Ligand Control of Agostic M···H···C Three-centre, Two-electron Bonding in Bicyclo[2.2.1]hept-2-yl Complexes of Platinum and Palladium. X-Ray Crystal Structures of $[Pt(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ and $[Pt(C_7H_{11})\{Bu^t_2P\text{-}(CH_2)_2PBu^t_2\}][BPh_4]$†

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The reaction of non-co-ordinating acids with the Pt^0 and Pd^0 alkene complexes $[M(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$ [M = Pt or Pd; L–L = $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$, **1a** or **1f**: $Bu^t_2P(CH_2)_2PBu^t_2$, **1b** or **1g**; and *o*-$C_6H_4(CH_2PBu^t_2)_2$, **1e** or **1h**; M = Pt, L–L = $(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$ **1c** or $Bu^t_2P(CH_2)_3PBu^t_2$ **1d**] affords a series of cationic bicyclo[2.2.1]hept-2-yl complexes **2a–2h** in which the otherwise electron-deficient metal centre is stabilized by a three-centre, two-electron (agostic) interaction with the *exo*-3-CH bond. The complexes were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy and for **1b** and **2b** by single-crystal X-ray crystallography. In complex **1b** the norborn-2-ene is bound to the platinum in a normal in-plane η^2-mode with equal Pt–C distances [2.110(7), 2.108(8) Å] and Pt–P distances [2.273(2), 2.274(2) Å]. For **2b** the crystallographic results reveal a long Pt–C_β contact of 2.309(5) Å which is bridged by a hydrogen atom forming the agostic bond, whereas the Pt–C_α bond is shortened to 2.096(4) Å. The Pt–P bond *trans* to the weak agostic bond is significantly shorter than the *cis* Pt–P bond [2.256(1) and 2.311(1) Å respectively], and this asymmetry in the co-ordination of the diphosphine is reflected in the ^{31}P NMR spectrum of **2b** for which $^1J(PtP_{trans}) \gg {}^1J(PtP_{cis})$. The extent of agostic interaction, as indicated by NMR parameters [$^1J(PtH)$, $^1J(PtP_{trans})$, *etc.*], depends on the bite angle of the diphosphine and the bulk of the substituents on phosphorus such that the smallest diphosphines induce the strongest M···H···C interaction. All the agostic complexes undergo a rapid intramolecular rearrangement on the NMR time-scale at room temperature involving β-elimination and alkene rotation. However, the ^{31}P nuclei remain non-equivalent up to 300 K.

Much of the interest in organometallic chemistry derives from the facilitity with which transition metal centres mediate bond formation and scission reactions between carbon and other light atoms. Archetypal reactions are those involving C–H bonds, as found in the transition-metal catalysed hydrogenation of alkenes and numerous other organometallic processes. Recent work has revealed crucial insights into the detail of the interaction of the transition metal atom with the C–H bond. In the case of alkene hydrogenation and related reactions, the concerted hydrogen transfer is believed to proceed through intermediates or transition states in which carbon, hydrogen and metal are linked by a three-centre, two-electron interaction (an agostic interaction). Of particular significance in extending the understanding of the intimate mechanism have been studies of model complexes in which the three-centre, two-electron interaction is present in the ground-state configuration of a stable molecule, rather than in short-lived transients. A considerable number of such complexes have been reported for metals from across the transition series, and the field has been recently reviewed by Brookhart *et al.*[1] However, despite this plethora of examples, there have been relatively few systematic studies of related compounds aimed at elucidating the factors which dictate the nature and stability of the agostic interaction.

Our earlier work on organocobalt complexes[2] was somewhat restricted by the tendency of the complexes to oxidize, and the limited scope for systematic structural change. This led us to consider the benefits of synthesizing a series of complexes of platinum(II) of the type $[PtR(L\text{–}L)]^+$ (R = hydrocarbon ligand, L–L = chelating diphosphine). In the absence of an agostic interaction between the metal and a C–H bond these would be 14-electron complexes, and such complexes are rare amongst the metals for which d^8 is a common electron configuration. There was thus the possibility that the electron deficiency of the metal could be reduced by interaction of the metal with either the α or β C–H bonds of the alkyl group. Another possibility was that the metal would remove the hydrogen entirely from the organic group affording, for example, a 16-electron metal hydridoalkene complex. Examples of *trans* hydridoalkene complexes of platinum are known,[3] for example, the cation *trans*-$[PtH(C_2H_4)(PEt_3)_2]^+$. In the latter case it seemed plausible that the *trans* orientation of the bulky phosphine ligands might be responsible for stabilizing the hydridoalkene form over an isomeric agostic alkyl form in which the PEt_3 groups would necessarily be in a *cis* relationship. We therefore chose to restrict the complexes to a *cis* geometry through the use of chelating diphosphines, which offered the added advantage of allowing quite subtle control over the steric and electronic factors through modifications to the length of the chain linking the two ligating atoms.[4] The choice of bicyclo[2.2.1]hept-2-ene (norborn-2-ene) as a suitable precursor was initially dictated by the ease of access to platinum(0) complexes of this strained alkene.[5] A preliminary report of this work has been published.[6]

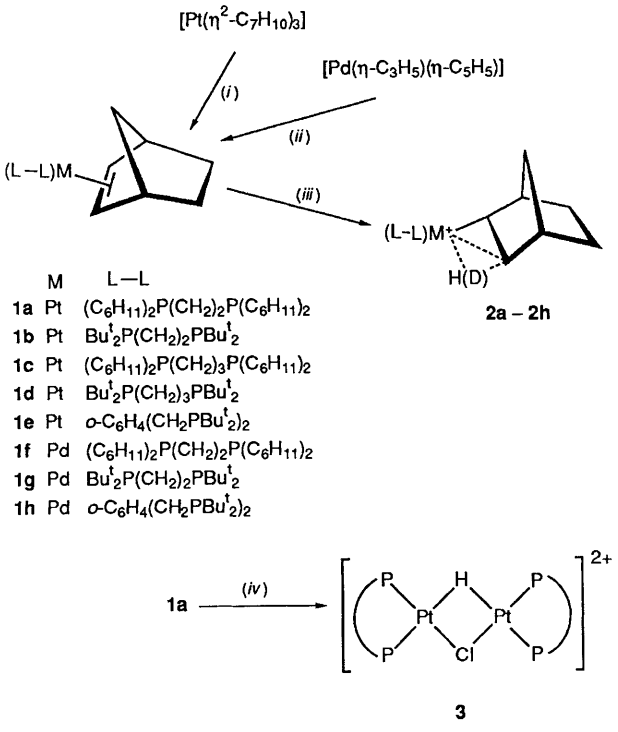
† η^2-Bicyclo[2.2.1]hept-2-ene-[1,2-bis(di-*tert*-butylphosphino)ethane-*P*,*P*′]platinum and bicyclo[2.2.1]hept-2-yl-C^1,C^2,H^β-[1,2-bis(di-*tert*-butylphosphino)ethane-*P*,*P*′]platinum tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Selected ^1H, ^{13}C and ^{31}P NMR data* for the compounds $[M(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$ (M = Pt, **1a**–**1e** or Pd, **1f**–**1h**)

Compound	Solvent	δ_H	J(PtH)	δ_C	J(PtC)	δ_P	J(PtP)
1a	C_6D_6	2.78	57.5	47.9	345	71.8	2982
1b	CD_2Cl_2	2.05	58.6	47.5	344	102.0	3067
1c	CD_2Cl_2	2.34	55.5	47.5	339	24.3	3116
1d	$C_6D_5CD_3$	2.16	58	48	333	46.5	3195
1e	C_6D_6	2.13	58.7	50.1	332	48.9	3331
1f	C_6D_6	3.6		62.4		77.0	
1g	C_6D_6	3.43		61.5		82.3	
1h	CD_2Cl_2	2.94		65.4		49.4	

* ^1H and ^{13}C NMR data refer to the alkene bond; δ (ppm) referenced as described in the Experimental section, coupling constants in Hz.



Scheme 1. (*i*) Diphosphine, L–L, hexane, 0 °C; (*ii*) L–L, norborn-2-ene, hexane, 20 °C; (*iii*) $HBF_4{\cdot}OEt_2$ (or CF_3SO_3D), diethyl ether, 0 °C; (*iv*) CH_2Cl_2, 20 °C

Results and Discussion

Treatment of tris(norborn-2-ene)platinum, $[Pt(\eta^2\text{-}C_7H_{10})_3]$, with diphosphines, L–L, in hexane readily affords the compounds $[Pt(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$ [L–L = $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$, **1a**; $Bu^t_2P(CH_2)_2PBu^t_2$, **1b**; $(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$, **1c**; $Bu^t_2P(CH_2)_3PBu^t_2$, **1d**; and *o*-$C_6H_4(CH_2PBu^t_2)_2$, **1e**], which have been characterized by microanalysis and NMR (^1H, ^{13}C, ^{31}P and ^{195}Pt) spectroscopy (Table 1 and Experimental section). Thus, the olefinic protons of the compounds **1** give rise to a distinctive signal in the proton NMR spectrum at δ *ca.* 2–3 with J(PtH) *ca.* 50 Hz, and the $^{13}C\text{-}\{^1H\}$ NMR spectra show characteristic resonances for the contact carbon atoms of the co-ordinated alkene at δ *ca.* 50 ppm [J(PtC) *ca.* 330 Hz]. The $^{31}P\text{-}\{^1H\}$ NMR spectra of the compounds **1** all show a single resonance (with ^{195}Pt satellites), as expected.

Surprisingly, the reaction between $[Pd(\eta^2\text{-}C_7H_{10})_3]$[5a] and the same diphosphines, L–L, was found not to be a suitable synthesis of the compounds $[Pd(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$. However, an alternative route to the palladium species was developed utilising the compound $[Pd(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$.[7] Thus, reaction of $[Pd(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ with the appropriate diphosphine in the presence of norbornene gives the compounds $[Pd(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$ [L–L = $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$, **1f**; $Bu^t_2P(CH_2)_2PBu^t_2$, **1g**; and *o*-$C_6H_4(CH_2PBu^t_2)_2$, **1h**]. The NMR (^1H, ^{13}C and ^{31}P) spectra of compounds **1f**–**1g** are similar to those of the platinum species **1a**, **1b** and **1e** and are entirely consistent with these compounds being formulated as η^2-norbornene complexes (see Table 1).

Protonation of $[Pt(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$ **1a**–**1e** with either $HBF_4{\cdot}OEt_2$ or CF_3SO_3H in OEt_2 at −0 °C affords microcrystalline complexes of formula $[Pt(C_7H_{11})(L\text{–}L)][Y]$ **2a**–**2e** (Y = BF_4 or CF_3SO_3) (Scheme 1) in *ca.* 75–95% yield. The palladium complexes $[Pd(C_7H_{11})(L\text{–}L)][BF_4]$ **2f**–**2h** are obtained similarly, but in lower yield (*ca.* 55–75%), by protonation of **1g**–**1h** with $HBF_4{\cdot}OEt_2$. It is noteworthy that protonation of **1g**–**1h** using CF_3SO_3H does not lead to isolation of the $CF_3SO_3^-$ salts of **2f**–**2h** but rather results in the formation of uncharacterized species.

Inspection of the IR spectra of the salts **2** is revealing in that no bands attributable to M–H stretches are observed for any of the compounds. Variable-temperature NMR spectroscopic studies show that the cations **2** undergo fluxional behaviour in solution (see below). However, throughout the temperature range 300–194 K the ^1H NMR spectra of all the compounds show a high-field signal (δ *ca.* −2), typical of discrete hydride ligands on platinum(II) *trans* to a soft ligand.[8] The high-field signal shows coupling to one phosphorus nucleus and, for the platinum species **2a**–**2e**, is weakly coupled to the metal (Table 2). For example, the resonance at δ −1.78 in the spectrum of the cation $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_3PBu^t_2\}]^+$ **2d** shows couplings of 51.3 and 85 Hz [J(PH) and J(PtH) respectively]. These may be compared with the corresponding values of 182 and 779 Hz for the compound $[PtH(O_3SCF_3)\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ which is known to contain a terminal hydride ligand.[9] Although these observations are indicative of the presence of a metal–hydrogen bond in the salts **2** the magnitudes of the platinum–hydrogen coupling constants suggest that this interaction is weak. Consistent with this, for all the compounds **2a**–**2e**, one of the platinum–phosphorus coupling constants [J(PtP)] is substantially larger than the other (*e.g.* 5067 and 2532 Hz for **2d**, Table 2), the large coupling constant being associated with the phosphorus nucleus *trans* to the weakly interacting hydrogen.

The implication of the IR and NMR spectroscopic data is that the norbornyl ligand in the salts **2** is bound to the metal *via* both σ-alkyl and β-agostic interactions. The presence of such an agostic bond would be expected to manifest itself in a reduced carbon–hydrogen coupling constant, ^1J(CH) for the agostic hydrogen atom.[1] Unfortunately, direct observation of ^1J(CH) for the agostic hydrogen has not proved possible due to the plethora of alkyl signals and complex (^{31}P and ^{195}Pt) couplings. Only in the case of $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}]^+$ **2b**, for which the β-carbon atom (δ 30.0 ppm) apparently shows proton couplings of 149 and 64 Hz at 195 K, has it proved possible to obtain an estimate of ^1J(CH) for the agostic hydrogen. The uncertainty arises due to severe overlap of signals in the region of the carbon-13 spectrum of interest. In order fully to characterize the nature of the interaction between the norbornyl

Table 2 Selected ^1H and ^{31}P NMR data* for the complex cations $[M(C_7H_{11})(L–L)]^+$ (M = Pt, **2a**–**2e** or Pd, **2f**–**2h**)

Compound	δ_H	$J(P_{trans}H)$	$J(PtH)$	$\delta(P_{trans})$	$\delta(P_{cis})$	$J(PP)$	$J(PtP_{trans})$	$J(PtP_{cis})$
2a	−1.84	80.1	324	64.3	74.8	8.5	3866	2695
2b	−1.05	56.7	136	90.2	89.1	17.9	4909	2577
2c	−1.42	52.7	102	24.7	17.8	9.1	4852	2564
2d	−1.78	51.3	85	47.4	37.5	9.8	5067	2532
2e	−2.14	52.2	79	52.6	37.4	—	5266	2620
2f	−1.30	59.7	—	63.6	70.4	15.3	—	—
2g	−1.65	59.6	—	92.5	97.6	13.3	—	—
2h	−2.38	58.0	—	67.4	38.5	33.4	—	—

* Measured in CD_2Cl_2 at ambient temperature; proton NMR data refers to the agostic hydrogen; P_{trans} and P_{cis} refer to the phosphorus atoms *trans* and *cis* respectively to the agostic hydrogen; for the palladium compounds assignment of the phosphorus spectrum was made by analogy with the appropriate platinum compound.

Table 3 Crystallographic data for $[Pt(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ **1b** and $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}][BPh_4]$ **2b***

Complex	**1b**	**2b**
Empirical formula	$C_{25}H_{50}P_2Pt$	$C_{49}H_{71}BP_2Pt$
Molecular weight	607.7	927.9
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
Cell dimensions		
a/Å	10.359(2)	13.996(4)
b/Å	18.016(3)	18.963(7)
c/Å	14.461(2)	18.615(6)
β/°	102.49(1)	114.31(2)
Z	4	4
U/Å^3	2635(1)	4503(2)
D_c/g cm^{-3}	1.53	1.37
μ(Mo-Kα)/cm^{-1}	54.8	32.5
2θ range/°	4–50	4–55
F(000)	1232	1912
No. of data collected	5080	9383
No. of unique data	4457	8371
No. with $F > n\sigma(F)$ (N_o)	3729	7985
No. of variables (N_v)	261	490
R	0.043	0.029
R'	0.059	0.037
S	2.03	1.35

* $R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$.

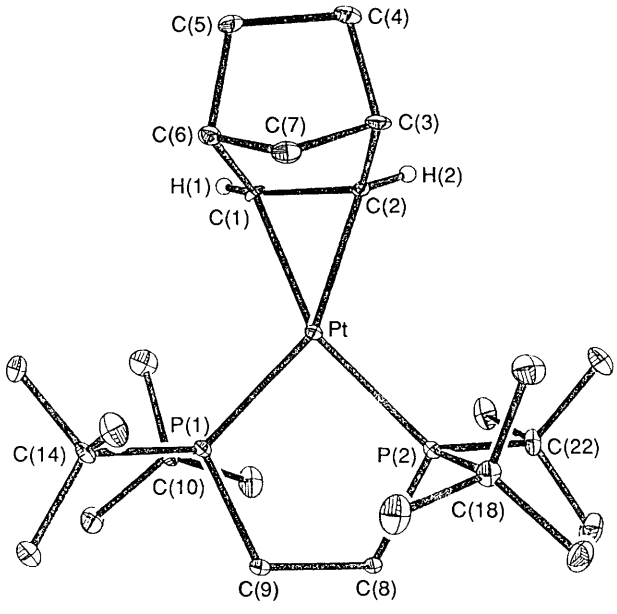


Fig. 1 Molecular structure of $[Pt(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ **1b**

ligand and the metal in the cations **2**, a low-temperature X-ray diffraction study was carried out on the tetraphenylborate salt of **2b**, $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}][BPh_4]$, the product of anion metathesis of **2b** (Y = BF_4) with $NaBPh_4$. For comparative reasons, the structure of the precursor alkene complex, **1b**, was also determined.

The solid-state structures of **1b** and **2b** are shown in Figs. 1 and 2 respectively, a summary of the crystallographic data is compiled in Table 3, and selected bond lengths and angles are collected in Table 4. The structure of **1b** displays the expected features of a zerovalent platinum alkene complex. Thus, the co-ordinated carbon atoms of the norbornene ligand lie in the co-ordination plane defined by Pt, P(1) and P(2) with an average Pt–C–C angle of 69.7(4)°. The platinum–carbon [Pt–C(1) 2.110(7), Pt–C(2) 2.108(8) Å] and carbon–carbon [C(1)–C(2) 1.46(1) Å] bond distances are similar to those found in related species.[10]

Wholly consistent with the solution NMR data, the solid-state structure of the cation $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}]^+$ **2b** shows that the norbornyl ligand is bound *via* both a σ bond and a β-agostic interaction. Hence, the atom C(2) is within the normal σ-bond distance of platinum [Pt–C(2) 2.096(4) Å] whereas C(1) is more remote [Pt–C(1) 2.309(5) Å], but is still close enough to interact with the metal. The agostic hydrogen was located directly [Pt–H(1a) 1.90(7), C(1)–H(1a) 1.28(6) Å] and lies in the co-ordination plane defined by Pt, P(1) and P(2).

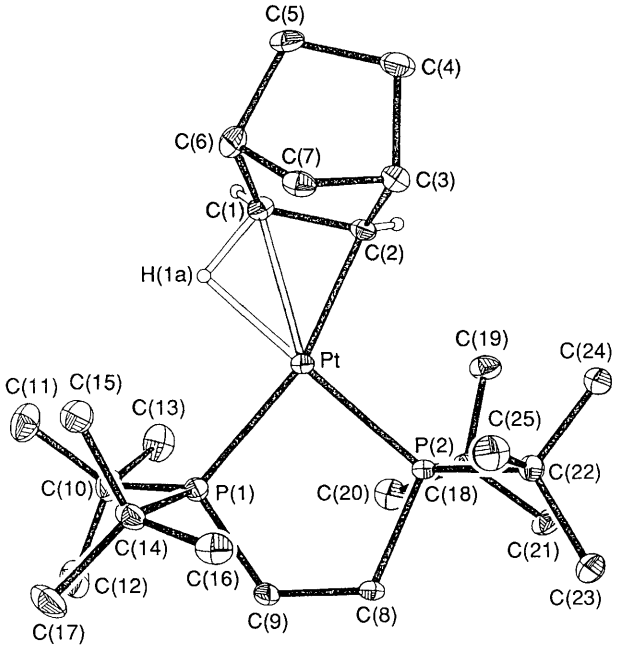
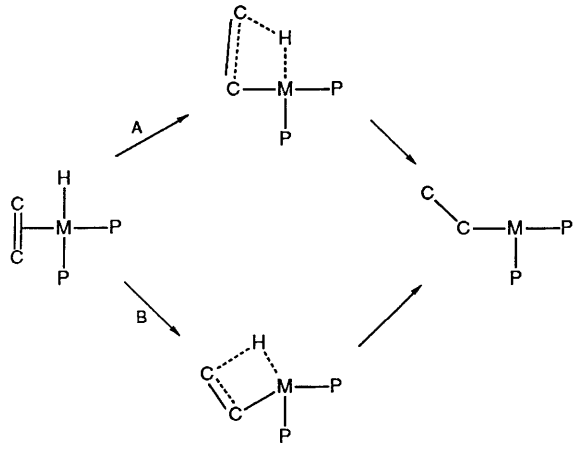


Fig. 2 Molecular structure of $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}]^+$ **2b**

Table 4 Selected interatomic distances (Å) and interbond angles (°) for $[Pt(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ **1b** and $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}][BPh_4]$ **2b**

	1b	**2b**		**1b**	**2b**
Pt–P(1)	2.273(2)	2.311(1)	P(1)–C(14)	1.884(9)	1.876(4)
Pt–P(2)	2.274(2)	2.256(1)	P(2)–C(8)	1.864(8)	1.849(4)
Pt–C(1)	2.110(7)	2.309(5)	P(2)–C(18)	1.885(8)	1.896(4)
Pt–C(2)	2.108(8)	2.096(4)	P(2)–C(22)	1.890(9)	1.868(4)
Pt–H(1a)	—	1.90(7)	C(1)–C(2)	1.460(11)	1.480(6)
P(1)–C(9)	1.850(8)	1.839(5)	C(1)–C(6)	1.516(11)	1.526(6)
P(1)–C(10)	1.884(9)	1.884(5)	C(1)–H(1a)	—	1.28(6)
C(2)–C(3)	1.533(12)	1.526(5)	C(5)–C(6)	1.558(11)	1.561(7)
C(3)–C(4)	1.542(11)	1.548(8)	C(6)–C(7)	1.508(12)	1.533(6)
C(3)–C(7)	1.508(13)	1.519(6)	C(8)–C(9)	1.555(11)	1.533(6)
C(4)–C(5)	1.557(12)	1.524(7)			
P(1)–Pt–P(2)	89.2(1)	89.3(1)	Pt–P(1)–C(14)	116.7(3)	111.4(1)
P(1)–Pt–C(1)	113.6(2)	124.7(1)	Pt–P(2)–C(8)	107.3(3)	106.7(2)
P(1)–Pt–C(2)	153.9(2)	163.1(1)	Pt–P(2)–C(18)	114.3(3)	111.6(2)
P(1)–Pt–H(1a)	—	91(2)	Pt–P(2)–C(22)	117.3(3)	117.4(2)
P(2)–Pt–C(1)	157.2(2)	145.6(1)	Pt–C(1)–C(2)	69.7(4)	62.7(3)
P(2)–Pt–C(2)	116.7(2)	107.4(1)	Pt–C(1)–C(6)	119.8(5)	123.0(3)
P(2)–Pt–H(1a)	—	170(1)	Pt–C(2)–H(1a)	—	55(3)
C(2)–Pt–H(1a)	—	72(3)	Pt–C(2)–C(1)	69.8(4)	78.3(2)
Pt–P(1)–C(9)	107.2(3)	105.9(1)	Pt–C(2)–C(3)	122.5(6)	120.2(3)
Pt–P(1)–C(10)	115.1(3)	117.9(2)	Pt–H(1a)–C(1)	—	91(3)
C(1)–C(2)–C(3)	104.4(7)	103.9(3)	C(5)–C(6)–C(7)	100.6(7)	100.4(3)
C(2)–C(3)–C(4)	106.3(7)	106.0(4)	C(1)–C(6)–C(5)	104.7(7)	104.8(3)
C(2)–C(3)–C(7)	101.5(7)	103.5(3)	C(1)–C(6)–C(7)	103.0(7)	102.3(4)
C(3)–C(4)–C(5)	102.3(7)	102.7(4)	C(3)–C(7)–C(6)	95.2(7)	94.2(3)
C(4)–C(5)–C(6)	102.7(7)	103.7(4)			



Scheme 2

The weak *trans* influence of the β-C–H bond is clearly demonstrated by comparison of the platinum–phosphorus bond lengths. Thus, Pt–P(2) which is *trans* to the agostic hydrogen [P(2)–Pt–H(1a) 170(1)°] is appreciably shorter than Pt–P(1) [2.256(1), *cf.* 2.311(1) Å], thereby explaining the difference in magnitude of the platinum–phosphorus coupling constants [$^1J(PtP_{trans})$ 4909, *cf.* $^1J(PtP_{cis})$ 2577 Hz] referred to above.

The dimensions of the norbornyl ligand in **2b** should be contrasted with those of the η^2-norbornene ligand in **1b** and those of the non-agostic ethyls in the compound $[Pt(C_2H_5)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$.[9] The C–C bond length [C(1)–C(2) 1.480(6) Å] in the agostic complex **2b** is midway between that of the co-ordinated alkene [C(1)–C(2) 1.46(1) Å] and those of the σ-ethyls [average C–C 1.50(1) Å]. These observations are consistent with the view that such agostic complexes provide a model for the intermediate stages of the β-elimination/alkene insertion reaction both in the sense that the β-hydrogen atom is within bonding distance of both metal and carbon atoms, and that the C–C bond order is intermediate between unity and that of an η^2-co-ordinated alkene. The implication of the geometry observed at platinum in **2b** (Fig. 2) is that in the β-elimination/hydride migration reaction it is the hydride that is 'fetched' by the alkene, and that at this stage when the C–H bond is almost fully formed the hydrogen is almost exactly where it started, *trans* to a phosphorus [P(2)–Pt–H(1a) 170(1)°]. This suggests that of the two limiting pathways A and B (Scheme 2), it is A that more accurately describes the course followed.

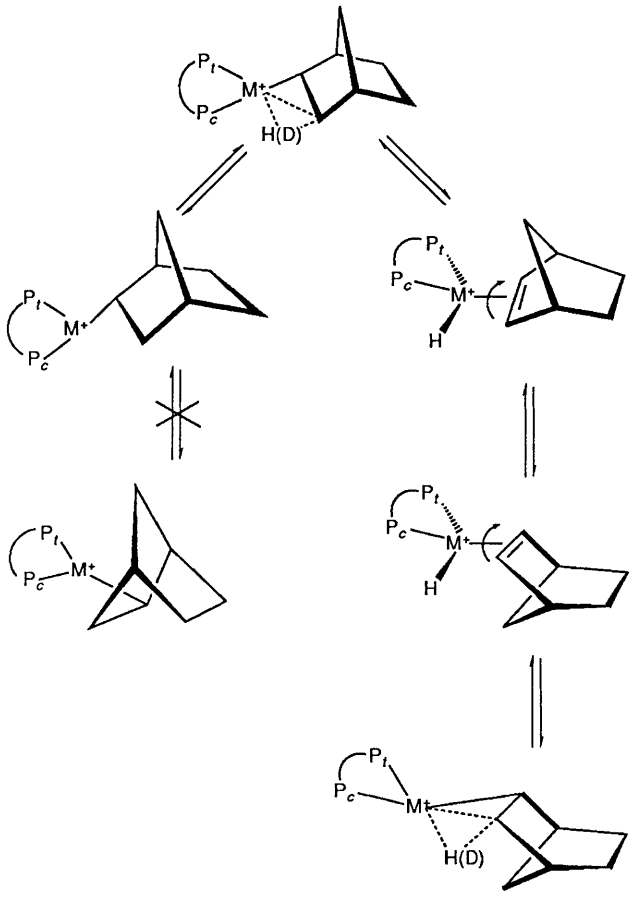
Whilst the insertion of an alkene into a metal–hydride bond has received much attention through the calculation of reaction pathways by molecular orbital theory[11,12] this work provides the first experimental evidence addressing the problem. In other β-agostic complexes the co-ordination geometry is less helpful than in the species described here where the movement of the alkene and hydride ligands can be judged relative to the 'fixed' diphosphine ligand.

The NMR data, particularly the platinum–phosphorus and platinum–hydrogen coupling constants (Table 2), show that the other cations have the same gross structure as **2b**, namely that they contain a β-agostic interaction. However, the strength of the platinum–hydrogen bond, *i.e.* the extent to which the β-hydrogen of the norbornyl group can be considered to have been transferred to the metal, clearly varies coherently as a function of the chelate ring size and the bulk of the substituents on phosphorus. Table 5 lists the coupling constants J(PtH) and J(PtP) as a function of the chelate ring size and it is immediately apparent that J(PtP) for the phosphorus *trans* to the agostic bond decreases dramatically with decreasing bite angle of the bidentate ligand. Complementary to this, J(PtH), which can be considered to be directly related to the strength of the agostic interaction, varies in the reverse manner. Whilst it may appear that the cation $[Pt(C_7H_{11})\{(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2\}]^+$ **2a** does not fit this sequence it should be pointed out that the P–Pt–P angle for this diphosphine was taken from a structural determination[14] of $[Pt(C_2H_4)\{(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2\}]$ which was found to be severely disordered and hence the bond angle is not as accurate as the others in the list. The implication is that the smaller of the diphosphines favour a structure in

Table 5 Comparison of $J(PtP_{trans})$ and $J(PtH)$ with the chelate ring size in the cations $[Pt(C_7H_{11})(L\text{–}L)]^+$

Diphosphine	P–Pt–P/°	$J(PtP_{trans})$/Hz	$J(PtH)$/Hz	Ref.
$(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$	87	3866	324	13
$Bu^t_2P(CH_2)_2PBu^t_2$	89	4909	136	6 and this work
$(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$	113*	4852	102	14
$Bu^t_2P(CH_2)_3PBu^t_2$	98–101	5067	85	9
$o\text{-}C_6H_4(CH_2PBu^t_2)_2$	105	5266	79	9

* This structure is disordered and is unlikely to be reliable for P–Pt–P angles; the true P–Pt–P angle is expected to be *ca.* 100°.



Scheme 3

which the norbornyl ligand is alkene-hydride-like in nature, the larger ones favouring alkyl-like structures. It has been postulated[12] that during the course of the reaction involving insertion of an alkene into the Pt–H bond of a four-co-ordinate *cis*-bis(phosphine) complex the P–Pt–P bond angle increases from an optimum value of 95° in the starting complex to 110° in the transition state, which would of course contain a β-agostic interaction. The results presented here and elsewhere are in complete accord with this in demonstrating experimentally that the strength of the agostic bond is highly dependent upon the angle subtended by the phosphorus atoms at the d^8 metal centre.

As mentioned earlier all the cations **2** undergo dynamic behaviour in solution. It is clear from Fig. 2 that the cation **2b** is asymmetric and that the four *tert*-butyl groups are not equivalent. However, in the ^1H and ^{13}C NMR spectra measured at 300 K only two *tert*-butyl groups are observed and the norbornyl C_7H_{11} framework is afforded a time-averaged plane of symmetry such that only four (rather than seven) carbon environments are discerned. The ^{31}P NMR spectrum shows two distinct signals throughout the temperature range 195–300 K. In addition, the reaction of compounds **1a–1e** with CF_3SO_3D is interesting in that deuteriation is observed to occur exclusively at the agostic position (as evidenced by ^2H NMR measurements): no H/D scrambling is observed even after extended periods of time. These observations can be explained by a rapid intramolecular rearrangement process *via* a mechanism involving transfer of the agostic hydrogen to the metal to give an intermediate alkene–hydride species in which rotation about the metal–alkene bond is facile (Scheme 3).

The free energy of activation ($\Delta G^\ddagger$) for these processes (β-H elimination/alkene rotation) has been calculated by measuring the temperature at which the signals due to the two bridgehead protons of the norbornyl group coalesce. Thus, for **2b** a value for $\Delta G^\ddagger$ of 47 ± 6 kJ mol^{-1} is calculated. The ^1H and ^{13}C NMR spectra of the other cations **2a** and **2c–2h** show the same temperature dependence and similar values of $\Delta G^\ddagger$ have been calculated. Although some variation in $\Delta G^\ddagger$ is observed within the series of compounds, the differences are very small and as would be anticipated: the species containing the smaller of the diphosphines have lower activation energies. For $[Pt(C_7H_{11})\{o\text{-}C_6H_4(CH_2PBu^t_2)_2\}]^+$ **2e** signals due to two species are observed in both the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra at temperatures below 240 K. The $^{31}P\text{-}\{^1H\}$ NMR spectrum however, shows resonances due to only one species. This is readily explained by the presence of two isomeric structures which differ in whether the methylene bridge of the norbornyl ligand and the *o*-xylyl group of the diphosphine both lie above the co-ordination plane defined by the metal and the two phosphorus atoms or one lies above and the other below this plane.

A second fluxional process involving detachment of the agostic interaction to give a 14-electron, T-shaped norbornyl intermediate (Scheme 3) cannot be ruled out. However, such a process occurring in isolation would not lead to the observed temperature dependence of the NMR spectra. If that process does occur then the norbornyl group does not flip from one co-ordination site to the other, at least not at temperatures below 300 K on the NMR time-scale, since the phosphorus atom environments are not averaged. This would be in disagreement with the theoretical study of Thorn and Hoffmann[12] who concluded that for the model species '$HPt(PH_3)_2$' the barrier to such a rearrangement should be very small (*ca.* 10 kJ mol^{-1}). However, it appears that flipping of the alkyl group in a T-shaped intermediate is observed[15] as a relatively high-energy process in the related ethyl complex $[Pt(C_2H_5)\{o\text{-}C_6H_4(CH_2PBu^t_2)_2\}]^+$.

The agostic cations **2** are on the whole stable both in the solid-state and in solution, the palladium complexes to a lesser extent than their platinum analogues. The exception to this is $[Pt(C_7H_{11})\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}]^+$ **2a** which upon crystallisation from chlorinated solvents gives a species which on the basis of NMR spectroscopy (^1H and ^{31}P) and microanalytical data has been characterized as the binuclear, hydride-bridged species $[Pt_2(\mu\text{-}H)(\mu\text{-}Cl)\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}_2]^{2+}$ **3** (Scheme 1). The formation of **3** presumably results from elimination of norbornene (from an intermediate alkene–hydride species) followed by reaction with the solvent. Similar reactivity has been observed[16] for the related ethyl species $[Pt(C_2H_5)\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}]^+$, but in this case loss of ethene is not followed by reaction with the solvent and the product is the dinuclear dihydride $[Pt_2(\mu\text{-}H)_2\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}_2]^{2+}$.

The presence in solution of an alkene–hydride species as indicated by the NMR studies is shown in the reactivity of the compounds **2**. Thus NMR measurements on solutions of $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}]^+$ in CD_3CN showed the presence of two species. One of these was readily identified as $[PtH(NCCD_3)\{Bu^t_2P(CH_2)_2PBu^t_2\}]^+$ **4a** [δ_P 88.4 and 91.5 ppm, J(PtP) 3945 and 1900 Hz respectively; δ_H −4.23, J(PH) 21 and 180 Hz, J(PtH) 915 Hz] and is formed by displacement of norbornene from the species $[PtH(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]^+$. The same species is also formed upon dissolution of $[Pt(C_2H_5)\{Bu^t_2P(CH_2)_2PBu^t_2\}][BF_4]$ in CD_3CN, thereby confirming the assignment. The ^{31}P NMR data for the other compound [δ_P 64.0 and 85.7 ppm, J(PtP) 4539 and 1433 Hz respectively] is consistent with it being formulated as the norbornyl complex $[Pt(NCCD_3)(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}]^+$ **4b** which presumably results from displacement of the agostic interaction *via* nucleophilic attack at the metal. This latter mode of reaction has been previously observed[2] with the compounds $[Co(\eta\text{-}C_5Me_5)\{PPh_2(o\text{-}C_6H_4CHCH_3)\}][BF_4]$ which also contain a β-agostic interaction.

In conclusion, this work has gone some way in assessing the influence of the ancillary ligands on the position of the alkene–hydride *versus* agostic alkyl equilibrium. In particular, it was clear that the bulky, large chelate ring-size diphosphines promote the insertion of alkenes into the M–H (M = Pt or Pd) bond, increasingly favouring the alkyl over the alkene–hydride form. Moreover, this system offers the possibility of very precise control of the degree of interaction between the β-C–H bond and the metal. The possible benefits that this might bestow on the design of homogeneous catalysts and in other aspects of organo-platinum chemistry will form the basis of future work in this area.

Experimental

All reactions were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques. Solvents were dried thoroughly over appropriate reagents and freshly distilled prior to use. The compounds $[Pt(\eta^2\text{-}C_7H_{10})_3]$,[5] $[Pd(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$,[7] $Bu^t_2P(CH_2)_2PBu^t_2$,[17] $(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$[18] and $o\text{-}C_6H_4(CH_2PBu^t_2)_2$[19] were prepared by published methods, the diphosphine $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$ was used as purchased from Strem Chemicals. NMR spectra were recorded on Bruker AC300, JEOL GX400 or JEOL FX90Q pulsed FT NMR spectrometers, at ambient temperature (unless otherwise stated). Proton (δ) and carbon-13 chemical shifts [δ (ppm)], are positive to high frequency of $SiMe_4$. Phosphorus-31 and platinum-195 chemical shifts are positive to high frequency of 85% H_3PO_4 (external) and Ξ(^{195}Pt) 21.4 MHz respectively. Though not reported, all ^{13}C NMR spectra showed the expected signals arising from the diphosphine ligands.

Synthesis of $Bu^t_2P(CH_2)_3PBu^t_2$.—To a solution of $PHBu^t_2$ (4.2 g, 29.0 mmol) in dry Et_2O (30 cm^3) stirred at 273 K, $LiBu^t$ (16 cm^3 of a 1.9 mol dm^{-3} solution) was added dropwise over a period of 5–10 min during which time the solution turned pale yellow. The compound $Cl(CH_2)_3Cl$ (1.7 g, 15 mmol) was added directly into the solution which was then left to stir at 273 K for 20 min. The reaction mixture was allowed to warm to ambient temperature and stir for 1 h. A gradual formation of a white precipitate was noted during this time. The solvent was then removed *in vacuo* and hexane (10 cm^3) was added followed by degassed water (20 cm^3). The organic layer was decanted off and the water layer extracted with hexane (3 × 10 cm^3). After removal of most of the hexane *in vacuo* the diphosphine was obtained by distillation in a Kugelrohr at 423 K (10^2 Pa) giving $Bu^t_2P(CH_2)_3PBu^t_2$ (2.0 g, 6 mmol) as a clear viscous liquid in 41% yield. The purity of the compound was checked by ^1H, ^{13}C and ^{31}P NMR. $\delta_H(C_6D_6)$: 1.1 [d, 36 H, J(PH) 11 Hz, $C(CH_3)_3$], 1.6 and 1.9 [m, 6 H, $P(CH_2)_3P$]; $\delta_C(C_6D_6)$: 23.6 [dd, J(PC) 23 and 13, $PCH_2CH_2CH_2P$], 29.9 [d, J(PC) 14, $C(CH_3)_3$], 31.4 [t, J(PC) 27, $PCH_2CH_2CH_2P$], 31.5 [d, J(PC) 23 Hz, $C(CH_3)_3$]; δ_P 24.6.

Synthesis of the Complexes $[Pt(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$ [L–L = $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$, $Bu^t_2P(CH_2)_2PBu^t_2$, $(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$, $Bu^t_2P(CH_2)_3PBu^t_2$ *or* $o\text{-}C_6H_4(CH_2PBu^t_2)_2$].—(*i*) The diphosphine $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$ (0.19 g, 0.45 mmol) was added to a cold (*ca.* 0 °C) solution of $[Pt(\eta^2\text{-}C_7H_{10})_3]$ (0.21 g, 0.44 mmol) in hexane (25 cm^3) and the resulting solution was stirred at this temperature for 30 min. After allowing to warm to ambient temperature, the solution was filtered through a Celite plug (*ca.* 2 cm depth), the volume of solvent reduced *in vacuo* to *ca.* 10 cm^3, and cooled (*ca.* −20 °C) to give $[Pt(\eta^2\text{-}C_7H_{10})\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}]$ **1a** (0.30 g, 96%) as an off-white microcrystalline *powder* (Found: C, 55.25; H, 8.20. $C_{33}H_{58}P_2Pt$ requires C, 55.70; H, 8.20%). NMR (C_6D_6): δ_H 0.81–2.20 (54 H, C_6H_{11}, PCH_2, CH_2 and CH_2-bridge), 2.78 [2 H, s, J(PtH) 58, HC=CH], 3.2 (2 H, s, CH); δ_C 34.3 [d, J(PC) 7, J(PtC) 57, CH_2], 42.2 [s, J(PtC) 59, CH_2-bridge] 46.6 (s, CH), 47.9 [vt, $|J(PC) + J(P'C)|$ 39, J(PtC) 345 Hz, C=C]; δ_{Pt} −713.

(*ii*) In an identical manner, $Bu^t_2P(CH_2)_2PBu^t_2$ (0.13 g, 0.41 mmol) and $[Pt(\eta^2\text{-}C_7H_{10})_3]$ (0.19 g, 0.40 mmol) gave $[Pt(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ **1b** (0.23 g, 94%) as a cream *powder* (Found: C, 49.10; H, 8.50. $C_{25}H_{50}P_2Pt$ requires C, 49.40; H, 8.30%). NMR (CD_2Cl_2): δ_H 0.28, 0.87 [2 H, AB, J(AB) 8, CH_2-bridge], 1.19 [36 H, d, J(PH) 6, CH_3], 1.28 (4 H, br, CH_2), 1.65 [4 H, d, J(PH) 4, PCH_2], 2.05 [2 H, s, J(PtH) 59, HC=CH], 2.71 (2 H, s, CH); δ_C 33.5 [d, J(PC) 6, J(PtC) 57, CH_2] 41.4 [s, J(PtC) 56, CH_2-bridge], 45.4 (s, CH), 47.5 [vt, $|J(PC) + J(P'C)|$ 41, J(PtC) 344 Hz, C=C]; δ_{Pt} −743.

(*iii*) By the same method $(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$ (0.20 g, 0.46 mmol) and $[Pt(\eta^2\text{-}C_7H_{10})_3]$ (0.22 g, 0.46 mmol) in hexane (25 cm^3) gave $[Pt(\eta^2\text{-}C_7H_{10})\{(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2\}]$ **1c** (0.32 g, 96%) as a white *powder* (Found: C, 56.10; H, 8.70. $C_{34}H_{60}P_2Pt$ requires C, 56.25; H, 8.35%). NMR (CD_2Cl_2): δ_H 0.66–2.10 (56 H, C_6H_{11}, PCH_2, CH_2 and CH_2-bridge), 2.34 [2 H, s, J(PtH) 56, HC=CH] 3.05 (2 H, s, CH); δ_C 33.8 [d, J(PC) 6, J(PtC) 54, CH_2], 41.6 [s, J(PtC) 55, CH_2-bridge], 46.2 (s, CH), 47.5 [vt, $|J(PC) + J(P'C)|$ 41, J(PtC) 339 Hz, C=C]; δ_{Pt} −685.

(*iv*) Similarly, $[Pt(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1d** (0.20 g, 96%) was obtained as a beige *powder* from $Bu^t_2P(CH_2)_3PBu^t_2$ (0.11 g, 0.33 mmol) and $[Pt(\eta^2\text{-}C_7H_{10})_3]$ (0.16, 0.34 mmol) (Found: C, 49.95; H, 8.60. $C_{26}H_{52}P_2Pt$ requires C, 50.2; H, 8.45%). NMR (CD_2Cl_2): $\delta_H(C_6D_5CD_3)$ 0.58, 0.94 [2 H, AB, J(AB) 8, CH_2-bridge], 1.15 [36 H, d, J(PC) 6, CH_3], 1.52 (2 H, br, PCH_2CH_2), 1.94–2.08 (8 H, br, PCH_2CH_2 and CH_2), 2.16 [2 H, d, J(PH) 1, J(PtH) 58, HC=CH], 3.02 (2 H, s, CH); δ_C 32.9 [d, J(PC) 5, J(PtC) 55, CH_2], 40.4 [s, J(PtC) 57, CH_2-bridge], 45.1 [s, J(PtC) 12, CH], 48.0 [vt, $|J(PC) + J(P'C)|$ 36, J(PtC) 333 Hz, C=C]; δ_{Pt} −759.

(*v*) In the same manner, $[Pt(\eta^2\text{-}C_7H_{10})_3]$ (0.16 g, 0.34 mmol) and $o\text{-}C_6H_4(CH_2PBu^t_2)_2$ (0.13 g, 0.33 mmol) gave $[Pt(\eta^2\text{-}C_7H_{10})\{o\text{-}C_6H_4(CH_2PBu^t_2)_2\}]$ **1e** (0.22 g, 96% as off-white *microcrystals* (Found: C, 54.20; H, 8.15. $C_{31}H_{54}P_2Pt$ requires C, 54.45; H, 7.95%). NMR (C_6D_6): δ_H 0.61, 1.13 [2 H, AB, J(AB) 7, CH_2-bridge], 1.28 (36 H, br, CH_3), 1.58 (4 H, m, CH_2), 2.13 [2 H, d, J(PH) 1, J(PH) 59, HC=CH], 3.06 (2 H, s, CH), 3.49 (4 H, br, PCH_2), 7.18 (4 H, br, C_6H_4); δ_C 32.7 [s, J(PtC) 56, CH_2], 40.2 [s, J(PtC) 50, CH_2-bridge], 45.0 [s, J(PtC) 13, CH], 50.1 [vt, $|J(PC) + J(P'C)|$ 35, J(PtC) 332 Hz, C=C]; δ_{Pt} −702.

Protonation Reactions of $[Pt(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$.—(*i*) A cold (*ca.* 0 °C) solution of $[Pt(\eta^2\text{-}C_7H_{10})\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}]$ **1a** (0.13 g, 0.18 mmol) in OEt_2 (15 cm^3) was treated with $HBF_4{\cdot}OEt_2$ (0.03 cm^3) and the resulting mixture allowed to warm to ambient temperature. The supernatant liquid was decanted off, the solid washed with OEt_2 (2 × 10 cm^3) and dried *in vacuo* to give slightly impure $[Pt(C_7H_{11})\{(C_6H_{11})_2P\text{-}$

$(CH_2)_2P(C_6H_{11})_2\}][BF_4]$ **2a**. Analytically pure samples of **2a** could not be obtained due to decomposition (see text). NMR (CD_2Cl_2): δ_H −1.84 [1 H, br, d, *J*(PH) 80, *J*(PtH) 324, Pt–H–C], 0.52, 0.77 [2 H, AB, *J*(AB) 10, CH_2-bridge], 1.05–2.40 (52 H, C_6H_{11}, PCH_2 and CH_2), 2.73 (2 H, br, Pt–CH), 2.99 (2 H, br, CH); δ_C 29.9 [s, *J*(PtC) 18, CH_2], 40.8 [s, *J*(PtC) 23, CH_2-bridge], 41.9 (br, Pt–C), 43.4 (s, CH); $\delta_P(CD_2Cl_2)$ 64.3 [d, *J*(PtP) 3866, *J*(PP) 9], 74.8 [d, *J*(PtP) 2695, *J*(PP) 9 Hz]; δ_{Pt} −1280. Crystallisation of **2a** (CF_3SO_3) from CH_2Cl_2–OEt_2 (10 cm^3, 1:2) gave yellow *microcrystals* of $[Pt_2(\mu\text{-}H)(\mu\text{-}Cl)\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}_2][CF_3SO_3]_2$ (Found: C, 41.50; H, 6.50; Cl, 3.20. $C_{54}H_{97}ClF_6O_6P_4Pt_2S_2$ requires C, 41.30; H, 6.25; Cl, 2.25%). NMR (CD_2Cl_2): δ_H −5.31 [1 H, 1:8:18:8:1 'quintet' of triplet triplets, *J*(PH) 72 and 8, *J*(PtH) 611, μ-H], 1.05–2.56 (96 H, overlapping, PCH_2 and C_6H_{11}); δ_P 59.7 [*J*(PtP) 3434] and 75.5 [*J*(PtP) 3430 and −81 Hz].

(*ii*) Addition of HBF_4·OEt_2 (0.04 cm^3) to a solution of $[Pt(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ **1b** (0.14 g, 0.23 mmol) in OEt_2 (15 cm^3) at *ca.* 0 °C gave an immediate cream precipitate. After allowing to warm to ambient temperature, the supernatant liquid was decanted off and the solid recrystallised from CH_2Cl_2–OEt_2 (1:4, 20 cm^3) to afford white *microcrystals* of $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}][BF_4]$ **2b** (0.15 g, 95%) (Found: C, 42.10; H, 7.25. $C_{25}H_{51}BF_4P_2Pt$ requires C, 43.15; H, 7.40%). NMR (CD_2Cl_2; −70 °C): δ_H −1.01 [1 H, br, d, *J*(PH) 53, *J*(PtH) 138, Pt–H–C], 0.42 and 0.74 [2 H, AB, *J*(AB) 10, CH_2-bridge], 1.19 (36 H, m, CH_3), 1.25–2.24 (10 H, br, Pt–C_α–H, Pt–C_β–H, CH_2 and PCH_2), 2.84 (1 H, s, CH), 3.06 (1 H, s, CH); δ_C 27.8 (s, CH_2), 30.0 (s, $C_\beta H$), 30.7 (s, CH_2), 39.3 (s, CH_2-bridge), 40.6 (s, CH), 43.9 (s, CH), 48.6 [d, *J*(PC) 47, *J*(PtC) 460, $C_\alpha H_2$]; δ_P 99.1 [d, *J*(PP) 18, *J*(PtP) 2577], 90.2 [d, *J*(PP) 18, *J* (PtP) 4909 Hz]; δ_{Pt} −1272. The deuteriated compound $[Pt(C_7H_{10}D)\{Bu^t_2P(CH_2)_2PBu^t_2\}][CF_3SO_3]$ was prepared in a similar manner by treating **1b** with one mole equivalent of CF_3SO_3D [generated *in situ* from $(CF_3SO_2)_2O$ and D_2O].

(*iii*) To a stirred, cold (*ca.* 0 °C) solution of $[Pt(\eta^2\text{-}C_7H_{10})\{(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2\}]$ **1c** (0.14 g, 0.19 mmol) in OEt_2 (15 cm^3) HBF_4·OEt_2 (0.03 cm^3) was added and the mixture was allowed to warm to ambient temperature. The supernatant liquid was removed by syringe and the solid was washed with OEt_2 (2 × 10 cm^3) to afford $[Pt(C_7H_{11})\{(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2\}][BF_4]$ **2c** (0.12 g, 76%) as a white *powder* (Found: C, 51.20; H, 7.85. $C_{34}H_{61}BF_4P_2Pt$ requires C, 50.20, H, 7.55%). NMR (CD_2Cl_2): δ_H −1.42 [1 H, d, *J*(PH) 53, *J*(PtH) 102, Pt–H–C], 0.65 and 0.86 [2 H, AB, *J*(AB) 10, CH_2-bridge], 0.92–2.35 (54 H, C_6H_{11}, PCH_2 and CH_2), 2.90 (2 H, br, Pt–CH), 3.32 (2 H, br, CH); δ_C 29.9 (s, CH_2), 35.5 [v br, (PtC)], 39.9 [s, *J*(PtC) 19, CH_2-bridge] 42.6 (s, CH); δ_P 52.7 [d, *J*(PP) 9, *J*(PtP) 4852], 24.7 [d, *J*(PP) 9, *J*(PtP) 2564 Hz].

(*iv*) An OEt_2 (15 cm^3) solution of $[Pt(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ **1d** (0.11 g, 0.18 mmol) was cooled to *ca.* 0 °C, HBF_4·OEt_2 (0.03 cm^3) was added and the resulting mixture allowed to warm to ambient temperature. After decanting off the supernatant liquid, the solid was washed with OEt_2 (2 × 10 cm^3) and dried *in vacuo* to give cream *microcrystals* of $[Pt(C_7H_{11})\{Bu^t_2P(CH_2)_3PBu^t_2\}][BF_4]$ **2d** (0.11 g, 88%) (Found: C, 44.95; H, 7.90. $C_{26}H_{53}BF_4P_2Pt$ requires C, 44.00; H, 7.55%). NMR (CD_2Cl_2): δ_H −1.78 [1 H, d, *J*(PH) 51, *J*(PtH) 85, Pt–H–C], 0.59 and 0.86 [2 H, AB, *J*(AB) 10, CH_2-bridge], 1.25 [18 H, d, *J*(PH) 14, CH_3], 1.34 [18 H, d, *J*(PH) 4, CH_3], 1.37–1.44 (4 H, m), 1.71 (2 H, br), 1.80–2.35 (6 H, m), 3.02 (2 H, br, CH); δ_C 24.2 [s, *J*(PtC) 54, CH], 26.3 [s, *J*(PtC) 53, CH] 29.4 (s, $C_\beta H$), 31.3 [s, *J*(PtC) 53], 38.4 (s), 38.7 [s, *J*(PtC) 18], 42.5 (br); δ_P 47.4 [d, *J*(PP) 10, *J*(PtP) 5067], 37.5 [d, *J*(PP) 10, *J*(PtP) 2532 Hz]; δ_{Pt} −1146.

(*v*) A solution of $[Pt(\eta^2\text{-}C_7H_{10})\{o\text{-}C_6H_4(Bu^t_2PCH_2)_2\}]$ **1e** (0.16 g, 0.23 mmol) in OEt_2 (20 cm^3) was cooled (*ca.* 0 °C) and HBF_4·OEt_2 (0.04 cm^3) was added. After allowing to warm to ambient temperature the supernatant liquid was decanted off and the residue recrystallised from CH_2Cl_2–OEt_2 (1:4, 10 cm^3) to give off-white *microcrystals* of $[Pt(C_7H_{11})\{o\text{-}C_6H_4(Bu^t_2PCH_2)_2\}][BF_4]$ **2e** (0.17 g, 94%) (Found: C, 48.50, H, 7.40. $C_{31}H_{55}BF_4P_2Pt$ requires C, 48.25; H, 7.20%). NMR (CD_2Cl_2): δ_H −2.14 [1 H, d, *J*(PH) 52, *J*(PtH) 29, Pt–H–C], 0.56 and 0.84 [2 H, AB, *J*(AB) 8, CH_2-bridge]; 1.36 [d, 18 H, *J*(PH) 15, $PC(CH_3)_3$], 1.68 (br, 2 H), 3.02 (br, 2 H), 3.80 [d, 2 H, *J*(PH) 11, *J*(PtH) 39], 3.99 [d, 2 H, *J*(PH) 12, *J*(PtH) 68 Hz], 7.2–7.5 (m, 4 H, C_6H_4); $\delta_C(CD_2Cl_2)$ 28.1 [d, *J*(PC) 15, *J*(PtC) 66, CH_2-bridge], 28.9 (s, CH_2-bridge), 30.6 [d, *J*(PC) 3, *J*(PtC) 30], 38.0 [s, *J*(PtC) 16 Hz, CH_2-bridge], 42.5 (br). The deuteriated compound $[Pt(C_7H_{10}D)\{o\text{-}C_6H_4(Bu^t_2PCH_2)_2\}][CF_3SO_3]$ was prepared in a similar manner by treating **1e** with 1 mole equivalent of CF_3SO_3D [generated *in situ* from $(CF_3SO_2)_2O$ and D_2O]. NMR (CH_2Cl_2): δ_{2H} −2.14 [d, *J*(PD) 7, Pt–D–C]; δ_P 52.6 [*J*(PtP) 5266], 37.4 [*J*(PtP) 2620 Hz]; δ_{Pt} −1031.

Synthesis of the Complexes $[Pd(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$ [L–L = $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$, $Bu^t_2P(CH_2)_2PBu^t_2$ *and* $o\text{-}C_6H_4(Bu^t_2PCH_2)_2$].—(*i*) A solution of the diphosphine $(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2$ (0.13 g, 0.31 mmol) and norbornene (0.04 g, 0.43 mmol) in hexane (15 cm^3) was added to a solution of $[Pd(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ (0.07 g, 0.33 mmol) also in hexane (15 cm^3) and the resulting mixture was stirred for 3 h to give a clear yellow solution. This was filtered through a Celite pad (*ca.* 3 cm), the volume of solvent was reduced to *ca.* 10 cm^3, and the solution cooled (*ca.* −30 °C) to give pale yellow *crystals* of $[Pd(\eta^2\text{-}C_7H_{10})\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}]$ **1f** (0.11 g, 54%) (Found: C, 63.75; H, 9.70. $C_{33}H_{58}P_2Pd$ requires C, 63.60; H, 9.40%). NMR (C_6D_6): δ_H 0.72 and 1.05 [2 H, AB, *J*(AB) 8, CH_2-bridge], 1.12–2.61 (52 H, C_6H_{11}, PCH_2, CH_2), 3.26 (2 H, CH), 3.60 [2 H, d, *J*(PH) 1, HC=CH]; δ_C 31.7 (s, CH_2), 41.8 (s, CH_2-bridge), 45.0 (s, CH), 62.4 [t, *J*(PC) 12 Hz, C=C].

(*ii*) Similarly, light brown *microcrystals* of $[Pd(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ **1g** (0.09 g, 61%) were obtained from $Bu^t_2P(CH_2)_2PBu^t_2$ (0.09 g, 0.28 mmol), norbornene (0.03 g, 0.32 mmol) and $[Pd(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ (0.06 g, 0.28 mmol) after recrystallisation from CH_2Cl_2 (5 cm^3; −30 °C) (Found: C, 58.25; H, 9.90. $C_{25}H_{50}P_2Pd$ requires C, 57.85; H, 9.70%). NMR (C_6D_6): δ_H 0.88 and 1.24 [2 H, AB, *J*(AB) 8, CH_2-bridge], 1.14 (36 H, br, CH_3), 1.60 (2 H, m, CH_2), 1.65 [4 H, d, *J*(PH) 3, PCH_2], 1.85 (2 H, m, CH_2), 3.17 (2 H, CH), 3.43 (2 H, br, HC=CH); δ_C 34.2 [d, *J*(PC) 4, CH_2], 43.0 (s, CH_2-bridge), 45.1 (s, CH), 61.5 [t, *J*(PC) 13 Hz, C=C].

(*iii*) In an identical manner, $o\text{-}C_6H_4(CH_2PBu^t_2)_2$ (0.15 g, 0.38 mmol), norbornene (0.06 g, 0.64 mmol) and $[Pd(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ (0.08 g, 0.38 mmol) gave $[Pd(\eta^2\text{-}C_7H_{10})\{o\text{-}C_6H_4(CH_2PBu^t_2)_2\}]$ **1h** (0.17, 76%) as a cream *powder* (Found: C, 62.85; H, 9.40. $C_{31}H_{54}P_2Pd$ requires C, 62.5; H, 9.15%). NMR (C_6D_6): δ_H 0.72 and 1.05 [2 H, AB, *J*(AB) 8, CH_2-bridge), 1.41 (2 H, m, CH_2), 2.70 (2 H, m, CH_2), 2.94 [2 H, d, *J*(PH) 2, HC=CH], 3.02 (s, CH); δ_C 35.8 (s, CH_2), 43.7 (s, CH_2-bridge), 46.2 (s, CH), 65.4 [t, *J*(PC) 11 Hz, C=C].

Protonation Reactions of $[Pd(\eta^2\text{-}C_7H_{10})(L\text{–}L)]$.—(*i*) Addition of HBF_4·OEt_2 (0.045 cm^3) to a cold (*ca.* 0 °C) solution of $[Pd(\eta^2\text{-}C_7H_{10})\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}]$ **1f** (0.16 g, 0.26 mmol) in OEt_2 (20 cm^3) gave an immediate precipitate from which the supernatant liquid was removed by syringe. After drying *in vacuo* $[Pd(C_7H_{11})\{(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2\}][BF_4]$ **2f** was obtained as a white *powder* (0.14 g, 77%). NMR (CD_2Cl_2): δ_H −1.30 [1 H, d, *J*(PH) 60, Pd–H–C], 0.47 and 1.03 [2 H, AB, *J*(AB) 10, CH_2-bridge], 1.11–2.23 (56 H, C_6H_{11}, PCH_2 and CH_2), 2.69 (1 H, br, CH), 2.95 (2 H, br, CH); δ_C 26.2 (s, CH_2), 29.8 (s, CH_2), 31.2 [d, *J*(PC) 4, Pd–C], 34.5 [d, *J*(PC) 18, CH_2-bridge], 36.1 [d, br, *J*(PC) 24, Pd–C], 40.5 (s, CH_2); δ_P 63.6, 70.3 [*J*(PP) 15 Hz].

(*ii*) In a similar manner, colourless *microcrystals* of $[Pd(C_7H_{11})\{Bu^t_2P(CH_2)_2PBu^t_2\}][BF_4]$ **2g** (0.16 g, 80%) were obtained from HBF_4·OEt_2 (0.06 cm^3) and $[Pd(\eta^2\text{-}C_7H_{10})\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ **1g** (0.18 g, 0.35 mmol). NMR (CD_2Cl_2, −70 °C): δ_H −1.75 [1 H, d, *J*(PH) 60, Pd–H–C], 0.20 and 1.01

Table 6 Atomic coordinates (× 10^4) for [Pt(η²-C_7H_{10}){$Bu^t_2P(CH_2)_2PBu^t_2$}]

Atom	x	y	z	Atom	x	y	z
Pt	7041(1)	2860(1)	−138(1)	C(12)	3036(9)	3221(6)	1130(8)
P(1)	5760(2)	3016(1)	940(2)	C(13)	3627(9)	3590(6)	−393(7)
P(2)	7482(2)	1680(1)	396(2)	C(14)	6208(9)	3808(5)	1801(6)
C(1)	7116(8)	3805(4)	−987(6)	C(15)	5710(11)	3731(6)	2725(7)
C(2)	7838(8)	3190(4)	−1298(6)	C(16)	5731(11)	4545(5)	1293(7)
C(3)	9255(8)	3480(5)	−1179(6)	C(17)	7730(9)	3841(6)	2081(7)
C(4)	9215(10)	4076(5)	−1950(7)	C(18)	9216(8)	1537(5)	1108(6)
C(5)	8457(10)	4722(5)	−1586(6)	C(19)	9571(10)	743(6)	1443(8)
C(6)	8156(8)	4396(5)	−657(6)	C(20)	10216(9)	1811(6)	560(8)
C(7)	9393(8)	3948(5)	−299(6)	C(21)	9359(10)	2025(6)	1986(8)
C(8)	6406(8)	1483(5)	1247(6)	C(22)	7036(8)	904(5)	−495(7)
C(9)	6017(9)	2196(5)	1728(6)	C(23)	5699(9)	1110(6)	−1136(7)
C(10)	3925(8)	3045(5)	431(7)	C(24)	6928(11)	128(6)	−113(8)
C(11)	3520(10)	2269(6)	4(9)	C(25)	8069(10)	913(6)	−1118(7)

Table 7 Atomic coordinates (× 10^4) for [Pt(C_7H_{11}){$Bu^t_2P(CH_2)_2PBu^t_2$}][BPh_4]

Atom	x	y	z	Atom	x	y	z
Pt	1337(1)	2224(1)	4954(1)	B	5515(3)	3190(2)	3310(2)
C(1)	240(3)	1898(2)	5543(3)	C(101)	5531(3)	2330(2)	3209(2)
C(2)	560(3)	1341(2)	5130(2)	C(102)	5224(3)	2015(2)	2460(2)
C(3)	−472(3)	1095(2)	4479(3)	C(103)	5221(4)	1289(2)	2357(2)
C(4)	−1035(4)	662(2)	4895(3)	C(104)	5540(3)	841(2)	2996(3)
C(5)	−1337(3)	1224(2)	5349(3)	C(105)	5852(3)	1128(2)	3737(2)
C(6)	−953(3)	1926(2)	5117(3)	C(106)	5855(3)	1857(2)	3840(2)
C(7)	−1138(3)	1760(2)	4264(2)	C(201)	6108(3)	3574(2)	2807(2)
C(8)	2890(3)	2632(2)	4077(2)	C(202)	5870(3)	4266(2)	2524(2)
C(9)	2933(3)	3298(2)	4555(2)	C(203)	6448(4)	4623(2)	2187(2)
P(1)	1856(1)	3368(1)	4875(1)	C(204)	7289(4)	4296(3)	2113(2)
C(10)	2432(4)	3898(2)	5813(3)	C(205)	7510(3)	3609(3)	2349(2)
C(11)	1569(4)	4201(3)	6029(3)	C(206)	6940(3)	3254(2)	2694(2)
C(12)	3151(4)	4493(3)	5768(3)	C(301)	4310(3)	3501(2)	2989(2)
C(13)	3077(4)	3390(3)	6478(3)	C(302)	3455(3)	3192(3)	2385(3)
C(14)	785(3)	3882(2)	4093(3)	C(303)	2464(4)	3489(3)	2060(3)
C(15)	−226(3)	3851(2)	4236(3)	C(304)	2284(4)	4120(4)	2345(4)
C(16)	554(3)	3512(2)	3307(2)	C(305)	3089(5)	4443(3)	2950(4)
C(17)	1064(4)	4654(2)	4031(3)	C(306)	4086(4)	4139(2)	3269(3)
P(2)	2427(1)	1841(1)	4420(1)	C(401)	6192(3)	3389(2)	4247(2)
C(18)	3637(3)	1403(2)	5183(2)	C(402)	5757(3)	3377(3)	4798(3)
C(19)	3294(4)	846(2)	5628(3)	C(403)	6334(4)	3482(3)	5602(3)
C(20)	4257(4)	1967(3)	5770(3)	C(404)	7394(4)	3611(2)	5888(2)
C(21)	4339(4)	1067(3)	4833(3)	C(405)	7858(3)	3630(2)	5368(2)
C(22)	1850(4)	1285(2)	3513(2)	C(406)	7269(3)	3525(2)	4571(2)
C(23)	2504(4)	1285(3)	3019(3)				
C(24)	1658(4)	525(2)	3715(3)				
C(25)	773(4)	1603(3)	2993(3)				

[2 H, AB, *J*(AB) 9, CH_2-bridge], 1.03–2.25 (46 H, br, overlapping), 2.82 (1 H, s, CH), 2.96 (1 H, s, CH); δ_C 25.9 (s, CH_2), 28.0 (s, $C_\beta H$), 28.5 (s, CH_2), 39.2 (s, CH_2-bridge), 40.0 (s, CH), 44.7 (s, CH), 57.4 [d of d, *J*(PC) 51 and 7, $C_\alpha H_2$]; δ_P 97.6, 92.5 [*J*(PP) 13 Hz].

(*iii*) Treatment of a cold (*ca.* 0 °C) solution of [Pd(η²-C_7H_{10}){*o*-$C_6H_4(CH_2PBu^t_2)_2$}] **1h** (0.21 g, 0.35 mmol) in OEt_2 (15 cm^3) with HBF_4·OEt_2 (0.061 cm^3) yielded [Pd(C_7H_{11})-{*o*-$C_6H_4(CH_2PBu^t_2)_2$}][BF_4] **2h** (0.19 g, 79%) as a white *powder* after 'work-up' as described above. NMR (CD_2Cl_2): δ_H −2.38 [1 H, d, *J*(PH) 57, Pd–H–C], 0.54 and 1.00 [2 H, AB, *J*(AB) 10, CH_2-bridge], 1.44 [18 H, d, *J*(PH) 3, CH_3], 1.46 [18 H, d, *J*(PH) 3, CH_3], 2.93 (1 H, s, CH), 3.05 (1 H, s, CH), 3.54 [1 H, d, *J*(PH) 4, PCH_2], 3.57 [1 H, d, *J*(PH) 4, PCH_2], 3.69 (1 H, s, PCH_2), 3.72 (1 H, s, PCH_2), 7.0–7.6 (4 H, m, C_6H_4); δ_C 29.2 (s, br, CH_2), 32.0 (s), 38.3 (m, CH), 42.9 (m, Pd–C), 128.0, 133.8 and 135.1 (C_6H_4); δ_P 67.4 and 38.5 [*J*(PP) 33 Hz].

Reactions of [Pt(C_7H_{11}){$Bu^t_2P(CH_2)_2PBu^t_2$}][BF_4] **2b**.—(*i*) The compound **2b** (*ca.* 0.15 mmol) was dissolved in CD_3CN (0.6 cm^3) and the resulting solution transferred to an NMR tube so that the progress of the reaction could be monitored by spectroscopy.

Crystal Structure Determinations.—Many of the details of the structure analyses carried out on **1b** and **2b** are listed in Table 3, selected bond lengths and angles are listed in Table 4. Crystals of [Pt(η²-C_7H_{10}){$Bu^t_2P(CH_2)_2PBu^t_2$}] **1b** and [Pt(C_7H_{11})-{$Bu^t_2P(CH_2)_2PBu^t_2$}][BPh_4] **2b** were grown (**1b**, light brown plates; **2b**, colourless prisms) from hexane at *ca.* −30 °C and by the slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex, respectively. The crystal chosen for study (**1b**, *ca.* 0.40 × 0.30 × 0.05 mm; **2b**, 0.56 × 0.40 × 0.30 mm) was sealed under N_2 in a thin-walled glass capillary tube for diffractometry. Cell dimensions for each analysis were determined from the setting angle values of 34 and 25 centred reflections respectively. Diffracted intensities (θ–2θ scans) were collected on Nicolet R3m four-circle diffractometers at *ca.* 200 K for a unique quadrant of reciprocal space using graphite monochromated Mo-Kα X-radiation ($\bar{\lambda}$ = 0.710 69 Å). Three check reflections remeasured after every 50 ordinary data showed no crystal decay but ±2% drift for **1b** and 8% decay for

2b, over the period of data collection; appropriate corrections were therefore applied. After deletion of these check intensity data, averaging of duplicate and equivalent measurements was carried out and systematic absences were deleted; of the unique data remaining, only data with $F \geqslant n\sigma(F)$ (**1b**, $n = 6$; **2b**, $n = 3$) were used in the solution and refinement of the structures. Corrections for Lorentz, polarisation and X-ray absorption effects were applied. The latter correction was based on a semi-empirical method using azimuthal scan data (221 such data for **1b**, and 400 for **2b**).

The structures were solved by conventional heavy-atom methods, and successive difference Fourier syntheses were used to locate all non-hydrogen atoms, which were refined with anisotropic thermal parameters. The hydrogen atoms on the contact carbon atoms [C(1) and C(2)] were directly located in difference Fourier syntheses and were refined without positional constraints. All other hydrogen atoms were included at calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (*ca.* 1.2 × U_{equiv} of the attached carbon atom). Refinement by full-matrix least squares on F with a weighting scheme of the form $w = [\sigma^2(F) + g|F|^2]^{-1}$ [where $\sigma_C^2(F_o)$ is the variance in F_o due to counting statistics; for **1b**, $g = 0.0005$; **2b**, $g = 0.000\,35$] gave satisfactory analyses of variance and converged to the residuals listed in Table 3. The final electron-density difference syntheses showed no peaks $\geqslant 2.86$ or $\leqslant -2.51$ for **1b** or $\geqslant 1.21$ or $\leqslant -1.77$ e Å^{-3} for **2b**. Calculations were performed using programs written by G. M. Sheldrick.[20] Complex neutral-atom scattering factors were taken from ref. 21. Tables 6 and 7 report the positional parameters for the non-hydrogen atoms of **1b** and **2b**.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom coordinates and remaining bond lengths and angles.

Acknowledgements

We thank the SERC for support.

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Received 19*th November* 1990; *Paper* 0/05208F