1–7.2 (br m, 6 H, Ph, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ )	30.0 [d, $J(\text{PC})$ 5, $\text{C}(\text{CH}_3)_3$ ], 30.3 [s, $\text{C}(\text{CH}_3)_3$ ], 30.6 [s, $\text{C}(\text{CH}_3)_3$ ], 32.4 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 33.1 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 35.5 [d, $J(\text{PtC})$ 212, $J(\text{PC})$ 31, alkene], 37.8 [br m, $\text{C}(\text{CH}_3)_3$ ], 46.6 [d, $J(\text{PtC})$ 232, $J(\text{PC})$ 29, alkene], 122.7 (s, $\text{CH}_2=\text{CHPh}$ ), 125.8 [d, $J(\text{PC})$ 3, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ], 126.3 [s, $J(\text{PtC})$ 22, $\text{CH}_2=\text{CHPh}$ ], 133.2 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 133.5 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 138.2 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 138.7 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 151.5 [s, $J(\text{PtC})$ 43, <i>ipso</i> - $\text{CH}_2=\text{CHPh}$ ]
<b>1f</b>	0.75 [d, 9 H, $J(\text{PH})$ 12.2, $\text{C}(\text{CH}_3)_3$ ], 1.09 [d, 9 H, $J(\text{PH})$ 12.0, $\text{C}(\text{CH}_3)_3$ ], 1.11 [d, 9 H, $J(\text{PH})$ 11.8, $\text{C}(\text{CH}_3)_3$ ], 1.14 [d, 9 H, $J(\text{PH})$ 12.0, $\text{C}(\text{CH}_3)_3$ ], 1.2–1.5 (br m, 4 H, $\text{PCH}_2\text{CH}_2\text{P}$ ), 3.19 (m, 1 H, $\text{CH}_2=\text{CH}$ ), 3.45 (m, 1 H, $\text{CH}_2=\text{CH}$ ), 4.69 (m, 1 H, $\text{CH}_2=\text{CH}$ ), 6.89 [t, 1 H, $J(\text{HH})$ 7.3, Ph], 7.16 [t, 2 H, $J(\text{HH})$ 7.5, Ph], 7.33 [d, 2 H, $J(\text{HH})$ 7.8, Ph]	23.7 [dd, $^1J(\text{PC})$ 19, $^2J(\text{PC})$ 10, $\text{PCH}_2\text{CH}_2\text{P}$ ], 24.1 [dd, $^1J(\text{PC})$ 20, $^2J(\text{PC})$ 10, $\text{PCH}_2\text{CH}_2\text{P}$ ], 29.8 [d, $J(\text{PC})$ 9, $\text{C}(\text{CH}_3)_3$ ], 30.3 [d, $J(\text{PC})$ 9, $\text{C}(\text{CH}_3)_3$ ], 30.5 [d, $J(\text{PC})$ 11, $\text{C}(\text{CH}_3)_3$ ], 30.7 [d, $J(\text{PC})$ 11, $\text{C}(\text{CH}_3)_3$ ], 34.1 [d, $J(\text{PC})$ 18, $\text{C}(\text{CH}_3)_3$ ], 40.5 [dd, $J(\text{P}_{\text{trans}}\text{C})$ 27, $J(\text{P}_{\text{cis}}\text{C})$ 5, alkene], 60.1 [dd, $J(\text{P}_{\text{trans}}\text{C})$ 25, $J(\text{P}_{\text{cis}}\text{C})$ 5, alkene], 121.6 [d, $J(\text{PC})$ 3, Ph], 124.5 [d, $J(\text{PC})$ 3, Ph], 149.5 (s, <i>ipso</i> -Ph)
<b>1g</b>	0.75 [d, 9 H, $J(\text{PH})$ 12.0, $\text{C}(\text{CH}_3)_3$ ], 1.11 [d, 9 H, $J(\text{PH})$ 11.8, $\text{C}(\text{CH}_3)_3$ ], 1.15 [d, 9 H, $J(\text{PH})$ 11.6, $\text{C}(\text{CH}_3)_3$ ], 1.19 [d, 9 H, $J(\text{PH})$ 11.8, $\text{C}(\text{CH}_3)_3$ ], 1.24–1.42 (br m, 4 H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 1.66–1.80 (br m, 2 H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 3.14 (m, 1 H, $\text{CH}_2=\text{CH}$ ), 3.33 (m, 1 H, $\text{CH}_2=\text{CH}$ ), 4.37 (m, 1 H, $\text{CH}_2=\text{CH}$ ), 6.89 [t, 1 H, $J(\text{HH})$ 7.3, Ph], 7.16 [t, partially obscured by solvent, 2 H, $J(\text{HH})$ 7.6, Ph], 7.29–7.32 (m, 2 H, Ph)	22.5 [d, $J(\text{PC})$ 16, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 24.5 [d, $J(\text{PC})$ 8, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 24.6 [d, $J(\text{PC})$ 6, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 29.8 [d, $J(\text{PC})$ 7, $\text{C}(\text{CH}_3)_3$ ], 30.0 [d, $J(\text{PC})$ 7, $\text{C}(\text{CH}_3)_3$ ], 30.2 [d, $J(\text{PC})$ 8, $\text{C}(\text{CH}_3)_3$ ], 34.4 [s, $\text{C}(\text{CH}_3)_3$ ], 35.0 [s, $\text{C}(\text{CH}_3)_3$ ], 44.1 [dd, $J(\text{P}_{\text{trans}}\text{C})$ 25, $J(\text{P}_{\text{cis}}\text{C})$ 6, alkene], 60.5 [dd, $J(\text{P}_{\text{trans}}\text{C})$ 24, $J(\text{P}_{\text{cis}}\text{C})$ 5, alkene], 122.1 (s, Ph), 125.0 (s, Ph), 128.1 (s, Ph), 149.8 (s, <i>ipso</i> -Ph)
<b>1h</b>	0.83 [d, 9 H, $J(\text{PH})$ 11.9, $\text{C}(\text{CH}_3)_3$ ], 1.19 [d, 9 H, $J(\text{PH})$ 11.8, $\text{C}(\text{CH}_3)_3$ ], 1.25 [d, 9 H, $J(\text{PH})$ 11.5, $\text{C}(\text{CH}_3)_3$ ], 1.29 [d, 9 H, $J(\text{PH})$ 10.9, $\text{C}(\text{CH}_3)_3$ ], 3.10–3.34 (br m, 6 H, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ , $\text{CH}_2=\text{CH}$ ), 4.25 (m, 1 H, $\text{CH}_2=\text{CH}$ ), 6.76–7.28 (m, 9 H, Ph, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ )	30.4–30.9 [br m, $\text{C}(\text{CH}_3)_3$ ], 31.7 [d, $J(\text{PC})$ 25, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ], 35.4 [s, $\text{C}(\text{CH}_3)_3$ ], 36.3 [s, $\text{C}(\text{CH}_3)_3$ ], 43.9 [dd, $J(\text{P}_{\text{trans}}\text{C})$ 25, $J(\text{P}_{\text{cis}}\text{C})$ 6, alkene], 62.1 [dd, $J(\text{P}_{\text{trans}}\text{C})$ 23, $J(\text{P}_{\text{cis}}\text{C})$ 4, alkene], 122.6 (s, Ph), 125.4 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 125.8 (s, Ph), 128.0 (s, partially obscured by solvent, Ph), 133.4 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 133.6 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 138.7 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 139.1 (s, $\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}$ ), 149.4 (s, <i>ipso</i> -Ph)
<b>2a</b>	0.5–1.5 (br, 22 H, $\text{C}_6\text{H}_{11}$ ), 1.5–2.1 (br, 27 H, $\text{C}_6\text{H}_{11}$ , $\text{PCH}_2\text{CH}_2\text{P}$ , $\text{CH}_3\text{CHPh}$ ), 2.2–2.4 (br m, 2 H, $\text{PCH}_2\text{CH}_2\text{P}$ ), 3.31 (m, 1 H, $\text{CH}_3\text{CHPh}$ ), 6.08 [m, 1 H, $J(\text{PtH})$ 23, Ph, $\text{H}^6$ ], 6.66 [d, 1 H, $J(\text{HH})$ 7.8, Ph], 7.11 [t, 1 H, $J(\text{HH})$ 3.0 and 1.1, Ph], 7.67 (m, 2 H, Ph)	15.2 (s, $\text{CH}_3\text{CHPh}$ ), 20.9 [dd, $J(\text{PtC})$ 90, $^1J(\text{PC})$ 32, $^2J(\text{PC})$ 4, $\text{PCH}_2\text{CH}_2\text{P}$ ], 24.3 [dd, $J(\text{PtC})$ 65, $^1J(\text{PC})$ 35, $^2J(\text{PC})$ 11, $\text{PCH}_2\text{CH}_2\text{P}$ ], 26.0–27.8 (m, $\text{C}_6\text{H}_{11}$ ), 28.5–30.4 (m, $\text{C}_6\text{H}_{11}$ ), 33.9 [d, $J(\text{PC})$ 27, $\text{C}_6\text{H}_{11}$ ], 34.0 [d, $J(\text{PC})$ 28, $\text{C}_6\text{H}_{11}$ ], 34.3 [d, $J(\text{PtC})$ 60, $J(\text{PC})$ 32, $\text{C}_6\text{H}_{11}$ ], 36.8 [d, $J(\text{PtC})$ 55, $J(\text{PC})$ 33, $\text{C}_6\text{H}_{11}$ ], 52.8 [dd, partially obscured, $J(\text{PtC})$ 167, $J(\text{PC})$ 44, $\text{CH}_3\text{CHC}_6\text{H}_5$ ], 106.0 [d, $J(\text{PtC})$ 23, $J(\text{PC})$ 11, Ph, $\text{C}^6$ ], 112.5 [d, $J(\text{PtC})$ 28, $J(\text{PC})$ 6, Ph, $\text{C}^2$ ], 120.5 [d, $J(\text{PC})$ 6, Ph, $\text{C}^1$ ], 127.9 (s, Ph, $\text{C}^4$ ), 135.3 [s, $J(\text{PtC})$ 20, Ph, $\text{C}^5$ ], 136.1 (s, Ph, $\text{C}^3$ )
<b>2b</b>	0.84 [d, 9 H, $J(\text{PH})$ 14.1, $\text{C}(\text{CH}_3)_3$ ], 1.23 [d, 9 H, $J(\text{PH})$ 14.7, $\text{C}(\text{CH}_3)_3$ ], 1.38 [d, 9 H, $J(\text{PH})$ 14.0, $\text{C}(\text{CH}_3)_3$ ], 1.44 [d, 9 H, $J(\text{PH})$ 14.7, $\text{C}(\text{CH}_3)_3$ ], 1.50 (m, partially obscured, 3 H, $\text{CH}_3\text{CHPh}$ ), 1.9–2.2 (br m, 2 H, $\text{PCH}_2\text{CH}_2\text{P}$ ), 2.2–2.5 (br m, 2 H, $\text{PCH}_2\text{CH}_2\text{P}$ ), 4.42 (m, 1 H, $\text{CH}_3\text{CHPh}$ ), 6.29 (br s, 1 H, Ph, $\text{H}^6$ ), 6.77 (br s, 1 H, Ph), 7.24 (m, 1 H, Ph, $\text{H}^4$ ), 7.46 (br s, 1 H, Ph), 7.89 (br s, 1 H, Ph)	17.7 [d, $J(\text{PtC})$ 22, $J(\text{PC})$ 6, $\text{CH}_3\text{CHPh}$ ], 22.4 [dd, $J(\text{PtC})$ 83, $^1J(\text{PC})$ 26, $^2J(\text{PC})$ 4, $\text{PCH}_2\text{CH}_2\text{P}$ ], 26.1 [dd, $J(\text{PtC})$ 85, $^1J(\text{PC})$ 30, $^2J(\text{PC})$ 8, $\text{PCH}_2\text{CH}_2\text{P}$ ], 29.6 [d, $J(\text{PC})$ 4, $\text{C}(\text{CH}_3)_3$ ], 30.0 [d, $J(\text{PC})$ 4, $\text{C}(\text{CH}_3)_3$ ], 30.4 [d, $J(\text{PC})$ 4, $\text{C}(\text{CH}_3)_3$ ], 36.7 [d, $J(\text{PC})$ 20, $\text{C}(\text{CH}_3)_3$ ], 38.2 [d, $J(\text{PC})$ 27, $\text{C}(\text{CH}_3)_3$ ], 39.1 [d, $J(\text{PC})$ 26, $\text{C}(\text{CH}_3)_3$ ], 51.2 [d, $J(\text{PtC})$ 179, $J(\text{PC})$ 43, $\text{CH}_3\text{CHPh}$ ], 97.4 (br, Ph, $\text{C}^6$ ), 118.2 (s, Ph, $\text{C}^1$ ), 127.9 (br, Ph, $\text{C}^2$ ), 129.6 [d, $J(\text{PC})$ 3, Ph, $\text{C}^4$ ], 133.8 (br, Ph, $\text{C}^3$ or $\text{C}^5$ ), 137.3 (br, Ph, $\text{C}^3$ or $\text{C}^5$ )

Table 1 (continued)

2c	0.8–1.5 (br, 22 H, C <sub>6</sub> H <sub>11</sub> ), 1.5–2.1 (br, 29 H, C <sub>6</sub> H <sub>11</sub> , PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P, CH <sub>3</sub> CHPh), 2.1–2.2 (br m, 2 H, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P), 3.49 (m, 1 H, CH <sub>3</sub> CHPh), 6.32 (br s, 1 H, Ph, H <sup>o</sup> ), 6.47 (br s, 1 H, Ph), 7.21 (br m, 1 H, Ph), 7.25 (m, 1 H, Ph, H <sup>a</sup> ), 7.60 (br m, 1 H, Ph)	15.5 [d, J(PC) 4, CH <sub>3</sub> CHPh], 17.4 [d, J(PtC) 32, J(PC) 28, PCH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> P], 18.6 [dd, J(PtC) 35, <sup>1</sup> J(PC) 34, <sup>2</sup> J(PC) 6, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P], 23.1 [s, J(PtC) 60, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P], 26.2 (s), 26.8 (s), 27.0 (s), 27.4 (s), 27.6 (s), 28.3 [d, J(PtC) 42, J(PC) 6], 29.0 [s, J(PtC) 13], 29.5 [s, J(PtC) 20], 30.0 (s), 30.3 (s) and 31.4 [s, J(PtC) 32] (all cyclohexyl CH <sub>2</sub> carbons), 34.2 [d, J(PtC) 16, J(PC) 28, C <sub>6</sub> H <sub>11</sub> ], 35.8 [d, J(PtC) 14, J(PC) 29, C <sub>6</sub> H <sub>11</sub> ], 36.5 [d, J(PtC) 47, J(PC) 31, C <sub>6</sub> H <sub>11</sub> ], 40.0 [d, J(PtC) 49, J(PC) 34, C <sub>6</sub> H <sub>11</sub> ], 52.9 [d, partially obscured, J(PtC) 163, J(PC) 41, CH <sub>3</sub> CHPh], 107.0 [br d, J(PtC) 40, J(PC) 8, Ph, C <sup>6</sup> ], 114.6 [br s, J(PtC) 35, Ph, C <sup>2</sup> ], 119.2 [d, J(PC) 4, Ph, C <sup>1</sup> ], 129.4 [d, J(PtC) 20, J(PC) 4, Ph, C <sup>4</sup> ], 134.7 (br s, Ph, C <sup>3</sup> or C <sup>5</sup> ), 135.4 (br s, Ph, C <sup>3</sup> or C <sup>5</sup> )
2e <sup>b</sup>	0.89 [br s, 9 H, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.17 [br s, 9 H, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.41 [d, 9 H, J(PH) 13.6, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.50 [d, 9 H, J(PH) 14.3, C(CH <sub>3</sub> ) <sub>3</sub> ], 3.5–3.9 [br m, 4 H, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P], 4.21 (m, 1 H, CH <sub>3</sub> CHPh), 7.11–7.56 (m, 9 H, Ph, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P)	2.02 (s, CH <sub>3</sub> CHPh), 28.1 (m, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 29.4 [s, C(CH <sub>3</sub> ) <sub>3</sub> ], 29.9 [s, C(CH <sub>3</sub> ) <sub>3</sub> ], 30.5 [s, C(CH <sub>3</sub> ) <sub>3</sub> ], 37.6 [br s, C(CH <sub>3</sub> ) <sub>3</sub> ], 38.8 [br s, C(CH <sub>3</sub> ) <sub>3</sub> ], 40.7 [d, J(PC) 25, C(CH <sub>3</sub> ) <sub>3</sub> ], 41.4 [br s, C(CH <sub>3</sub> ) <sub>3</sub> ], 44.6 [d, J(PtC) 162, J(PC) 34, CH <sub>3</sub> CHPh], 118.0 (br, Ph), 127.4 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 127.6 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 130.8 (br s, Ph), 132.6 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 133.2 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 133.5 (br s, Ph), 134.4 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 134.6 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P)
2f	0.83 [d, 9 H, J(PH) 13.7, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.25 [d, 9 H, J(PH) 14.2, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.33 [d, 9 H, J(PH) 13.6, C(CH <sub>3</sub> ) <sub>3</sub> ], ca. 1.4 (partially obscured, 3 H, CH <sub>3</sub> CHPh), 1.41 [d, 9 H, J(PH) 14.3, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.95–2.18 (br m, 2 H, PCH <sub>2</sub> CH <sub>2</sub> P), 2.20–2.45 (br m, 2 H, PCH <sub>2</sub> CH <sub>2</sub> P), 4.98 (m, 1 H, CH <sub>3</sub> CHPh), 6.57 [t, 1 H, J(HH) 6.6, H <sup>o</sup> , Ph], 6.90 [d, 1 H, J(HH) 7.4, Ph], 7.49 (m, 2 H, Ph), 7.86 [t, 1 H, J(HH) 7.2, Ph]	18.0 [d, J(PC) 6, CH <sub>3</sub> CHPh], 21.5 [dd, <sup>1</sup> J(PC) 20, <sup>2</sup> J(PC) 8, PCH <sub>2</sub> CH <sub>2</sub> P], 26.1 [dd, partially obscured, <sup>1</sup> J(PC) 22, <sup>2</sup> J(PC) 16, PCH <sub>2</sub> CH <sub>2</sub> P], 29.6 [d, J(PC) 5, C(CH <sub>3</sub> ) <sub>3</sub> ], 30.2 [d, J(PC) 4, C(CH <sub>3</sub> ) <sub>3</sub> ], 30.4 [d, J(PC) 4, C(CH <sub>3</sub> ) <sub>3</sub> ], 30.5 [d, J(PC) 6, C(CH <sub>3</sub> ) <sub>3</sub> ], 35.6 [d, J(PC) 11, C(CH <sub>3</sub> ) <sub>3</sub> ], 36.3 [d, J(PC) 10, C(CH <sub>3</sub> ) <sub>3</sub> ], 38.2 [d, J(PC) 15, C(CH <sub>3</sub> ) <sub>3</sub> ], 38.7 [d, J(PC) 14, C(CH <sub>3</sub> ) <sub>3</sub> ], 58.6 [d, J(P <sub>trans</sub> C) 45, J(P <sub>cis</sub> C) 10, CH <sub>3</sub> CHPh], 104.4 [d, J(PC) 13, Ph, C <sup>6</sup> ], 121.1 (s, Ph, C <sup>1</sup> ), 126.6 [d, J(PC) 4, Ph, C <sup>2</sup> ], 130.0 [vt,  J(PC + P'C)  10, Ph, C <sup>4</sup> ], 132.9 (s, Ph, C <sup>3</sup> or C <sup>5</sup> ), 135.5 [vt,  J(PC) + J(P'C)  10, Ph, C <sup>3</sup> or C <sup>5</sup> ]
2g <sup>c</sup>	0.69 [d, 9 H, J(PH) 13.8, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.30 [d, 9 H, J(PH) 14.2, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.35 [d, 9 H, J(PH) 13.8, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.41 [d, 9 H, J(PH) 14.0, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.49 (partially obscured, 3 H, CH <sub>3</sub> CHPh), 1.7–1.8 (br m, 2 H, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P), 1.9–2.2 (br m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> P), 5.24 (m, 1 H, CH <sub>3</sub> CHPh), 6.65 [t, 1 H, J(HH) 6.5, Ph, H <sup>o</sup> ], 7.08 [d, 1 H, J(HH) 7.4, Ph], 7.44 [t, 1 H, J(HH) 7.5, Ph], 7.54 (m, 1 H, Ph), 7.67 [t, 1 H, J(HH) 7.3, Ph]	18.1 [d, J(PC) 5, CH <sub>3</sub> CHPh], 21.0 [d, J(PC) 15, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P], 21.9 [dd, <sup>1</sup> J(PC) 19, <sup>2</sup> J(PC) 7, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P], 22.5 [d, J(PC) 3, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P], 29.0 [s, C(CH <sub>3</sub> ) <sub>3</sub> ], 29.4 [s, C(CH <sub>3</sub> ) <sub>3</sub> ], 29.6 [s, C(CH <sub>3</sub> ) <sub>3</sub> ], 33.9 [d, J(PC) 13, C(CH <sub>3</sub> ) <sub>3</sub> ], 37.4 [d, J(PC) 15, C(CH <sub>3</sub> ) <sub>3</sub> ], 39.6 [d, J(PC) 14, C(CH <sub>3</sub> ) <sub>3</sub> ], 53.8 [dd, partially obscured by solvent, <sup>1</sup> J(PC) 42, <sup>2</sup> J(PC) 11, CH <sub>3</sub> CHPh], 111.0 [d, J(PC) 9, Ph, C <sup>6</sup> ], 120.0 [d, J(PC) 6, C <sup>1</sup> ], 128.8 (s, Ph), 130.9 [d, J(PC) 6, Ph], 132.7 [d, J(PC) 7, Ph, C <sup>4</sup> ], 133.2 [d, J(PC) 6, Ph]
2h	0.64 [d, 9 H, J(PH) 13.4, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.37 [d, 18 H, J(PH) 13.1, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.44 [d, 9 H, J(PH) 14.6, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.77 [d, 3 H, J(PH) 10, CH <sub>3</sub> CHPh], 3.28–4.00 [br m, 4 H, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P], 5.25 [m, 1 H, CH <sub>3</sub> CHPh], 7.23–7.72 [m, 9 H, Ph, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub> P]	18.0 [d, J(PC) 4, CH <sub>3</sub> CHPh], 28.1 [d, J(PC) 8, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P], 30.4 [br s, C(CH <sub>3</sub> ) <sub>3</sub> ], 31.1 [d, J(PC) 3, C(CH <sub>3</sub> ) <sub>3</sub> ], 37.0 [br, C(CH <sub>3</sub> ) <sub>3</sub> ], 40.9 [d, J(PC) 8, C(CH <sub>3</sub> ) <sub>3</sub> ], 51.7 [dd, J(P <sub>trans</sub> C) 42, J(P <sub>cis</sub> C) 13, CH <sub>3</sub> CHPh], 119.0 [d, J(PC) 6, Ph, C <sup>1</sup> ], 127.6 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 128.0 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 130.5 (br, Ph), 133.1 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 133.8 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 134.5 [d, J(PC) 6, Ph, C <sup>4</sup> ], 134.8 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P), 135.5 (s, PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P)

Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, vt = virtual triplet, br = broad.

<sup>a</sup> Chemical shifts (δ) in ppm positive to high frequency of SiMe<sub>4</sub>, coupling constants in Hz, measurements at room temperature, unless otherwise stated and in C<sub>6</sub>D<sub>6</sub> (**1a–1h**) or CD<sub>2</sub>Cl<sub>2</sub> (**2a–2c** and **2e–2h**). <sup>b</sup> Recorded at 245 K. <sup>c</sup> Recorded at 200 K.

Table 2 <sup>31</sup>P-{<sup>1</sup>H} NMR data for the complexes [M(η<sup>2</sup>-CH<sub>2</sub>=CHPh)(L-L)] [M = Pt (**1a–1e**) or Pd (**1f–1h**)] and [M(η<sup>3</sup>-MeCPh)(L-L)] [BF<sub>4</sub>]<sup>-</sup> [M = Pt (**2a–2e**) or Pd (**2f–2h**)]<sup>a</sup>

Complex	L-L	δ(P <sup>1</sup> )	J(PtP <sup>1</sup> )	δ(P <sup>2</sup> )	J(PtP <sup>2</sup> )	J(PP)	Δ <sup>b</sup>
1a	(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	66.4	3157	70.1	3177	64	20
1c	(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> P(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	19.8	3256	22.9	3279	26	23
1b	Bu <sup>t</sup> <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PBu <sup>t</sup> <sub>2</sub>	94.3	3236	98.6	3233	72	3
1d	Bu <sup>t</sup> <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PBu <sup>t</sup> <sub>2</sub>	42.9	3356	44.6	3326	41	30
1e	Bu <sup>t</sup> <sub>2</sub> PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> PBu <sup>t</sup> <sub>2</sub>	45.6	3452	46.6	3506	43	54
1f	Bu <sup>t</sup> <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PBu <sup>t</sup> <sub>2</sub>	74.5		84.6		59	
1g	Bu <sup>t</sup> <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PBu <sup>t</sup> <sub>2</sub>	42.0		48.5		27	
1h	Bu <sup>t</sup> <sub>2</sub> PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> PBu <sup>t</sup> <sub>2</sub>	46.2		50.5		24	
2a	(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> P(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	65.0	4727	63.9	2933	10	1794
2c	(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> P(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	21.9	4764	7.5	2948	16	1816
2b	Bu <sup>t</sup> <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PBu <sup>t</sup> <sub>2</sub>	90.7	5004	88.3	3002	14	2002
2d	Bu <sup>t</sup> <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PBu <sup>t</sup> <sub>2</sub>	48.3	5293	38.0	2995	7	2298
2e <sup>c</sup>	Bu <sup>t</sup> <sub>2</sub> PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> PBu <sup>t</sup> <sub>2</sub>	57.6	5524	45.3	2954	0	2570
2f	Bu <sup>t</sup> <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PBu <sup>t</sup> <sub>2</sub>	89.7		93.8		29	
2g	Bu <sup>t</sup> <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PBu <sup>t</sup> <sub>2</sub>	40.0		59.6		51	
2h	Bu <sup>t</sup> <sub>2</sub> PCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> PBu <sup>t</sup> <sub>2</sub>	44.4		71.5		43	

<sup>a</sup> Chemical shifts (δ) in ppm positive to high frequency of 85% H<sub>3</sub>PO<sub>4</sub>, coupling constants in Hz, measurements at room temperature, unless otherwise stated and in C<sub>6</sub>D<sub>6</sub> (**1a–1f**) or CD<sub>2</sub>Cl<sub>2</sub> (**2a–2f**). <sup>b</sup> Δ = |<sup>1</sup>J(PtP<sup>1</sup>) - <sup>1</sup>J(PtP<sup>2</sup>)|. <sup>c</sup> Recorded at 245 K.

observed in the <sup>13</sup>C spectrum and the key resonances for C<sup>2</sup> and C<sup>6</sup> which at 293 K are at δ 112.5 and 106.0 respectively move only to δ 113.7 and 104.2 at 353 K. It is possible, though unlikely, that the equilibrium proportions of the two isomers

remain almost constant over the accessible temperature range. We conclude, therefore, that although the evidence points strongly towards an *anti* η<sup>3</sup>-methylbenzyl structure for **2b** and **2d–2h**, there remains doubt about the structures of **2a** and **2c**.

**Table 3** Proton and  $^{13}\text{C}\{-^1\text{H}\}$  NMR data for the complex  $[\text{Pt}(\eta^3\text{-MeCHPh})\{\text{Bu}'_2\text{P}(\text{CH}_2)_3\text{PBu}'_2\}][\text{BF}_4] \mathbf{2d}^*$ 

$T/\text{K}$	$^1\text{H}$ ( $\delta$ )	$^{13}\text{C}\{-^1\text{H}\}$ ( $\delta$ )
200	0.63 [d, 9 H, $J(\text{PH})$ 13.0, $\text{C}(\text{CH}_3)_3$ ], 1.19 [d, 9 H, $J(\text{PH})$ 10.2, $\text{C}(\text{CH}_3)_3$ ], 1.30 [d, 18 H, $J(\text{PH})$ 13.0, $\text{C}(\text{CH}_3)_3$ ], 1.5–2.4 [br m, 9 H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ , $\text{CH}_3\text{CHPh}$ ], 4.55 (br m, 1 H, $\text{CH}_3\text{CHPh}$ ), 6.27 (br s, 1 H, Ph, $\text{H}^6$ ), 6.86 (br s, 1 H, Ph, $\text{H}^2$ ), 7.29 (br m, 1 H, Ph, $\text{H}^4$ ), 7.39 (br m, 1 H, Ph, $\text{H}^3$ or $\text{H}^5$ ), 7.68 (br s, 1 H, Ph, $\text{H}^3$ or $\text{H}^5$ )	17.2 (s, $\text{CH}_3\text{CHPh}$ ), 19.0 [d, $J(\text{PC})$ 23, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 20.0 [d, $J(\text{PC})$ 28, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 22.1 (s, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ), 28.7 [br s, $\text{C}(\text{CH}_3)_3$ ], 29.3 [br s, $\text{C}(\text{CH}_3)_3$ ], 35.8 [d, $J(\text{PC})$ 22, $\text{C}(\text{CH}_3)_3$ ], 37.7 [d, $J(\text{PC})$ 26, $\text{C}(\text{CH}_3)_3$ ], 39.1 [d, $J(\text{PC})$ 17, $\text{C}(\text{CH}_3)_3$ ], 40.6 [d, $J(\text{PC})$ 26, $\text{C}(\text{CH}_3)_3$ ], 47.6 [d, $J(\text{PtC})$ 180, $J(\text{PC})$ 40, $\text{CH}_3\text{CHPh}$ ], 103.1 [br d, $J(\text{PC})$ 10, Ph, $\text{C}^6$ ], 115.2 [d, $J(\text{PC})$ 4, Ph, $\text{C}^1$ ], 128.8 (s, Ph, $\text{C}^2$ ), 130.4 (s, Ph, $\text{C}^4$ ), 132.4 (s, Ph, $\text{C}^3$ or $\text{C}^5$ ), 134.8 (s, Ph, $\text{C}^3$ or $\text{C}^5$ )
245	0.69 [d, 9 H, $J(\text{PH})$ 13.8, $\text{C}(\text{CH}_3)_3$ ], 1.25 [d, 9 H, $J(\text{PH})$ 13.4, $\text{C}(\text{CH}_3)_3$ ], 1.36 [d, 18 H, $J(\text{PH})$ 14.0, $\text{C}(\text{CH}_3)_3$ ], 1.37 [d, 18 H, $J(\text{PH})$ 14.1, $\text{C}(\text{CH}_3)_3$ ], 1.5–2.4 (br m, 9 H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ , $\text{CH}_3\text{CHPh}$ ), 4.62 (br m, 1 H, $\text{CH}_3\text{-CHPh}$ ), 6.65 (br s, 2 H, Ph, $\text{H}^2$ and $\text{H}^6$ ), 7.35 (br s, 1 H, Ph, $\text{H}^4$ ), 7.57 (br m, 2 H, Ph, $\text{H}^3$ and $\text{H}^5$ )	17.6 [d, $J(\text{PC})$ 3, $\text{CH}_3\text{CHPh}$ ], 19.8 [d, $J(\text{PC})$ 24, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 20.7 [d, $J(\text{PC})$ 29, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 22.5 [s, $J(\text{PtC})$ 57, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 29.2 [s, $\text{C}(\text{CH}_3)_3$ ], 29.5 [s, $\text{C}(\text{CH}_3)_3$ ], 29.7 [s, $\text{C}(\text{CH}_3)_3$ ], 36.3 [d, $J(\text{PC})$ 22, $\text{C}(\text{CH}_3)_3$ ], 38.3 [d, $J(\text{PC})$ 25, $\text{C}(\text{CH}_3)_3$ ], 39.1 [d, $J(\text{PC})$ 17, $\text{C}(\text{CH}_3)_3$ ], 40.9 [d, $J(\text{PC})$ 26, $\text{C}(\text{CH}_3)_3$ ], 47.8 [d, $J(\text{PtC})$ 179, $J(\text{PC})$ 40, $\text{CH}_3\text{CHPh}$ ], 115.7 [d, $J(\text{PC})$ 3, Ph, $\text{C}^1$ ], 130.9 [d, $J(\text{PC})$ 3, Ph, $\text{C}^4$ ], 133.6 (br s, Ph, $\text{C}^3$ and $\text{C}^5$ )
303	1.07 [d, 18 H, $J(\text{PH})$ 13.9, $\text{C}(\text{CH}_3)_3$ ], 1.37 [d, 18 H, $J(\text{PH})$ 14.4, $\text{C}(\text{CH}_3)_3$ ], 1.8–2.3 (br m, 10 H, $\text{PCH}_2\text{-CH}_2\text{CH}_2\text{P}$ , $\text{CH}_3\text{CHPh}$ ), 6.73 (br s, 2 H, Ph, $\text{H}^2$ and $\text{H}^6$ ), 7.40 (br m, 1 H, Ph, $\text{H}^4$ ), 7.58 [br m, 2 H, $J(\text{HH})$ 7.4, Ph, $\text{H}^3$ and $\text{H}^5$ ]	18.1 [d, $J(\text{PtC})$ 25, $J(\text{PC})$ 3, $\text{CH}_3\text{CHPh}$ ], 20.7 [d, $J(\text{PtC})$ 26, $J(\text{PC})$ 23, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 21.5 [dd, $J(\text{PtC})$ 56, $^1J(\text{PC})$ 29, $^2J(\text{PC})$ 6, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 23.0 [s, $J(\text{PtC})$ 57, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$ ], 30.0 [d, $J(\text{PC})$ 4, $\text{C}(\text{CH}_3)_3$ ], 30.4 [d, $J(\text{PtC})$ 10, $J(\text{PC})$ 2, $\text{C}(\text{CH}_3)_3$ ], 38.0 [br, $\text{C}(\text{CH}_3)_3$ ], 40.0 [br, $\text{C}(\text{CH}_3)_3$ ], 48.2 [d, $J(\text{PtC})$ 180, $J(\text{PC})$ 41, $\text{CH}_3\text{CHPh}$ ], 116.5 (s, Ph, $\text{C}^1$ ), 119.7 (br, Ph, $\text{C}^2$ and $\text{C}^6$ ), 131.7 [d, $J(\text{PtC})$ 30, $J(\text{PC})$ 4, Ph, $\text{C}^4$ ], 133.8 [s, $J(\text{PtC})$ 20, Ph, $\text{C}^3$ and $\text{C}^5$ ]

\* Chemical shifts ( $\delta$ ) in ppm positive to high frequency of  $\text{SiMe}_4$ , coupling constants in Hz, recorded in  $\text{CD}_2\text{Cl}_2$ .

The fluxional processes occurring in **2** were studied by variable-temperature  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectroscopy. For example, as a sample of **2d** dissolved in  $\text{CD}_2\text{Cl}_2$  is slowly warmed from 200 K to 303 K in the spectrometer, a number of spectral changes are observed (Table 3). The signals for the two *ortho* ( $\delta$  6.27 and 6.86) and two *meta* ( $\delta$  7.39 and 7.68) protons broaden, disappear into the baseline at 250 K and then reappear at 270 K as two multiplets at  $\delta$  6.73 and 7.58 respectively. The four signals for the  $\text{Bu}'$  protons observed at 200 K are also affected as the temperature is raised and by 303 K resonate as two doublets at  $\delta$  1.07 and 1.37 with  $J(\text{PH})$  of 13.9 and 14.4 Hz respectively. More interestingly, the signal for the benzyl proton broadens and then disappears into the baseline at 280 K, but at 303 K no new signals are apparent. Similarly, in the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum, the signals for the phenyl carbon atoms  $\text{C}^2$  and  $\text{C}^6$ , at  $\delta$  103.1 and 128.8 and  $\text{C}^3$  and  $\text{C}^5$  at  $\delta$  132.4 and 134.8 broaden and collapse at 245 K and then reappear as signals at  $\delta$  119.7 and 133.8 [ $J(\text{PtC}) = 20$  Hz] respectively. The  $\text{Bu}'$  carbon resonances are also affected as the temperature is raised: in the static spectrum there are four  $\text{Bu}'$  environments, but at 298 K two resonances for the methyl carbons at  $\delta$  30.0 [ $J(\text{PC}) = 4$  Hz] and 30.4 [ $J(\text{PtC}) = 10$ ,  $J(\text{PC}) = 2$  Hz] are observed with two broad signals for the quaternary carbon atoms at  $\delta$  38.0 and 40.0. All other carbon resonances remain unaffected.

In order to find an explanation for the apparent absence of a signal for the benzyl proton at temperatures above 280 K,  $[\text{Pt}(\eta^2\text{-CD}_2=\text{CDC}_6\text{D}_5)\{\text{Bu}'_2\text{P}(\text{CH}_2)_3\text{PBu}'_2\}] \mathbf{1d}'$  was prepared and protonated with  $\text{HBF}_4 \cdot \text{OME}_2$ . At 250 K there are two signals in the  $^2\text{H}$  NMR spectrum of **2d'** at  $\delta$  4.64 and 1.22. On the basis of relative intensity and chemical shift, the higher frequency signal can be assigned to the *syn* proton and the other to the *anti* methyl group. As the temperature is raised, the two signals broaden and coalesce to a broad signal at  $\delta$  2.05, the weighted average chemical shift of the two signals at 250 K. In the  $^1\text{H}$  NMR spectrum of **2d**, this averaged signal would be obscured by the diphosphine bridge protons.

The other  $\eta^3$ -benzyl complexes display similar dynamic behaviour, although the activation barriers differ between platinum and palladium and as the diphosphine backbone increases in length, a point which is discussed below. Mechanisms to account for the dynamic behaviour of **2d** must therefore explain the following features. (i) The equivalence of the *o*- and, separately, the *m*-carbons and attached protons of the phenyl ligand above 235 K. (ii) The exchange of the three *anti* methyl protons and *syn* benzyl proton at temperatures above 280 K. (iii) The time-averaged plane of symmetry in the

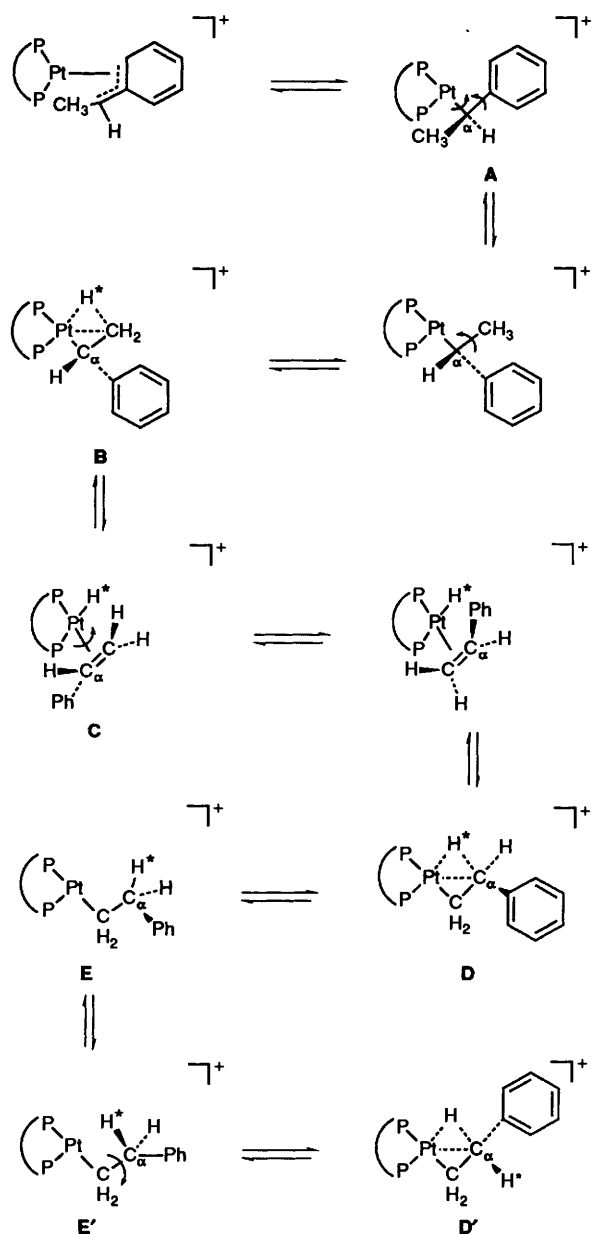
molecule which renders equivalent the two  $\text{Bu}'$  groups on one phosphorus atom and, separately, the two  $\text{Bu}'$  groups on the other phosphorus. (iv) The inequivalence of the phosphorus nuclei and their substituents throughout the temperature range studied.

The dynamics of  $\eta^3$ -benzyl complexes have been studied by a number of workers. Mechanisms involving  $\eta^3 \rightleftharpoons \sigma$  conversions<sup>4,18–21</sup> and suprafacial [1,5] shifts, with<sup>22</sup> or without<sup>6</sup> allyl rotation, have been proposed to account for the spectroscopic observations. However, none of these mechanisms can satisfactorily explain all the behaviour observed in **2**.

In order to account for the dynamic behaviour of **2**, we postulate a complex process involving  $\eta^3 \rightleftharpoons \sigma$  conversion, rotation about C–C single bonds,  $\beta$  elimination/hydride migration, and alkene rotation (Scheme 2). Previous work on related systems<sup>10,11</sup> has shown that species with agostic  $\text{Pt} \cdots \text{H} \cdots \text{C}$  bonds are important and relatively stable, and therefore intermediates with agostic structures are included in the scheme, although there is no direct evidence implicating them.

Initially, the formation of a  $\sigma$  intermediate, **A**, allows rotation around the  $\text{C}_\alpha$ -phenyl bond leading to the exchange of the two pairs of phenyl carbon atoms and the attendant protons referred to in (i) above. Three-co-ordinate intermediates have been long sought after in the chemistry of platinum(II) complexes,<sup>23</sup> but only recently a substantial body of results has emerged which supports the existence of reduced co-ordination number intermediates. A  $\sigma$  intermediate also allows rotation about the  $\text{Pt}-\text{C}_\alpha$  bond to bring the methyl group into the correct orientation to fill the vacant co-ordination site by forming a  $\beta$ -agostic  $\text{Pt}-\text{H}-\text{C}$  bond (**B**). From the evidence of other agostic systems,<sup>1,11,12</sup> **B** would be in rapid equilibrium with an alkene-hydride complex **C** through a  $\beta$ -elimination process. The styrene-hydride species **C** can then undergo alkene rotation followed by partial hydride migration to form **D**. Full transfer of the agostic hydrogen  $\text{H}^*$  from the metal to form a  $\sigma$  2-phenylethyl intermediate **E** allows rotation of the C–C single bond and exchanges  $\text{H}^*$  with the other proton attached to  $\text{C}_\alpha$ . Overall this results in the exchange of the three protons of the *anti* methyl group and the *syn* proton in **2** as required by the observations described in (ii). Furthermore, rotation about the C–C single bond in **E** gives the molecule a time-averaged plane of symmetry (**E'**) in the plane defined by the platinum and the two phosphorus atoms and so this dynamic process leads to a loss of chirality at  $\text{C}_\alpha$  as required (iii).

Two separate parts of Scheme 2 are distinguished by the rates of exchange determined from the line broadening and coalescence of signals in the NMR spectra. The lowest energy process



Scheme 2

is that described by the first equilibrium in Scheme 2 in which the benzyl ligand changes from an  $\eta^3$  to a  $\sigma$  co-ordination mode, followed by free rotation about the  $C_\alpha$ -phenyl bond. The free energy of activation for this process determined from the coalescence temperature of  $H^2$  and  $H^6$  measured from the proton spectrum at 230 K is  $44.4 \pm 1.0$  kJ mol $^{-1}$ . The corresponding value determined from the  $^{13}C$  spectrum is  $45.5 \pm 1.0$  kJ mol $^{-1}$  at 230 K.

The two other changes described in (ii) and (iii) above are observed in the  $^1H$  spectrum at higher temperatures. The free energy of activation for the exchange of methyl and benzyl protons (ii) was determined from the line broadening of the benzyl proton signal over a range of temperature 238–282 K. There was little sensitivity to temperature and a value of  $54.0 \pm 1.3$  kJ mol $^{-1}$  was determined at 269 K. The activation energy for the pairwise exchange of the  $Bu^1$  groups was determined as  $53.4 \pm 0.9$  kJ mol $^{-1}$  from the coalescence of the  $Bu^1$  signals. The good agreement between these activation energies suggests that (ii) and (iii) are two effects of the same process, consistent with Scheme 2 in which the methyl and benzyl proton exchange, and pairwise exchange of  $Bu^1$  groups, are consequences of the equilibria linking **D** and **D'**.

The importance of T-shaped intermediates in the chemistry of square-planar platinum(II) complexes has recently become clear,<sup>24</sup> particularly in respect of the mechanisms of metal alkyl decomposition<sup>23</sup> and *cis-trans* isomerization.<sup>25</sup> The mechanisms of Scheme 2 involve species with three-co-ordinate, 14-electron Pt $^{II}$  centres which would be expected to adopt a T-shaped structure and which might also be expected to undergo rearrangement *via* Y-shaped transition states, thereby exchanging the environments of the  $^{31}P$  nuclei. Thorn and Hoffmann<sup>26</sup> have calculated a relatively low activation energy for this process in a model complex, in contrast to our observations which suggest a barrier of  $>60$  kJ mol $^{-1}$ . In a similar system where a three-co-ordinate intermediate was postulated,<sup>11</sup> [PtEt(L-L)]BF $_4$ , we also noted that the phosphorus environments remained distinct at temperatures up to 300 K, with the possible exception of the compound with L-L =  $Bu^1_2PCH_2C_6H_4CH_2PBu^1_2$  which displayed a broadening of the signals in the  $^{31}P$  NMR spectrum at room temperature. Significantly, complex **2e** has broad peaks in the spectrum which may indicate that the T-Y-T process is occurring at room temperature. Presumably the bulk of the large diphosphine destabilizes the T-shaped structure relative to the Y-shaped transition state and so lowers the activation energy.

The conclusions drawn above are consistent with the findings of other investigators. Wrighton and co-workers<sup>27</sup> have postulated a mechanism for the isomerization of the alkyl group in the photogenerated complex [W( $\eta$ -C $_5$ H $_5$ )(CO) $_2$ ( $\sigma$ -CH $_2$ CH $_2$ Ph)] to give [W( $\eta$ -C $_5$ H $_5$ )(CO) $_2$ ( $\eta^3$ -MeCHPh)]. Since the  $\sigma$  species contains both a benzyl functionality and  $\beta$ -hydrogens, rearrangement can lead to either  $\eta^3$ -benzyl formation or a  $\beta$ -agostic interaction. The experimental evidence suggests that  $\eta^3$ -benzyl formation is the preferred outcome even at temperatures as low as 77 K. The photochemical reactions of [W( $\eta$ -C $_5$ H $_5$ )(CO) $_3$ (CD $_2$ CH $_2$ Ph)] and [W(C $_5$ H $_5$ )(CO) $_3$ (CDHCDHPh)] have been studied by Su and Wojcicki,<sup>28</sup> who also postulated a mechanism involving  $\beta$  elimination and hydride migration to account for the essentially statistical distribution of  $^1H$  between the (CH $_{1-y}$ D $_y$ )(CH $_3-x$ D $_x$ ) positions.

The series of complexes **2a-2h** can now be viewed as a whole and the influence of the chelating diphosphine assessed. Both the bulk of the substituents on the phosphorus and the bite angle of the diphosphine ligand may have an effect on the degree of  $\eta^3$ -benzyl interaction. The values of  $^1J(PtP^2)$  are all relatively constant, but as the substituents on phosphorus become more bulky, and as the number of carbon atoms in the diphosphine backbone increases, the value of  $^1J(PtP^1)$  changes considerably. One can envisage that as the bulkiness of the diphosphine increases there is less space for the benzyl moiety on the opposite side of the molecule. Thus the benzyl ligand becomes more asymmetrically bonded and a shift in the extent of interaction towards the 14-electron  $\sigma$  limit occurs. This is supported by considering the activation energies for the intramolecular dynamic processes of Scheme 2 for **2a-2h**. Two trends are readily discerned by noting the temperatures at which the NMR signals broaden and collapse: the rates of exchange increase with increasing bulk of the diphosphine and decrease on changing the metal from Pt to Pd with the same ligands. For example, of the complexes with a trimethylene bridged diphosphine, **2d** is the most fluxional, whereas **2g** is less so ( $\Delta G^\ddagger = 58.3 \pm 1.1$  and  $61.0 \pm 1.5$  kJ mol $^{-1}$  respectively at 295 K for the two processes described above for **2d**), and **2c** barely shows the effect of the  $\eta^3 \rightleftharpoons \sigma$  process at room temperature ( $\Delta G^\ddagger \geq 63$  kJ mol $^{-1}$ ).

Mann and Shaw<sup>22</sup> have studied the dynamic behaviour of [M( $\eta^3$ -CPh $_3$ )(acac)] (M = Pd or Pt, acac = pentane-2,4-dionate). In their system it is the palladium complex that has the lower energy barrier for each of the three exchange processes observed in solution. Work on co-ordinatively unsaturated diphosphine complexes of the nickel group<sup>11,12</sup> has shown that activation barriers to  $\beta$  elimination/ethene rotation in

$[\text{M}(\text{C}_2\text{H}_5)(\text{L}-\text{L})]^+$  [ $\text{L}-\text{L} = \text{Bu}'_2\text{P}(\text{CH}_2)_n\text{PBu}'_2$ ,  $n = 2$  or  $3$ ;  $\text{Bu}'_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}'_2$ ] are in the order  $\text{M} = \text{Ni} > \text{Pd} > \text{Pt}$ , highlighting the differences between the nickel group metals with respect to these dynamic processes.

In conclusion, this paper has described a series of closely related  $\eta^3$ -benzyl complexes in which the degree of interaction of the ligand with the metal is dependent on the bite angle and/or the bulk of substituents on the diphosphine. It has been shown that, like many other  $\eta^3$ -benzyl complexes, complexes **2** are fluxional on the NMR time-scale. More importantly, mechanisms have been proposed to account for the dynamic behaviour that involve an  $\eta^3$  to  $\sigma$  conversion followed by single-bond rotation,  $\beta$  elimination, alkene rotation and hydride migration. The activation energies for the internal rearrangements depend both on the metal centre ( $\text{Pd} > \text{Pt}$ ) and on the steric effect of the diphosphine ligands. For the complexes with the smaller chelate angle and less bulky substituents,  $\Delta G^\ddagger$  is highest.

## Experimental

All reactions were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques. Solvents were thoroughly dried over appropriate reagents: tetrahydrofuran (thf) and diethyl ether over Na/benzophenone, toluene over Na, hexane and  $\text{CH}_2\text{Cl}_2$  over  $\text{CaH}_2$ , and freshly distilled prior to use. Solvents for NMR spectra were degassed by the freeze-pump-thaw method. The diphosphines 1,3-bis(dicyclohexylphosphino)propane,<sup>29</sup> 1,3-bis(di-*tert*-butylphosphino)propane,<sup>10</sup> 1,2-bis(di-*tert*-butylphosphino)ethane<sup>30</sup> and 1,2-bis(di-*tert*-butylphosphinomethyl)benzene<sup>31</sup> and the complexes  $[\text{Pt}(\text{C}_6\text{H}_{11})_2]$ ,<sup>32</sup>  $[\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)]$ ,<sup>33</sup>  $[\text{PtCl}_2(\eta^2\text{-CH}_2=\text{CHPh})_2]$ <sup>16</sup> were prepared by published methods. The diphosphine 1,2-bis(dicyclohexylphosphino)ethane was used as purchased from Strem Chemicals. Infrared spectra were recorded on a Perkin Elmer 1710 FTIR instrument as KBr discs, and NMR spectra on Bruker AC 300 or JEOL EX90 spectrometer at ambient temperature unless otherwise stated. All  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are expressed in  $\delta$  relative to  $\text{SiMe}_4$  (0.0 ppm). Chemical shifts in  $^{31}\text{P}$  NMR spectra are positive to high frequency of 85%  $\text{H}_3\text{PO}_4$  (external). Calculations of activation energies were based on the coalescence of signals or on line broadening close to the slow exchange limit and followed standard procedures.<sup>34</sup>

**Synthesis of the Complexes  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})(\text{L}-\text{L})]$  **1a-1e**.**—The platinum(0) alkene complexes were prepared either from  $[\text{Pt}(\text{cod})_2]$  by displacement (Method A) or by the reduction of  $[\text{PtCl}_2(\text{L}-\text{L})]$  (Method B).

**Method A.** An excess (*ca.* 2 mole equivalents) of the appropriate styrene was added to a cold (*ca.* 273 K) solution of diphosphine in hexane (20  $\text{cm}^3$ ) and  $[\text{Pt}(\text{cod})_2]$  was then added in portions. The reaction flask was stirred at this temperature for *ca.* 1 h and after allowing to warm to ambient temperature, the solvent was removed under reduced pressure and the residue extracted with diethyl ether. The diethyl ether was removed *in vacuo* and the product held under vacuum for *ca.* 2 h to remove the excess of styrene. Recrystallization from diethyl ether at 253 K afforded the platinum(0) alkene complex in good yield.

**Method B.** To a Na/Hg amalgam (1%, *ca.* 30 g) in thf (*ca.* 30  $\text{cm}^3$ ) was added an excess (*ca.* 2 mole equivalents) of the appropriate styrene followed by  $[\text{PtCl}_2(\text{L}-\text{L})]$ . The reaction flask was stirred at ambient temperature, typically for 2 h. After filtration, the solvent was removed *in vacuo* and the crude product dried under vacuum for *ca.* 2 h to remove the excess of styrene. If necessary, the product may be filtered on a 5  $\text{cm}^3$  plug of neutral alumina, eluted with diethyl ether. Recrystallization from diethyl ether at 253 K gave the product in fair yield.

(i) Using Method A,  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})\{\text{Bu}'_2\text{P}(\text{CH}_2)_3\text{PBu}'_2\}]$  **1d** (0.341 g, 88%) was obtained from  $\text{Bu}'_2\text{P}(\text{CH}_2)_3\text{PBu}'_2$  (0.203 g, 0.61 mmol),  $\text{CH}_2=\text{CHPh}$  (0.20  $\text{cm}^3$ , 1.75 mmol)

and  $[\text{Pt}(\text{cod})_2]$  (0.251 g, 0.61 mmol) as a white *microcrystals*. Alternatively, by method B  $[\text{PtCl}_2\{\text{Bu}'_2\text{P}(\text{CH}_2)_3\text{PBu}'_2\}]$  (0.300 g, 0.50 mmol) and  $\text{CH}_2=\text{CHPh}$  (0.10  $\text{cm}^3$ , 0.87 mmol) gave **1d** (0.170 g, 54%) (Found: C, 51.0; H, 8.4.  $\text{C}_{27}\text{H}_{50}\text{P}_2\text{Pt}$  requires C, 51.3; H, 8.0%).

(ii) The reaction of  $\text{Bu}'_2\text{P}(\text{CH}_2)_3\text{PBu}'_2$  (0.093 g, 0.28 mmol) with  $\text{CD}_2=\text{CDC}_6\text{D}_5$  (0.06  $\text{cm}^3$ , 0.54 mmol) and  $[\text{Pt}(\text{cod})_2]$  (0.115 g, 0.28 mmol) (Method A) afforded **1d'** as a cream *powder* (0.175 g, 0.27 mmol) in 96% yield. The spectroscopic data for this complex are analogous to those for **1d**.

(iii) Following Method A,  $\text{Bu}'_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}'_2$  (0.099 g, 0.25 mmol),  $\text{CH}_2=\text{CHPh}$  (0.10  $\text{cm}^3$ , 0.87 mmol) and  $[\text{Pt}(\text{cod})_2]$  (0.103 g, 0.25 mmol) gave  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})(\text{Bu}'_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}'_2)]$  **1e** (0.164 g, 94%) as a cream *solid* (Found: C, 54.5; H, 7.7.  $\text{C}_{32}\text{H}_{52}\text{P}_2\text{Pt}$  requires C, 55.4; H, 7.6%).

(iv) Following method A,  $(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2$  (0.166 g, 0.39 mmol),  $\text{CH}_2=\text{CHPh}$  (0.10  $\text{cm}^3$ , 0.87 mmol) and  $[\text{Pt}(\text{cod})_2]$  (0.162 g, 0.39 mmol) gave  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2\}]$  **1a** as a pale brown *solid* (0.224 g, 80%). The compound was characterized by NMR spectroscopy.

(v) The reaction of  $\text{Bu}'_2\text{P}(\text{CH}_2)_2\text{PBu}'_2$  (0.129 g, 0.41 mmol),  $\text{CH}_2=\text{CHPh}$  (0.10  $\text{cm}^3$ , 0.87 mmol) and  $[\text{Pt}(\text{cod})_2]$  (0.167 g, 0.41 mmol) (Method A) afforded **1b** as an orange *powder* (0.206 g, 82%). Alternatively, the reduction of  $[\text{PtCl}_2\{\text{Bu}'_2\text{P}(\text{CH}_2)_2\text{PBu}'_2\}]$  (0.212 g, 0.36 mmol) in the presence of an excess of  $\text{CH}_2=\text{CHPh}$  (0.10  $\text{cm}^3$ , 0.87 mmol) (Method B) gave  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})\{\text{Bu}'_2\text{P}(\text{CH}_2)_2\text{PBu}'_2\}]$  **1b** (0.136 g, 62%). Spectroscopic data support the proposed formula.

(vi) The complex  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_{11})_2\}]$  **1c** was prepared from  $[\text{PtCl}_2\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_{11})_2\}]$  (0.316 g, 0.45 mmol) and  $\text{CH}_2=\text{CHPh}$  (0.2  $\text{cm}^3$ , 1.75 mmol) by Method B, as a white *powder* (0.246 g, 74%). The compound was characterized by NMR spectroscopy.

**Synthesis of  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})(\text{L}-\text{L})]$  **1f-1h**.**—(i) To a solution of  $[\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)]$  (0.112 g, 0.34 mmol) in hexane (1  $\text{cm}^3$ ) was added  $\text{CH}_2=\text{CHPh}$  (0.1  $\text{cm}^3$ , 0.87 mmol). The red solution was stirred and  $\text{Bu}'_2\text{P}(\text{CH}_2)_3\text{PBu}'_2$  (0.134 g, 0.41 mmol) in hexane (1  $\text{cm}^3$ ) added. After 1 h the resulting solution was cooled (*ca.* 253 K) to give yellow-orange *crystals* of  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})\{\text{Bu}'_2\text{P}(\text{CH}_2)_3\text{PBu}'_2\}]$  **1g** (0.112 g, 62%) (Found: C, 59.3; H, 9.4.  $\text{C}_{27}\text{H}_{50}\text{P}_2\text{Pd}$  requires C, 59.7; H, 9.3%).

(ii) A solution of the diphosphine  $\text{Bu}'_2\text{P}(\text{CH}_2)_2\text{PBu}'_2$  (0.068 g, 0.21 mmol) in hexane (0.5  $\text{cm}^3$ ) was added to a solution of  $[\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)]$  (0.046 g, 0.21 mmol) and  $\text{CH}_2=\text{CHPh}$  (0.10  $\text{cm}^3$ , 0.87 mmol), also in hexane (2  $\text{cm}^3$ ). After stirring for 15 min a precipitate formed. The solution was cooled (*ca.* 253 K) to give brown *crystals* of  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})\{\text{Bu}'_2\text{P}(\text{CH}_2)_2\text{PBu}'_2\}]$  **1f** (0.105 g, 93%). The compound was characterized by NMR spectroscopy.

(iii) To a solution of  $[\text{Pd}(\eta\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)]$  (0.046 g, 0.21 mmol) in hexane (3  $\text{cm}^3$ ) was added  $\text{CH}_2=\text{CHPh}$  (0.1  $\text{cm}^3$ , 0.87 mmol) followed by  $\text{Bu}'_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}'_2$  (0.085 g, 0.21 mmol). The red solution was stirred for 30 min during which time a solid precipitated. The solution was cooled (*ca.* 253 K) to afford  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})(\text{Bu}'_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}'_2)]$  **1h** as a pale orange *powder* (0.110 g, 85%). Spectroscopic data support the proposed formula.

**Protonation of  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})(\text{L}-\text{L})]$  **1a-1e**.** **Synthesis of the Complexes  $[\text{Pt}(\eta^3\text{-MeCHPh})(\text{L}-\text{L})][\text{BF}_4]$  **2a-2e**.**—The experimental procedure for the synthesis of complexes **2a-2d** was essentially identical. Typically, an approximately equimolar amount of  $\text{HBF}_4\cdot\text{Ome}_2$  was added to a cold (*ca.* 273 K) solution of the styrene complex **1** in diethyl ether (*ca.* 10  $\text{cm}^3$ ). A precipitate formed immediately and the reaction flask was stirred for *ca.* 15 min and then allowed to warm to room temperature. The precipitate was allowed to settle and the mother-liquors were then decanted. The product was washed with diethyl ether (3  $\times$  5  $\text{cm}^3$ , discarded) and dried *in vacuo*.



(i) The complex  $[\text{Pt}(\eta^3\text{-MeCHPh})\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2\}][\text{BF}_4]$  **2a** was obtained as pale yellow crystals from the protonation of  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2\}][\text{BF}_4]$  **1a** (0.117 g, 85%). It is stable in  $\text{CH}_2\text{Cl}_2$  and can be recrystallized from  $\text{CH}_2\text{Cl}_2$ -diethyl ether (Found: C, 47.3; H, 6.7.  $\text{C}_{34}\text{H}_{57}\text{BF}_4\text{P}_2\text{Pt}\cdot\text{CH}_2\text{Cl}_2$  requires C, 47.0; H, 6.7%).

(ii) The complex  $[\text{Pt}(\eta^3\text{-MeCHPh})\{\text{Bu}^t\text{P}(\text{CH}_2)_2\text{PBu}^t\}][\text{BF}_4]$  **2b** (0.215 g, 90%) was obtained from the protonation of **1b**. Recrystallization from  $\text{CH}_2\text{Cl}_2$ -diethyl ether afforded orange crystals that are stable in  $\text{CH}_2\text{Cl}_2$  solution (Found: C, 43.9; H, 7.1.  $\text{C}_{26}\text{H}_{49}\text{BF}_4\text{P}_2\text{Pt}$  requires C, 44.3; H, 7.0%).

(iii) Protonation of  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_{11})_2\}][\text{BF}_4]$  **1c** (0.176 g, 0.24 mmol) afforded  $[\text{Pt}(\eta^3\text{-MeCHPh})\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_{11})_2\}][\text{BF}_4]$  **2c** (0.163 g, 83%). Recrystallization from  $\text{CH}_2\text{Cl}_2$ -diethyl ether gave **2c** as yellow crystals (Found: C, 51.4; H, 7.6.  $\text{C}_{38}\text{H}_{59}\text{BF}_4\text{P}_2\text{Pt}$  requires C, 51.0; H, 7.2%).

(iv) The complex  $[\text{Pt}(\eta^3\text{-MeCHPh})\{\text{Bu}^t\text{P}(\text{CH}_2)_3\text{PBu}^t\}][\text{BF}_4]$  **2d** (0.303 g, 90%) was obtained as pale yellow-green dichroic crystals which, in solution in the absence of excess of styrene, partially decompose to form the compound  $[\text{Pt}_2(\mu\text{-H})_2\{\text{Bu}^t\text{P}(\text{CH}_2)_3\text{PBu}^t\}_2][\text{BF}_4]_2$  (Found: C, 43.9; H, 7.1.  $\text{C}_{27}\text{H}_{51}\text{BF}_4\text{P}_2\text{Pt}\cdot 0.5\text{CH}_2\text{Cl}_2$  requires C, 43.3; H, 6.9%).

(v) A solution of  $[\text{Pt}(\eta^2\text{-CD}_2=\text{CDC}_6\text{D}_5)\{\text{Bu}^t\text{P}(\text{CH}_2)_3\text{PBu}^t\}][\text{BF}_4]$  (0.175 g, 0.27 mmol) in diethyl ether (10  $\text{cm}^3$ ) was cooled (ca. 273 K) and  $\text{HBF}_4\cdot\text{OMe}_2$  (0.04  $\text{cm}^3$ , 0.03 mmol) added. A yellow precipitate formed immediately. After stirring for 15 min, the flask was warmed to ambient temperature and the supernatant liquid was decanted. The product was washed with diethyl ether (3  $\times$  3  $\text{cm}^3$ ) and dried *in vacuo* to give yellow microcrystals of **2d'** (0.187 g, 96% yield). The spectroscopic data support a structure identical to that for the undeuterated complex.

(vi) A solution of  $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})(\text{Bu}^t\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-PBu}^t)]$  **1e** (0.145 g, 0.19 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.5  $\text{cm}^3$ ) in an NMR tube was protonated at 195 K with an equimolar amount of  $\text{HBF}_4\cdot\text{OMe}_2$ . The tube was shaken briefly and then placed into a pre-cooled NMR probe. Since the product  $[\text{Pt}(\eta^3\text{-MeCHPh})\{\text{Bu}^t\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}^t\}][\text{BF}_4]$  **2e** is temperature sensitive in both solution and solid state, elemental analysis could not be obtained.

*Protonation of  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})(\text{L-L})]$  **1f-1h**. Synthesis of the Complexes  $[\text{Pd}(\eta^3\text{-MeCHPh})(\text{L-L})][\text{BF}_4]$  **2f-2h**.*—The experimental procedure for the synthesis of complexes **2f-2h** was essentially identical. Typically, an equimolar equivalent of  $\text{HBF}_4\cdot\text{OMe}_2$  was added to a cold (ca. 273 K) solution of  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})(\text{L-L})]$  **1f-1h** (0.280 g, 0.53 mmol) in diethyl ether (10  $\text{cm}^3$ ). A precipitate formed and the reaction flask was stirred at this temperature for 15 min. The precipitate was then allowed to settle and the supernatant liquid decanted and the product washed with diethyl ether (3  $\times$  5  $\text{cm}^3$ , discarded). Recrystallization from  $\text{CH}_2\text{Cl}_2$ -diethyl ether afforded the product in good yield.

(i) Protonation of  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})\{\text{Bu}^t\text{P}(\text{CH}_2)_2\text{-PBu}^t\}][\text{BF}_4]$  **1f** (0.300 g, 0.53 mmol) gave a dark precipitate. Recrystallization from  $\text{CH}_2\text{Cl}_2$ -diethyl ether afforded  $[\text{Pd}(\eta^3\text{-MeCHPh})\{\text{Bu}^t\text{P}(\text{CH}_2)_2\text{PBu}^t\}][\text{BF}_4]$  **2f** (0.303 g, 94% yield) as orange-brown crystals (Found: C, 50.2; H, 8.1.  $\text{C}_{26}\text{H}_{49}\text{BF}_4\text{P}_2\text{Pd}$  requires C, 50.6; H, 8.0%).

(ii) Protonation of the complex  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})\{\text{Bu}^t\text{-P}(\text{CH}_2)_3\text{PBu}^t\}][\text{BF}_4]$  **1g** (0.050 g, 0.09 mmol) afforded  $[\text{Pd}(\eta^3\text{-MeCHPh})\{\text{Bu}^t\text{P}(\text{CH}_2)_3\text{PBu}^t\}][\text{BF}_4]$  **2g** (0.045 g, 60%) as a mustard yellow powder (Found: C, 50.7; H, 8.2.  $\text{C}_{27}\text{H}_{51}\text{BF}_4\text{P}_2\text{Pd}$  requires C, 51.4; H, 8.2%).

(iii) Protonation of  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CHPh})(\text{Bu}^t\text{PCH}_2\text{C}_6\text{H}_4\text{-}$

$\text{CH}_2\text{PBu}^t)]$  **1h** (0.110 g, 0.18 mmol) in diethyl ether gave a red-brown precipitate. The product was dried *in vacuo* to give  $[\text{Pd}(\eta^3\text{-MeCHPh})(\text{Bu}^t\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}^t)][\text{BF}_4]$  **2h** (0.081 g, 78%) as an orange powder. The compound was characterized by NMR spectroscopy.

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