Effect of Phenyl Substitution on Bonding in η^3-Benzyl Complexes of Platinum

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Reaction of the platinum(0) styrene complexes $[Pt(\eta^2\text{-}CH_2{=}CHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1a–1f** (X = Br-3, Br-4, Me-4, F-4, F-3 or MeO-4) with HBF_4 in diethyl ether afforded the η^3-methylbenzyl complexes $[Pt(\eta^3\text{-}MeCHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2a–2f**. The effect of phenyl substitution on the asymmetry of the η^3-methylbenzyl interaction was measured by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy and it was found that, in general, the more electron releasing the substituent, X, the more asymmetric is the bonding. Complexes **2a–2f** lose styrene reversibly to form the hydride-bridged dinuclear platinum complex $[Pt_2(\mu\text{-}H)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}_2][BF_4]_2$. Displacement of styrenes from **2a–2f** by ethene and bicyclo[2.2.1]hept-2-ene affords known complexes stabilized by a three-centre, two-electron (agostic) bond.

Few η^3-benzyl complexes of transition metals have been reported over the past 25 years,[1] although numerous examples of η^3-allyl species have been made and studied in detail.[2] Of the Group 10 metals, palladium and platinum, benzyl complexes of the former have received the greatest attention.[3] Furthermore, whilst a number of reports have discussed the structural features of η^3-benzyl complexes[1,4,5] and studied the dynamic behaviour,[1,6] few systematic studies of substitution effects on the bonding and stability have been made.[6,7] During an investigation of the chemistry of electrophilic platinum(II) complexes we discovered straightforward syntheses of η^3-methylbenzyl complexes, and bearing in mind the paucity of detailed evidence on the factors controlling the metal–η^3-benzyl bond we sought to characterize a series of platinum η^3-benzyl complexes with various substituents on the phenyl ring, and thereby elucidate some of the factors which dictate stability and the nature of the bonding in the ground state. We considered it possible that the ground state might be affected by phenyl substitution to the extent that an alternative bonding mode was preferred. Previous work on the synthesis of electronically unsaturated complexes of Pt^{II} has shown that complexes with three-centre, two-electron Pt···H···C (β-agostic) bonding are relatively stable. In this context it was of interest to explore the relative stabilities of the β-agostic and η^3-benzyl bonding modes with ligands derived from styrene. An earlier paper[8] described the effect of the ancillary chelating diphosphine ligands on the bonding and dynamic behaviour of a series of η^3-benzyl complexes. This paper describes the synthesis and NMR analysis of the platinum(0) styrene complexes $[Pt(\eta^2\text{-}CH_2{=}CHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1a–1f** (X = Br-3, Br-4, Me-4, F-4, F-3 or MeO-4) and the platinum(II) η^3-benzyl complexes, $[Pt(\eta^3\text{-}MeCHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2a–2f**, formed by protonation of **1a–1f**. The use of substituted styrenes allowed the influence of the various electron-donating or -withdrawing substituents on the nature of the platinum(II) complex formed to be monitored. The ease of displacement of styrenes from **2** was noted and the synthetic application of this facile elimination has been explored through reaction with various alkenes. A preliminary report of this work has been published.[9]

Results and Discussion

Treatment of $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene) with the diphosphine $Bu^t_2P(CH_2)_3PBu^t_2$ and an excess of the substituted styrene in hexane solution readily affords the complexes $[Pt(\eta^2\text{-}CH_2{=}CHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1a–1c**. A similar method has been used successfully to prepare the complexes $[Pt(\eta^2\text{-}CH_2{=}CHPh)(L\text{–}L)]$ [L–L = $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$, $Bu^t_2P(CH_2)_nPBu^t_2$, n = 2 or 3 or $Bu^t_2PCH_2C_6H_4CH_2PBu^t_2$].[8] Unfortunately, this method did not work well for the synthesis of **1d–1f** since in these cases the styrene did not displace completely the second cod molecule and $[Pt(cod)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ was also formed in the reaction. For these compounds an alternative method of preparation was applied which involved the reduction of $[PtCl_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ by Na/Hg amalgam in the presence of an excess of the appropriate styrene. The latter method can only be used with styrenes which can withstand the strong reducing environment of a Na/Hg amalgam and thus the preparation of **1c–1f** is possible by this route, but not that of the bromostyrene derivatives **1a** and **1b**.

The characterization of complexes **1a–1f** is based on multinuclear NMR spectroscopy. The alkene protons of the co-ordinated styrenes give rise to three distinctive signals in the ^1H NMR spectra with coupling to platinum (Table 1), whilst the $^{13}C\text{-}\{^1H\}$ NMR spectra also show the features expected for platinum(0) styrene diphosphine complexes, *i.e.* signals arising from the diphosphine ligand and the co-ordinated styrene are observed. Values of $^1J(PtC)$ for the contact carbon atoms of the styrene show little variation within the series **1a–1f**, the unsubstituted carbon atom, C^1, having a $^1J(PtC^1)$ value in the range 220 ± 2 Hz and C^2 a value for $^1J(PtC^2)$ in the range 228 ± 4 Hz (Table 1). The $^{31}P\text{-}\{^1H\}$ NMR spectra of the compounds **1a–1f** all show two resonances with ^{195}Pt satellites, as expected, and these signals appear to be sensitive to the nature of the substituent on the phenyl ring (Table 2). A general trend is observed, with the magnitude of $J(PtP^1) - J(PtP^2)$ increasing as the overall electron-donating ability of the substituent (as measured by the modified Hammett substituent constant,[10] σ_p^+) increases. Similar correlations of NMR parameters with σ_p^+ have been observed by Cooper and Powell[10] in platinum(II) styrene complexes for which electron-releasing substituents on the phenyl ring promote more asymmetric bonding of the alkene to Pt^{II}. As noted above, other NMR parameters associated with the metal–alkene bond, for example δ_C(alkene) and $^1J(PtC)$, are remarkably insensitive to the phenyl substituent which is in marked contrast to the platinum(II) examples of Cooper and Powell where significant trends were observed.

Table 1 Proton and ^{13}C-{^{1}H} NMR data for the complexes [Pt(η^2-CH_2=CHC_6H_4X){$Bu^t_2P(CH_2)_3PBu^t_2$}] **1a**–**1f** and [Pt(η^3-$MeCHC_6H_4X$){Bu^t_2-$P(CH_2)_3PBu^t_2$}][BF_4] **2a** and **2c**–**2f***

Complex	$^{1}H(\delta)$	^{13}C-{^{1}H}(δ)
1a	0.74 [d, 9 H, *J*(PH) 12.4, $C(CH_3)_3$], 1.09 [d, 9 H, *J*(PH) 12.2, $C(CH_3)_3$], 1.10 [d, 9 H, *J* (PH) 12.1, $C(CH_3)_3$], 1.16 [d, 9 H, *J*(PH) 12.3, $C(CH_3)_3$], 1.2–1.5 (br m, 4 H, $PCH_2CH_2CH_2P$), 1.6–1.8 (br m, 2 H, $PCH_2CH_2CH_2P$), 2.44 [m, 1 H, *J*(PtH) 48, CH_2=CH], 2.53 [m, 1 H, *J*(PtH) 52, CH_2=CH], 3.33 [m, 1 H, *J*(PtH) 62, CH_2=CH], 6.81 [t, 1 H, *J*(HH) 7.8, Ph], 6.95–6.98 (m, 1 H, Ph), 7.38 (m, 1 H, Ph)	20.8 [d, *J*(PC) 14, $PCH_2CH_2CH_2P$], 21.4 [d, *J*(PC) 16, $PCH_2CH_2CH_2P$], 25.9 [s, *J*(PtC) 36, $PCH_2CH_2CH_2P$], 29.5 [d, *J*(PC) 7, $C(CH_3)_3$], 29.6 [d, *J*(PC) 7, $C(CH_3)_3$], 29.9 [d, *J*(PC) 8, $C(CH_3)_3$], 30.0 [d, *J*(PC) 8, $C(CH_3)_3$], 32.6 [dd, *J*(PtC) 222, $J(P_{trans}C)$ 38, $J(P_{cis}C)$ 6, alkene], 35.2 [d, *J*(PtC) 40, *J*(PC) 15, $C(CH_3)_3$], 36.2 [d, *J*(PtC) 42, *J*(PC) 17, $C(CH_3)_3$], 44.4 [dd, *J*(PtC) 225, $J(P_{trans}C)$ 36, $J(P_{cis}C)$ 6, alkene], 122.0 (s, Ph), 124.0 [s, *J*(PtC) 22, Ph], 124.6 (s, Ph), 128.8 [s, *J*(PtC) 23, Ph], 129.0 (s, Ph), 155.2 [d, *J*(PtC) 48, *J*(PC) 4, *ipso*-C of Ph]
1b	0.70 [d, 9 H, *J*(PH) 12.3, $C(CH_3)_3$], 1.10 [d, 9 H, *J*(PH) 12.1, $C(CH_3)_3$], 1.11 [d, 9 H, *J*(PH) 12.0, $C(CH_3)_3$], 1.15 [d, 9 H, *J*(PH) 12.4, $C(CH_3)_3$], 1.2–1.4 (br m, 4 H, $PCH_2CH_2CH_2P$), 1.6–1.8 (br m, 2 H, $PCH_2CH_2CH_2P$), 2.50 [m, 1 H, *J*(PtH) 55, CH_2=CH], 2.60 [m, 1 H, *J*(PtH) 55, CH_2=CH], 3.38 [m, 1 H, *J*(PtH) 66, CH_2=CH], 6.93 (m, 2 H, Ph), 7.28 [d, 2 H, *J*(HH) 8.4, Ph]	20.9 [d, *J*(PC) 14, $PCH_2CH_2CH_2P$], 21.3 [d, *J*(PC) 15, $PCH_2CH_2CH_2P$], 25.9 [s, *J*(PtC) 37, $PCH_2CH_2CH_2P$], 29.6 [d, *J*(PC) 7, $C(CH_3)_3$], 29.8 [d, *J*(PC) 6, $C(CH_3)_3$], 30.0 [d, *J*(PC) 6, $C(CH_3)_3$], 32.6 [dd, *J*(PtC) 222, $J(P_{trans}C)$ 39, $J(P_{cis}C)$ 6, alkene], 35.1–35.2 [br m, $C(CH_3)_3$], 44.5 [dd, *J*(PtC) 226, $J(P_{trans}C)$ 35, $J(P_{cis}C)$ 6, alkene], 115.0 (s, Ph), 127.4 [d, *J*(PtC) 21, *J*(PC) 4, Ph], 130.5 (s, Ph), 151.4 [d, *J*(PtC) 47, *J*(PC) 6, *ipso*-C of Ph]
1c	0.80 [d, 9 H, *J*(PH) 12.1, $C(CH_3)_3$], 1.14 [d, 9 H, *J*(PH) 12.7, $C(CH_3)_3$], 1.18 [d, 9 H, *J*(PH) 12.1, $C(CH_3)_3$], 1.21 [d, 9 H, *J*(PH) 11.9, $C(CH_3)_3$], 1.3–1.5 (br m, 4 H, $PCH_2CH_2CH_2P$), 1.6–1.8 (br m, 4 H, $PCH_2CH_2CH_2P$), 2.24 [d, 3 H, *J*(HH) 1.4, Me-4], 2.64 [m, 2 H, *J*(PtH) 60, CH_2=CH], 3.60 [m, 1 H, *J*(PtH) 70, CH_2=CH], 7.10 [d, 2 H, *J*(HH) 7.9, Ph], 7.1–7.2 (br m, 2 H, Ph)	21.0 {d, *J*(PC) 11, $PCH_2CH_2CH_2P$], 21.1 (s, partially obscured, Me-4), 21.5 [d, *J*(PC) 14, $PCH_2CH_2CH_2P$], 26.1 [s, *J*(PtC) 35, $PCH_2CH_2CH_2P$], 29.6 [d, *J*(PC) 6, $C(CH_3)_3$], 29.7 [d, *J*(PC) 5, $C(CH_3)_3$], 29.8 [d, *J*(PC) 5, $C(CH_3)_3$], 30.0 [d, *J*(PC) 7, $C(CH_3)_3$], 32.9 [dd, *J*(PtC) 218, $J(P_{trans}C)$ 38, $J(P_{cis}C)$ 6, alkene], 35.0–35.2 [br m, $C(CH_3)_3$], 45.6 [dd, *J*(PtC) 228, $J(P_{trans}C)$ 35, $J(P_{cis}C)$ 6, alkene], 125.9 [d, *J*(PtC) 19, *J*(PC) 3, Ph], 130.9 [d, *J*(PC) 4, Ph], 148.9 [d, *J*(PtC) 43, *J*(PC) 3, *ipso*-C of Ph]
1d	0.73 [d, 9 H, *J*(PH) 12.2, $C(CH_3)_3$], 1.12 [d, 9 H, *J*(PH) 12.0, $C(CH_3)_3$], 1.13 [d, 9 H, *J*(PH) 12.6, $C(CH_3)_3$], 1.18 [d, 9 H, *J*(PH) 12.5, $C(CH_3)_3$], 1.3–1.5 (br m, 4 H, $PCH_2CH_2CH_2P$), 1.6–1.8 (br m, 2 H, $PCH_2CH_2CH_2P$), 2.50 [m, 1 H, *J*(PtH) 47, CH_2=CH], 2.60 [m, 1 H, *J*(PtH) 65, CH_2=CH], 3.45 [m, 1 H, *J*(PtH) 63, CH_2=CH], 6.86 [t, 2 H, *J*(HH) 8.8, Ph], 6.98–7.04 (br m, 2 H, Ph)	21.1 [d, *J*(PC) 13, $PCH_2CH_2CH_2P$], 21.7 [d, *J*(PC) 16, $PCH_2CH_2CH_2P$], 26.1 [d, *J*(PtC) 35, *J*(PC) 3, $PCH_2CH_2CH_2P$], 29.7 [d, *J*(PC) 7, $C(CH_3)_3$], 29.9 [d, *J*(PC) 5, $C(CH_3)_3$], 30.1 [d, *J*(PC) 6, $C(CH_3)_3$], 32.7 [dd, *J*(PtC) 218, $J(P_{trans}C)$ 37, $J(P_{cis}C)$ 6, alkene], 35.1–36.5 [br m, $C(CH_3)_3$], 44.5 [dd, *J*(PtC) 234, $J(P_{trans}C)$ 35, $J(P_{cis}C)$ 6, alkene], 114.1 [d, *J*(PtC) 10, *J*(FC) 21, Ph], 126.6 [dd, *J*(PC) 4, *J*(FC) 7, Ph], 147.8 (s, *ipso*-C of Ph)
1e	0.74 [d, 9 H, *J*(PH) 12.3, $C(CH_3)_3$], 1.09 [d, 9 H, *J*(PH) 12.2, $C(CH_3)_3$], 1.11 [d, 9 H, *J*(PH) 11.9, $C(CH_3)_3$], 1.14 [d, 9 H, *J*(PH) 12.2, $C(CH_3)_3$], 1.2–1.5 (br m, 4 H, $PCH_2CH_2CH_2P$), 1.6–1.8 (br m, 2 H, $PCH_2CH_2CH_2P$), 2.50 [m, 1 H, *J*(PtH) 48, CH_2=CH], 2.57 [m, 1 H, *J*(PtH) 63, CH_2=CH], 3.39 [m, 1 H, *J*(PtH) 63, CH_2=CH], 6.55 (m, 1 H, Ph), 6.89–7.00 (m, 3 H, Ph)	20.9 [d, *J*(PC) 14, $PCH_2CH_2CH_2P$], 21.4 [d, *J*(PC) 15, $PCH_2CH_2CH_2P$], 26.0 [s, *J*(PtC) 36, $PCH_2CH_2CH_2P$], 29.6 [d, *J*(PC) 7, $C(CH_3)_3$], 29.8 [d, *J*(PC) 5, $C(CH_3)_3$], 30.0 [d, *J*(PC) 6, $C(CH_3)_3$], 31.1 [dd, *J*(PtC) 262, $J(P_{trans}C)$ 38, $J(P_{cis}C)$ 6, alkene], 35.0–37.0 [br m, $C(CH_3)_3$], 44.9 [dd, *J*(PtC) 227, $J(P_{trans}C)$ 35, $J(P_{cis}C)$ 7, alkene], 108.5 [d, *J*(PtC) 13, *J*(FC) 21, Ph], 112.0 [d, *J*(PtC) 21, *J*(FC) 21, Ph], 121.5 [s, *J*(PtC) 19, Ph], 155.2 (s, *ipso*-C of Ph)
1f	0.75 [d, 9 H, *J*(PH) 12.1, $C(CH_3)_3$], 1.12 [d, 9 H, *J*(PH) 11.8, $C(CH_3)_3$], 1.14 [d, 9 H, *J*(PH) 11.7, $C(CH_3)_3$], 1.19 [d, *J*(PH) 11.9, $C(CH_3)_3$], 1.3–1.5 (br m, 4 H, $PCH_2CH_2CH_2P$), 1.6–1.9 (br m, 2 H, $PCH_2CH_2CH_2P$), 2.44 [m, 1 H, *J*(PtH) 50, CH_2=CH], 2.53 [m, 1 H, *J*(PtH) 54, CH_2=CH], 3.32 (s, 4 H, OMe-4, CH_2=CH), 7.01–7.19 (m, 4 H, Ph)	21.0 [d, *J*(PC) 13, $PCH_2CH_2CH_2P$], 21.5 [d, *J*(PC) 15, $PCH_2CH_2CH_2P$], 26.5 [s, *J*(PtC) 35, $PCH_2CH_2CH_2P$], 29.7 [d, *J*(PC) 6, $C(CH_3)_3$], 29.9 [s, $C(CH_3)_3$], 30.0 [d, *J*(PC) 7, $C(CH_3)_3$], 32.4 [dd, *J*(PtC) 220, $J(P_{trans}C)$ 38, $J(P_{cis}C)$ 6, alkene], 34.9–35.2 [br m, $C(CH_3)_3$], 36.0–36.4 [br m, $C(CH_3)_3$], 44.7 [dd, *J*(PtC) 232, $J(P_{trans}C)$ 36, $J(P_{cis}C)$ 6, alkene], 54.9 (s, OMe-4), 126.4 [d, *J*(PtC) 21, *J*(PC) 4, Ph], 144.2 [d, *J*(PtC) 42, *J*(PC) 4, *ipso*-C of Ph]
2a	1.10 [d, 18 H, *J*(PH) 14.1, $C(CH_3)_3$], 1.38 (d, 18 H, *J*(PH) 14.6, $C(CH_3)_3$], 1.9–2.4 (br m, $PCH_2CH_2CH_2P$), 6.59 (br m, 2 H, Ph), 7.36 (m, 1 H, partially obscured by CH_2=CHC_6H_4Br-3, Ph), 7.54 (m, 1 H, partially obscured by CH_2=CHC_6H_4Br-3, Ph)	18.6 [s, *J*(PtC) 21, $CH_3CHC_6H_4$Br-3], 20.6 [d, *J*(PtC) 25, *J*(PC) 23, $PCH_2CH_2CH_2P$], 21.5 [dd, *J*(PtC) 29, ^{1}J(PC) 29, ^{2}J(PC) 6, $PCH_2CH_2CH_2P$], 23.0 [s, *J*(PtC) 58, $PCH_2CH_2CH_2P$], 29.9 [s, $C(CH_3)_3$], 30.0 [d, *J*(PC) 5, $C(CH_3)_3$], 38.0 [d, *J*(PC) 20, $C(CH_3)_3$], 40.5 [d, *J*(PC) 25, $C(CH_3)_3$], 47.6 [d, *J*(PtC) 180, *J*(PC) 40, $CH_3CHC_6H_4$Br-3], 114.5 (br s, Ph, C^6), 120.1 [d, *J*(PC) 4, Ph, C^1], 127.4 (s, Ph, C^3 or C^5), 128.9 [d, *J*(PtC) 34, *J*(PC) 3, Ph, C^2 or C^4], 134.5 [s, *J*(PtC) 25, Ph, C^2 or C^4], 135.2 [s, *J*(PtC) 19, Ph, C^3 or C^5]
2c	0.7–1.1 [br, 18 H, $C(CH_3)_3$], 1.38 [d, 18 H, *J*(PH) 15.2, $C(CH_3)_3$], 1.8–2.3 (br m, 9 H, $PCH_2CH_2CH_2P$, $CH_3CHC_6H_4$Me-4), 2.42 [d, 3 H, *J*(PH) 4.0, Me-4], 4.5 (br, 1 H, $CH_3CHC_6H_4$Me-4), 6.72 (m, 2 H, Ph), 7.38 [d, 2 H, *J*(HH) 7.9, Ph]	17.9 [d, *J*(PtC) 18, *J*(PC) 4, $CH_3CHC_6H_4$Me-4], 20.9 [d, *J*(PtC) 25, *J*(PC) 23, $PCH_2CH_2CH_2P$], 21.6 (s, Me-4), 21.7 [d, partially obscured, *J*(PC) 5, $PCH_2CH_2CH_2P$], 23.1 [s, *J*(PtC) 57, $PCH_2CH_2CH_2P$], 29.9 [s, $C(CH_3)_3$], 30.5 [s, $C(CH_3)_3$], 36.0–42.0 [br, $C(CH_3)_3$], 47.8 [d, *J*(PtC) 194, *J*(PC) 42, $CH_3CHC_6H_4$Me-4], 112.0 [d, *J*(PC) 3, Ph, C^3], 133.9 [d, *J*(PtC) 18, *J*(PC) 4, Ph, C^4]

Table 1 (*continued*)

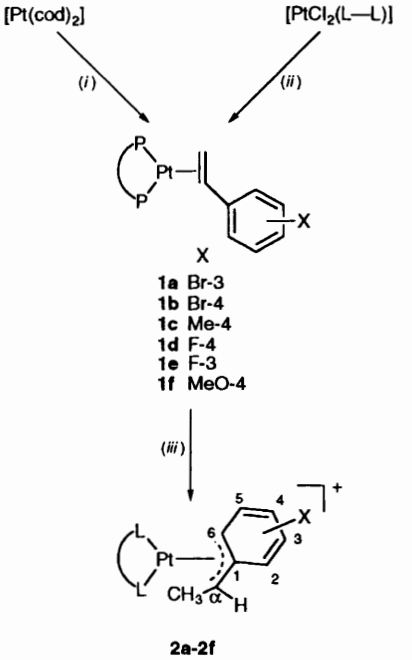
Complex	$^1H(\delta)$	$^{13}C\{^1H\}(\delta)$
2d	0.8 [br d, 18 H, *J*(PH) 12.8, $C(CH_3)_3$], 1.38 [d, 22 H, *J*(PH) 14.4, $C(CH_3)_3$, $CH_3CHC_6H_4F$-4], 1.8–2.4 (br m, 6 H, $PCH_2CH_2CH_2P$), 6.91 (m, 2 H, Ph), 7.26 (m, 2 H, Ph)	18.8 (s, $CH_3CHC_6H_4F$-4), 20.7 [d, *J*(PtC) 25, *J*(PC) 23, $PCH_2CH_2CH_2P$], 21.6 [dd, ^1J(PC) 29, ^2J(PC) 6, $PCH_2CH_2CH_2P$], 23.1 [s, *J*(PtC) 58, $PCH_2CH_2CH_2P$], 29.9 [d, *J*(PC) 4, $C(CH_3)_3$], 30.5 [s, $C(CH_3)_3$], 37.8 [br d, *J*(PC) 18, $C(CH_3)_3$], 39.5–41.0 [br m, partially obscured, $C(CH_3)_3$], 47.7 [d, *J*(PtC) 189, *J*(PC) 42, $CH_3CHC_6H_4F$-4], 112.1 (s, Ph, C^1), 120.0 [d, *J*(FC) 22, Ph, C^3 and C^5], 126.3 (br, Ph, C^2 and C^6), C^4 obscured by $CH_2{=}CHC_6H_4F$-4
2e	1.13 [br d, 18 H, *J*(PH) 13.5, $C(CH_3)_3$], 1.37 [d, 22 H, *J*(PH) 14.5, $C(CH_3)_3$, $CH_3CHC_6H_4F$-3], 1.9–2.5 (br m, 6 H, $PCH_2CH_2CH_2P$), 6.40 (m, 2 H, Ph), remaining Ph signals obscured by $CH_2{=}CHC_6H_4F$-3	18.5 [s, *J*(PtC) 25, $CH_3CHC_6H_4F$-3], 20.6 [d, *J*(PtC) 26, *J*(PC) 24, $PCH_2CH_2CH_2P$], 21.4 [dd, ^1J(PC) 29, ^2J(PC) 6, $PCH_2CH_2CH_2P$], 23.0 [s, *J*(PtC) 57, $PCH_2CH_2CH_2P$], 30.1 [d, *J*(PC) 4, $C(CH_3)_3$], 30.4 [s, *J*(PtC) 22, $C(CH_3)_3$], 38.2 [br d, *J*(PC) 19, $C(CH_3)_3$], 40.4 [br d, *J*(PC) 25, $C(CH_3)_3$], 48.2 [d, *J*(PtC) 170, *J*(PC) 40, $CH_3CHC_6H_4F$-3], 105.8 [br d, *J*(FC) 22, Ph, C^2 or C^6], 110.0 (br, Ph, C^2 or C^6), 118.4 [br d, *J*(FC) 23, Ph, C^4], 137.2 [br d, *J*(FC) 8, Ph, C^3 or C^5]
2f	0.74 [br s, 18 H, $C(CH_3)_3$], 1.38 [br d, 18 H, *J*(PH) 14.3, $C(CH_3)_3$], 1.8–2.3 (br m, 6 H, $PCH_2CH_2CH_2P$), 3.86 (s, 3 H, OMe-4), 4.27 (br, 1 H, $CH_3CHC_6H_4OMe$-4), 6.5–7.5 (m, 4 H, Ph)	17.8 [d, *J*(PtC) 10, *J*(PC) 4, $CH_3CHC_6H_4OMe$-4], 20.9 [d, *J*(PC) 23, $PCH_2CH_2CH_2P$], 21.7 [dd, *J*(PtC) 52, ^1J(PC) 29, ^2J(PC) 6, $PCH_2CH_2CH_2P$], 23.2 [s, *J*(PtC) 56, $PCH_2CH_2CH_2P$], 29.8 [br s, $C(CH_3)_3$], 30.6 [br s, $C(CH_3)_3$], 35.0–41.5 [br, $C(CH_3)_3$], 47.6 [d, *J*(PtC) 216, *J*(PC) 45, $CH_3CHC_6H_4OMe$-4], 56.2 (s, OMe-4), 103.4 [d, *J*(PC) 5, Ph, C^1], 117.3 (br s, Ph, C^2 and C^6), 131.8 (br s, Ph, C^3 and C^5)

* Chemical shifts (δ) in ppm positive to high frequency of $SiMe_4$, coupling constants in Hz, measurements at room temperature, unless otherwise stated and in C_6D_6 **1a–1f** or CD_2Cl_2 **2a** and **2c–2f**. For some samples the signals of the complex are obscured by the presence of free styrene.

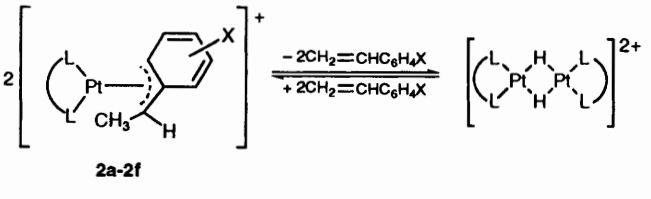
Table 2 $^{31}P\{^1H\}$ NMR data for the complexes $[Pt(\eta^2\text{-}CH_2{=}CHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **1a–1f**, $[Pt(\eta^3\text{-}MeCHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2a–2f** and $[Pt(\eta^3\text{-}MeCHPh)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **3d**[a]

Complex	$\delta(P^1)$	$J(PtP^1)$	$\delta(P^2)$	$J(PtP^2)$	$J(PP)$	Δ[b]
1a	44.3	3369	41.1	3317	38	52
1e	44.4	3360	42.4	3329	39	31
1b	44.5	3346	43.2	3335	40	11
1d	44.3	3306	43.0	3347	41	−41
1c	44.4	3302	43.1	3363	43	−61
1f	44.7	3272	43.5	3374	44	−102
2e	47.8	5156	38.1	3009	10	2156
2b	49.3	5256	36.0	2998	9	2258
3d[c]	48.3	5293	38.0	2995	7	2298
2a	51.6	5264	41.8	2960	9	2304
2c	49.9	5362	36.6	2972	7	2390
2d	51.2	5365	38.6	2944	6	2421
2f	53.8	5492	40.7	2909	4	2583

[a] Chemical shifts (δ) in ppm positive to high frequency of 85% H_3PO_4, coupling constants in Hz, measurements at room temperature, unless otherwise stated and in C_6D_6 **1a–1f** or CD_2Cl_2 **2a–2f** and **3d**. [b] $\Delta = {}^1J(PtP^1) - {}^1J(PtP^2)$. [c] Taken from ref. 9.



Scheme 1 (*i*) $Bu^t_2(CH_2)_3Bu^t_2$, L–L, styrene, hexane, 273 K; (*ii*) 1% Na/Hg amalgam, styrene, tetrahydrofuran (thf), 298 K; (*iii*) $HBF_4{\cdot}OEt_2$, diethyl ether, 273 K



Scheme 2 L–L = $Bu^t_2P(CH_2)_3PBu^t_2$

Protonation of $[Pt(\eta^2\text{-}CH_2{=}CHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1a–1f** with $HBF_4{\cdot}OEt_2$ in Et_2O at 273 K affords the cationic complexes $[Pt(\eta^3\text{-}MeCHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}]^+$ **2a–2f** (Scheme 1). Complexes **2a–2f** are all unstable in dichloromethane solution: a hydrogen is transferred from the benzyl ligand to the metal and the styrene is lost reversibly to give the dinuclear species $[Pt_2(\mu\text{-}H)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}_2][BF_4]_2$[11] (Scheme 2). However, the equilibrium can be shifted in favour of the benzyl complex by addition of the appropriate styrene and consequently **2a–2f** may be recrystallized by vapour diffusion of Et_2O into a solution of the compound in CH_2Cl_2–styrene. The reversibility of this reaction offers a route to the benzyl complexes from the diplatinum dihydride cation, a reaction which possibly involves the intermediacy of a mononuclear platinum species, $[PtH(solv)\{Bu^tP(CH_2)_3$

Table 3 Proton and ^{13}C-{^1H} NMR data for the complex $[Pt(\eta^3\text{-}MeCHC_6H_4Br\text{-}4)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2b***

T/K	^1H (δ)	^{13}C-{^1H}
195	0.73 [d, 9 H, *J*(PH) 13.9, $C(CH_3)_3$], 1.21 [d, 9 H, *J*(PH) 13.9, $C(CH_3)_3$], 1.34 [d, 18 H, *J*(PH) 13.3, $C(CH_3)_3$], 1.6–2.8 (br m, 2 H, $PCH_2CH_2CH_2P$), 2.0–2.4 (br m, 7 H, $PCH_2CH_2CH_2P$, $CH_3CHC_6H_4Br$-4), 4.54 (br m, 1 H, $CH_3CHC_6H_5$), 6.19 (m, 1 H, Ph, H^6), 6.80 [br d, 1 H, *J*(HH) 8.1, Ph, H^2], 7.50 [br d, 1 H, *J*(HH) 8.2, H^3 or H^5], 7.80 [br d, 1 H, *J*(HH) 6.4, Ph, H^3 or H^5]	17.2 (s, $CH_3CHC_6H_4Br$-4), 18.9 [d, *J*(PC) 24, $PCH_2CH_2CH_2P$], 19.9 [d, *J*(PC) 30, $PCH_2CH_2CH_2P$], 22.1 [s, *J*(PtC) 55, $PCH_2CH_2CH_2P$], 28.7 [s, $C(CH_3)_3$], 29.1 [s, $C(CH_3)_3$], 29.4 [s, $C(CH_3)_3$], 29.8 [s, $C(CH_3)_3$], 35.8 [d, *J*(PC) 22, $C(CH_3)_3$], 37.9 [d, *J*(PC) 18, $C(CH_3)_3$], 38.3 [d, *J*(PC) 26, $C(CH_3)_3$], 41.0 [d, *J*(PC) 26, $C(CH_3)_3$], 47.3 [d, *J*(PtC) 164, *J*(PC) 40, $CH_3CHC_6H_4Br$-4], 105.6 (br s, Ph, C^6), 113.5 (s, Ph, C^1), 124.6 (s, Ph, C^4), 130.8 (br s, Ph, C^2), 135.6 (br s, Ph, C^3 or C^5), 136.2 (br s, Ph, C^3 or C^5)
260	0.85 [br, 9 H, $C(CH_3)_3$], 1.33 [br s, $C(CH_3)_3$], 1.37 [br s, $C(CH_3)_3$], 1.39 [br s, 9 H, $C(CH_3)_3$], 1.8–2.7 [br m, 9 H, $PCH_2CH_2CH_2P$, $CH_3CHC_6H_4Br$-4], 4.62 (br, 1 H, $CH_3CHC_6H_4Br$-4), 6.60 (br s, 2 H, Ph, H^2 and H^6), 7.35 (br s, 1 H, Ph, H^4), 7.69 [br d, 2 H, *J*(HH) 8.2, Ph, H^3 and H^5]	17.6 [d, *J*(PC) 4, $CH_3CHC_6H_4Br$-4], 19.8 [d, *J*(PC) 24, $PCH_2CH_2CH_2P$], 20.1 [dd, ^1J(PC) 24, ^2J(PC) 5, PCH_2CH_2-CH_2P], 22.5 [s, *J*(PtC) 58, $PCH_2CH_2CH_2P$], 29.4 [br s, $C(CH_3)_3$], 47.6 [d, *J*(PtC) 164, *J*(PC) 40, $CH_3CHC_6H_4Br$-4], 114.2 (s, Ph, C^1), 125.3 [d, *J*(PC) 6, Ph, C^4], 136.2 (s, Ph, C^3 and C^5)
298	1.15 [br d, 18 H, *J*(PH) 11.1, $C(CH_3)_3$], 1.38 [d, 18 H, *J*(PH) 13.9, $C(CH_3)_3$], 1.8–2.3 (br m, 10 H, $PCH_2CH_2CH_2P$, $CH_3CHC_6H_4$-Br-4), 6.64 (m, 2 H, partially obscured, Ph), 7.69 (m, 2 H, Ph)	18.0 (s, $CH_3CHC_6H_4Br$-4), 20.2 [d, *J*(PC) 24, $PCH_2CH_2CH_2P$], 21.1 [dd, ^1J(PC) 29, ^2J(PC) 5, $PCH_2CH_2CH_2P$], 23.1 [s, *J*(PtC) 58, $PCH_2CH_2CH_2P$], 30.01 [s, $C(CH_3)_3$], 30.6 [s, $C(CH_3)_3$], 37.5 [d, *J*(PtC) 20, *J*(PC) 19, $C(CH_3)_3$], 40.1 [m, partially obscured, $C(CH_3)_3$], 48.5 [d, *J*(PtC) 175, *J*(PC) 40, $CH_3CHC_6H_4Br$-4), 115.9 (s, Ph, C^1), 122.3 (br, Ph, C^2 and C^6), 126.4 [d, *J*(PC) 3, Ph, C^4], 136.4 [s, *J*(PtC) 19, Ph, C^3 and C^5]

* Chemical shifts (δ) in ppm positive to high frequency of $SiMe_4$, coupling constants in Hz, recorded in CD_2Cl_2.

$PBu^t_2\}]^+$ (solv = solvent). Musco and co-workers[5] have recently reported the reaction of an analogous species $[PdMe(solv)L_2]^+$ with styrene in which the methyl group migrates to the co-ordinated styrene forming an η^3-ethylbenzyl ligand. Subsequent elimination of the methylstyrene is believed to generate a hydridosolvate species which may react with excess of styrene to afford methylbenzyl derivatives similar to those reported here.

As we reported previously,[9] a single-crystal X-ray diffraction study of complex **2b** confirmed the bonding mode of the η^3-methylbenzyl moiety, the phenyl ring lying perpendicular to the plane defined by the platinum and phosphorus atoms. The study also illustrated that the methyl group occupies an *anti* position. This is consistent with the low-temperature ^1H NMR data for **2b** (Table 3) which revealed a signal at δ 4.54, the chemical shift typical of a *syn*-allylic proton.[12] In η^3-allyl complexes substituted at a terminal carbon atom, the isomer with the bulkiest substituent in the *syn* position is expected to predominate because of lower steric interaction with the metal.[13] Likewise, in substituted η^3-benzyl complexes the *syn* isomer would normally also allow the lowest possible interaction of the substituent with the *meta* atom.[3] However, it is possible that steric interaction between a methyl group in the *syn* position and the bulky Bu^t groups on the diphosphine ligand forces the adoption of an *anti* configuration in complexes **2a**–**2f**.[14] It is interesting that the substituted palladium benzyl complexes reported by Musco and co-workers[5] adopt an *anti* geometry.

The crystal structure of complex **2b** also showed that the methylbenzyl group is bonded to the platinum atom with Pt–η^3-C distances of 2.163(11), 2.242(10) and 2.446(9) Å in the sequence C_α, C^1, C^2. This asymmetry is not untypical and a number of compounds containing the η^3-benzyl moiety exhibit a similar trend.[1,3,4] The asymmetric bonding of the η^3-methylbenzyl moiety is reflected in the Pt–P bond lengths. Thus Pt–P(1), which is *trans* to the longest Pt–C bond [P(1)–Pt–C(64) 160.9(3)°], is appreciably shorter than Pt–P(2) [2.295(3) *vs.* 2.349(3) Å]. This in turn explains the difference in magnitude of the Pt–P coupling constants which are discussed below.

The low-temperature limiting ^{13}C-{^1H} NMR spectra of complexes **2b** (Table 3), **2d** and **2f** are consistent with the solid-state structure and hence six resonances are observed for the inequivalent phenyl carbon atoms. Although the assignments for C^3 and C^5 may be reversed, the carbon atoms C^2 and C^6 can be assigned on the basis of chemical shift and coupling to other spin-active nuclei. The ^1H NMR spectra of **2b** and **2f**, recorded at 195 and 225 K respectively, also show characteristic signals for the *syn*-benzylic proton at δ 4.54 and 4.27 respectively. However, as the temperature is raised, a number of spectral changes occur: at 298 K the ^1H and ^{13}C-{^1H} NMR spectra of **2b**, **2d** or **2f** show that these complexes possess an apparent plane of symmetry passing through C_α, C^1 and C^4 (Table 1). Thus averaged parameter values are observed for C^2 and C^6 and, separately, C^3 and C^5. At this temperature the spectrum of **2c** is still below the fast-exchange rate limit and signals for C^2, C^6, C^3 and C^5 are collapsed into the baseline. For each of **2a** and **2e**, substituted in the 3 position, only one set of signals is observed at 298 K (Table 1) and not two sets corresponding to the two possible orientations of the 3-substituent.

In each of the complexes **2** the *syn*-benzyl proton exchanges sufficiently rapidly on the NMR time-scale with the *anti*-methyl protons that at 298 K the averaged signal is broad and difficult to observe, being also obscured in part by the other ligand signals. An earlier paper[8] presented experimental evidence suggesting that the fluxional behaviour of the complexes $[Pt(\eta^3\text{-}MeCHPh)(L\text{–}L)][BF_4]$ [L–L = $(C_6H_{11})_2P(CH_2)_n$-$P(C_6H_{11})_2$, n = 2 **3a** or 3 **3c**, $Bu^t_2P(CH_2)_nPBu^t_2$, n = 2 **3b** or 3 **3d** or $Bu^t_2PCH_2C_6H_4CH_2PBu^t_2$ **3e**] could be explained by a mechanism that involved an $\eta^3 \rightleftharpoons \eta^1$ conversion followed by β elimination and hydride migration. On the basis of variable-temperature NMR spectroscopy, we postulate that the dynamic processes occurring in **2** are similar to those of **3** and can hence be interpreted by the same mechanism.

It is particularly interesting to compare the NMR parameters for the complex $[Pt(\eta^3\text{-}MeCHPh)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **3d** and **2a**–**2f** to examine the effect, if any, the phenyl ring substituent X has on the degree of Pt–η^3-$MeCHC_6H_4X$ interaction. As expected, the ^{31}P-{^1H} NMR data for these complexes (Table 3) show that there are two inequivalent phosphorus environments with a large difference in ^1J(PtP) values. The spectra also remain unchanged down to 200 K. This is fully consistent with one phosphorus atom lying *trans* to a

weakly co-ordinating C_6H_4X group and is also supported by the unequal Pt–P bond lengths found in the crystal structure of **2b**. Moreover, the larger of the coupling constants, $^1J(PtP^1)$, is particularly sensitive to the electron-donating ability of the substituent X, whereas the other value, $^1J(PtP^2)$, remains relatively constant. The magnitude of the difference between these two coupling constants may be taken as a measure of the asymmetry in the Pt–η^3-methylbenzyl bond. Interestingly there appears to be a correlation between this and ease of loss of styrenes from **2**. Indeed, **2c**, **2d** and **2f**, with the largest values for $[^1J(PtP^1) - {}^1J(PtP^2)]$, lose styrene most readily, with the equilibrium in Scheme 2 lying to the right for these complexes. Taking the substituent constant σ_p^+ as a guide to the overall electron-donating ability of X, it appears that the more electron donating the substituent the more asymmetric is the bond and the more facile the loss of styrene. Conversely, styrenes with electron-withdrawing substituents form the least-reactive complexes with regard to styrene displacement. This is somewhat surprising since it might be expected that σ (ligand to metal) donation is more important in platinum(II) complexes than π-back bonding. Any effect which increases the tendency for electronic charge to be donated to the metal might therefore be expected to stabilize the bonding and *vice versa*. For example, Mann *et al.*[3] found that electron-donating substituents favoured the binding of the metal to the substituted phenyl group in [Pd(η^3-$CPh_2C_6H_4X$-4)(acac)] (X = F, Me or OMe; acac = acetylacetonate). Conversely, electron-withdrawing substituents disfavoured the binding of the metal.

The ease of displacement of styrenes from complexes **2** prompted us to consider the usefulness of these species as intermediates in the preparation of other complexes. The displacement by alkenes such as bicyclo[2.2.1]hept-2-ene (norbornene) and ethene was explored with the intention of preparing complexes stabilized by β-*agostic* interactions. On treatment with norbornene, **2** lost styrene irreversibly and the known complex $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$,[15,16] stabilized by a β-agostic bond, was produced. In a similar displacement reaction using ethene (1 atm, *ca.* 10^5 Pa), the conversion into $[PtEt\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$[17] was reversible. Once it had been established that complexes **2** could be useful precursors to platinum(II) monoalkyl complexes, we became interested in tailoring their reactivity. The ^{31}P-$\{^1H\}$ NMR spectroscopic evidence suggested that the substituted styrenes CH_2=CHC_6H_4X where X = F-4 or MeO-4 were the most weakly bound and hence most readily displaced. This was indeed found to be the case, for example, displacement of CH_2=CHC_6H_4Br-4 from **2b** by a variety of alkenes was unsuccessful, but when **2d** was employed complete conversion into new products was possible.

To conclude, this work has established that although variation in the phenyl substituent does not affect the ground-state structure or mechanism of the dynamic behaviour of platinum η^3-methylbenzyl complexes for the range of substituents tested, it does affect the asymmetry of the Pt–η^3-$MeCHC_6H_4X$ interaction and the elimination of styrene from the complex. Furthermore the ease with which some of the compounds lose styrene has led to a convenient route to new platinum(II) monoalkyl complexes, and other electrophilic complexes.

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: thf and diethyl ether over sodium–benzophenone, toluene over Na, hexane and CH_2Cl_2 over CaH_2, and freshly distilled prior to use. Solvents for NMR spectra were degassed by the freeze–pump–thaw method. Both 1,3-bis(di-*tert*-butylphosphino)propane[16] and $[Pt(C_8H_{12})_2]$[18] were prepared by the published methods, and $[PtCl_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$[19] was prepared by the reaction of the diphosphine with $[PtCl_2(CH_2CHPh)_2]$.[20] Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR instrument as KBr discs, and NMR spectra on a Bruker AC 300 or JEOL EX90 spectrometer at ambient temperature unless otherwise stated (Tables 1–3). All ^1H and ^{13}C NMR chemical shifts are expressed in δ relative to $SiMe_4$ (δ 0.0). Chemical shifts in ^{31}P NMR spectra are positive to high frequency of 85% H_3PO_4 (external).

Synthesis of the Complexes $[Pt(\eta^2$-CH_2=$CHC_6H_4X)\{Bu^t_2$-$P(CH_2)_3PBu^t_2\}]$ **1a–1f**.—The platinum(0) alkene complexes were prepared either from $[Pt(cod)_2]$ by displacement (Method A) or by reduction of $[PtCl_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ (Method B) with sodium amalgam.

Method A. An excess (*ca.* 2 mole equivalents) of the appropriate styrene was added to a cold (*ca.* 273 K) solution of $Bu^t_2P(CH_2)_3PBu^t_2$ in hexane (20 cm^3) and $[Pt(cod)_2]$ was then added in portions. The reaction mixture was stirred at this temperature for *ca.* 1 h and after allowing it 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 or toluene 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 cm^3) was added an excess (*ca.* 2 mole equivalents) of the appropriate styrene followed by $[PtCl_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$. 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. Where necessary, the product was filtered through a 5 cm^3 pad of neutral alumina, eluted with diethyl ether. Recrystallization from diethyl ether at 253 K gave the product in fair yield.

(*i*) The reaction of $Bu^t_2P(CH_2)_3PBu^t_2$ (0.149 g, 0.45 mmol) with CH_2=CHC_6H_4Br-3 (0.10 cm^3, 0.77 mmol) and $[Pt(cod)_2]$ (0.184 g, 0.45 mmol) (method A) gave $[Pt(\eta^2$-CH_2=CHC_6H_4Br-3)$\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1a** (0.249 g, 78%) as colourless *crystals* (Found: C, 45.7, H, 7.1. $C_{27}H_{49}BrP_2Pt$ requires C, 45.7; H, 7.0%).

(*ii*) Pale cream *crystals* of $[Pt(\eta^2$-CH_2=CHC_6H_4Br-4)-$\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1b** (0.088 g, 52%) were prepared from $Bu^t_2P(CH_2)_3PBu^t_2$ (0.075 g, 0.23 mmol), CH_2=CHC_6H_4Br-4 (0.20 cm^3, 1.53 mmol) and $[Pt(cod)_2]$ (0.093 g, 0.23 mmol) (method A) (Found: C, 45.9; H, 7.2. $C_{27}H_{49}BrP_2Pt$ requires C, 45.6; H, 7.0%).

(*iii*) Pale cream, *crystals* of $[Pt(\eta^2$-CH_2=CHC_6H_4Me-4)-$\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1c** (0.737 g, 82%) were obtained from the reaction of $Bu^t_2P(CH_2)_3PBu^t_2$ (0.465 g, 1.40 mmol), CH_2=CHC_6H_4Me-4 (0.40 cm^3, 3.04 mmol) and $[Pt(cod)_2]$ (0.574 g, 1.40 mmol) following method A. The reduction of $[PtCl_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ (0.700 g, 1.20 mmol) in the presence of CH_2=CHC_6H_4Me-4 (0.30 cm^3, 2.83 mmol) also gave complex **1c** (0.389 g, 50% yield) (method B) (Found: C, 51.9; H, 8.2. $C_{28}H_{51}P_2Pt$ requires C, 52.1; H, 8.0%).

(*iv*) The reaction of $[PtCl_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ (0.287 g, 0.48 mmol) and CH_2=CHC_6H_4F-4 (0.20 cm^3, 1.68 mmol) (method B) afforded white *crystals* of $[Pt(\eta^2$-CH_2=CHC_6H_4F-4)$\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1d** (0.246 g, 79%). The compound was characterized by NMR spectroscopy.

(*v*) Following method B, $[PtCl_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ (0.210 g, 0.35 mmol) and CH_2=CHC_6H_4F-3 (0.20 cm^3, 1.68 mmol) gave $[Pt(\eta^2$-CH_2=CHC_6H_4F-3)$\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1e** as a cream *solid* (0.141 g, 62%). The compound was characterized by NMR spectroscopy.

(*vi*) The reduction of $[PtCl_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ (0.202 g, 0.34 mmol) in the presence of an excess of CH_2=CHC_6H_4OMe-4 (0.20 cm^3, 1.50 mmol) for 16 h (method B) afforded $[Pt(\eta^2$-CH_2=CHC_6H_4OMe-4)$\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1f** as a yellow

powder (0.106 g, 47%). The compound was characterized by NMR spectroscopy.

Protonation of $[Pt(\eta^2\text{-}CH_2{=}CHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1a–1f**. *Synthesis of the Complexes* $[Pt(\eta^3\text{-}MeCHC_6H_4X)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2a–2f**.—The experimental procedures for the synthesis of complexes **2a–2f** were essentially identical. Typically, an approximately equimolar amount of $HBF_4{\cdot}OMe_2$ was added to a cold (*ca.* 273 K) solution of the styrene complex **1** in diethyl ether (*ca.* 10 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 (3×5 cm^3, discarded) and dried *in vacuo*.

(*i*) The complex $[Pt(\eta^3\text{-}MeCHC_6H_4Br\text{-}4)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **2a** (0.105 g, 80%) was obtained as orange *microcrystals*. In solution, in the absence of excess of $CH_2{=}CHC_6H_4Br$-3, the compound is in equilibrium with $[Pt_2(\mu\text{-}H)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}_2][BF_4]_2$. The compound was characterized by NMR spectroscopy.

(*ii*) The complex $[Pt(\eta^3\text{-}MeCHC_6H_4Br\text{-}4)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2b** (0.120 g, 85%) was obtained from the protonation of **1b**. Recrystallization from CH_2Cl_2–diethyl ether in the presence of an excess (*ca.* 2 molar) of $CH_2{=}CHC_6H_4Br$-4 afforded **2b** as orange-green dichroic *crystals* (Found: C, 38.5; H, 6.4. $C_{27}H_{51}BF_4P_2Pt{\cdot}CH_2Cl_2$ requires C, 38.1; H, 5.9%).

(*iii*) The complex $[Pt(\eta^3\text{-}MeCHC_6H_4Me\text{-}4)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2c** (0.111 g, 85%) was obtained as pale orange-green dichroic *crystals*. In solution, in the absence of $CH_2{=}CHC_6H_4Me$-4, an equilibrium is established with the compound $[Pt_2(\mu\text{-}H)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}_2][BF_4]_2$ (Found: C, 45.9; H, 7.7. $C_{28}H_{52}BF_4P_2Pt$ requires C, 45.8; H, 7.3%).

(*iv*) Protonation of $[Pt(\eta^2\text{-}CH_2{=}CHC_6H_4F\text{-}4)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1d** (0.222 g, 0.34 mmol) afforded pale yellow-green dichroic *crystals* of $[Pt(\eta^3\text{-}MeCHC_6H_4F\text{-}4)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2d** (0.208 g, 83%). During recrystallization from CH_2Cl_2–diethyl ether the presence of a small excess of $CH_2{=}CHC_6H_4F$-4 prevented partial conversion into $[Pt_2(\mu\text{-}H)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}_2][BF_4]_2$. The compound crystallized as a hemisolvate (Found: C, 44.0; H, 6.9. $C_{27}H_{50}BF_5P_2Pt{\cdot}0.5CH_2Cl_2$ requires C, 43.4; H, 6.8%).

(*v*) The complex $[Pt(\eta^3\text{-}MeCHC_6H_4F\text{-}3)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2e** (0.115 g, 80%) was prepared as an orange *powder*. In solution, in the absence of excess of $CH_2{=}CHC_6H_4F$-3, the compound partially decomposes to give $[Pt_2(\mu\text{-}H)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}_2][BF_4]_2$. The instability of the complex made it difficult to prepare an analytically pure sample and the characterization rests on the spectroscopic data.

(*vi*) The protonation of $[Pt(\eta^2\text{-}CH_2{=}CHC_6H_4OMe\text{-}4)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1f** affords the product $[Pt(\eta^3\text{-}MeCHC_6H_4OMe\text{-}4)\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2f** (0.131 g, 90%) as a mustard yellow *powder*. In solution, in the absence of $CH_2{=}CHC_6H_4OMe$-4, an equilibrium is established with the dinuclear complex $[Pt_2(\mu\text{-}H)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}_2][BF_4]_2$. The compound was isolated with 1 equivalent of diethyl ether of crystallization [Found: C, 46.6; H, 7.4. $C_{28}H_{53}BF_4OP_2Pt{\cdot}O(CH_2CH_3)_2$ requires C, 46.7; H, 7.7%].

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