Effect of Bulky Alkyl Substituents on the Dynamics and Stability of Platinum Complexes with β-Agostic Bonding

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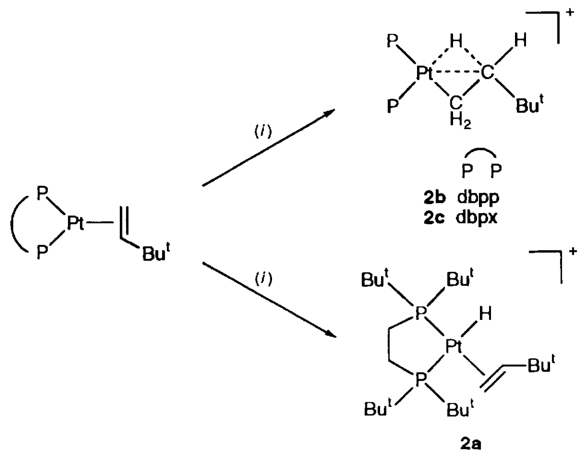
Protonation of the platinum(0) compounds $[Pt(CH_2{=}CHBu^t)(P\text{–}P)]$ [P–P = $Bu^t_2P(CH_2)_nPBu^t_2$, $n = 2$ **1a** or 3 **1b**, or $Bu^t_2PCH_2C_6H_4CH_2PBu^t_2$ **1c**] with $HBF_4{\cdot}OMe_2$ in diethyl ether at 273 K afforded the pale yellow cationic complexes $[PtH(CH_2{=}CHBu^t)\{Bu^t_2P(CH_2)_2PBu^t_2\}][BF_4]$ **2a** and $[Pt(C_6H_{13})(P\text{–}P)][BF_4]$ [P–P = $Bu^t_2P(CH_2)_3PBu^t_2$ **2b** or $Bu^t_2PCH_2C_6H_4CH_2PBu^t_2$ **2c**] respectively. Complex **2a** has been shown by IR and NMR studies to possess a *cis* alkene–hydride ground-state structure, whilst **2b** and **2c** achieve a 16-electron configuration *via* a β-C–H agostic interaction. The reaction between the red dinuclear complex $[Pt_2(\mu\text{-}H)_2(dbpp)_2][BF_4]_2$ [dbpp = $Bu^t_2P(CH_2)_3PBu^t_2$] and 2,3,3-trimethylbut-1-ene afforded the complex $[Pt(CH_2CHMeBu^t)(dbpp)][BF_4]$ **2d** which also exhibits a β-C–H agostic interaction.

Complexes with three-centre, two-electron (agostic) interactions have been the subject of several reports, which have been reviewed in 1983[1] and 1988.[2] Our detailed systematic studies[3–6] have highlighted some of the factors which determine the nature and stability of the ground states of agostic complexes of the type $[M(Et)(P\text{–}P)][BF_4]$ and $[M(C_7H_{11})(P\text{–}P)][BF_4]$ (M = Ni, Pd or Pt; P–P = chelating diphosphine, C_7H_{11} = *exo*-norborn-2-yl). In particular we have shown that the strength of the agostic interaction depends on the bite angle of the chelating diphosphine ligand and the nature of the central metal atom. In our continued investigation of the stability of these agostic complexes, we considered what effect bulky alkyl substituents on the alkyl fragment would have on the structure and dynamics of such systems. Work by Brookhart *et al.*[7] has shown that the β-carbon of the major isomer of the propyl ligand in the agostic cobalt complex $[Co(CH_2CH_2Me)\{P(OMe)_3\}(\eta\text{-}C_5Me_5)]^+$ possesses more olefinic character compared to the ethyl analogue. We were interested in exploring the generality of this observation in the context of the Group 10 metal(II) complexes. This paper describes the preparation and properties of new agostic complexes which possess bulky alkyl substituents on the β-carbon of the alkyl fragment.

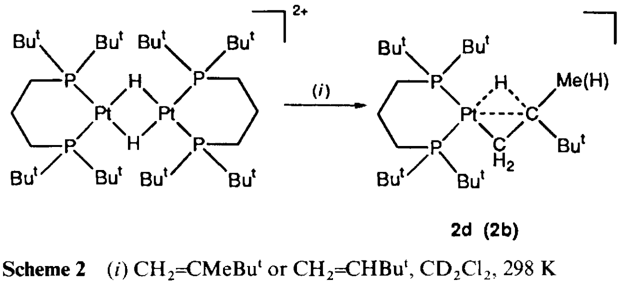
Results and Discussion

Preparations.—Reduction of the diphosphineplatinum(II) dichloride complexes $[PtCl_2(P\text{–}P)]$ [P–P = $Bu^t_2P(CH_2)_2PBu^t_2$, (dbpe); $Bu^t_2P(CH_2)_3PBu^t_2$ (dbpp) and $1,2\text{-}(Bu^t_2PCH_2)_2C_6H_4$ (dbpx)] by 1% Na–Hg amalgam in the presence of a large excess of 3,3-dimethylbut-1-ene at room temperature, afforded the platinum(0) complexes $[Pt(CH_2{=}CHBu^t)(P\text{–}P)]$ (P–P = dbpe **1a**, dbpp **1b** or dbpx **1c**) as pale yellow, air-sensitive crystalline solids in good yields (60–74%). Complex **1c** decomposes in solution within 2–3 h unless stabilized by an excess of 3,3-dimethylbut-1-ene. The bite angle and bulkiness of the chelating diphosphines increase in the order dbpe < dbpp < dbpx, and it seems likely that steric factors affect the stability of the largest diphosphine complex **1c**. The NMR spectroscopic data for **1a**–**1c** are typical of platinum(0) alkene complexes (see Experimental section).

Reaction of compounds **1a**–**1c** with $HBF_4{\cdot}OMe_2$ in diethyl ether at 273 K afforded the cationic complexes **2a**–**2c** respectively in good yields (80–90%) (Scheme 1). Complex **2b** could also be prepared by the reaction of the diplatinum complex $[Pt_2(\mu\text{-}H)_2(dbpp)_2][BF_4]_2$[5] with an excess of 3,3-dimethylbut-1-ene. The complex $[Pt(CH_2CHMeBu^t)(dbpp)][BF_4]$ **2d** was obtained by the reaction between $[Pt_2(\mu\text{-}H)_2(dbpp)_2][BF_4]_2$ and an excess of 2,3,3-trimethylbut-1-ene (Scheme 2). This reaction was performed and the product identified in an NMR tube as attempts to isolate the solid resulted in decomposition to other unidentified products. For example, attempted crystallization of the complex from $CH_2Cl_2\text{–}Et_2O$ by vapour diffusion in the presence of an excess of the alkene resulted in a mixture of unidentified products.



Scheme 1 (*i*) H^+, Et_2O, 273 K



Scheme 2 (*i*) $CH_2{=}CMeBu^t$ or $CH_2{=}CHBu^t$, CD_2Cl_2, 298 K

Complex **2a** possesses a *cis*-alkene–hydride ground-state structure whilst for **2b**–**2d** the platinum achieves a 16-electron configuration *via* a β-C–H agostic Pt ··· H ··· C interaction. The cations **2a**–**2d** are soluble in dichloromethane at room temperature. Solutions of **2a**–**2c** are indefinitely stable at room

Table 1 Selected ^1H and ^{13}C NMR data for complexes **2a**–**2d**[a]

Complex	P–P	T/K	δ_H	J(PH)	J(PtH)	$\delta(C_\alpha)$	$J(PtC_\alpha)$	$\delta(C_\beta)$	$J(PtC_\beta)$	$J(C_\beta H)$
2a	dbpe	293	*b*			42.2[c]	112	89.6[c]	< 10	87[d]
		205	−4.80	107	492	44.8	95	95.6	< 10	159
2b	dbpp	293	−0.65[d]	27	42	23.7	217	45.8	51	103[d]
		190	−3.20	48	77	*b*		47.6	*b*	41, 155
2c	dbpx	293	−0.85[d]	*e*	*e*	33.7	187	43.4	60	101[d]
		195	−3.45	*e*	*e*					
2d	dbpp	293	−3.90	62	142	34.3	208	65.7	43	55
		205	−3.75	58	115					

[a] ^1H NMR data refer to the hydridic or agostic proton chemical shifts (δ) in ppm positive to high frequency of $SiMe_4$, coupling constants in Hz, solvent CD_2Cl_2. [b] Not observed. [c] Refers to alkene carbons: CH_2 is C_α. [d] Averaged values: see text. [e] Broad signal, unresolved.

Table 2 ^{31}P-{^1H} NMR data for complexes **2a**–**2d** at various temperatures[a]

Complex	P–P	T/K	$\delta(P_c)$	$J(PtP_c)$	$\delta(P_t)$	$J(PtP_t)$
2a	dbpe	293	101.4	2934	87.6	2997
		213	100.0	2940	86.9	2718
2b	dbpp	293	39.1	2711	46.7	4837
		193	36.2[b]	2693	44.3[b]	4850
2c	dbpx	293	43.1	3268	53.1	4865
		213	41.1	3275	49.0	4789
2d	dbpp	293	44.2[c]	2757	45.4[c]	4513
		203	40.0[b]	2707	43.6[b]	4655

[a] Chemical shifts (δ) in ppm positive to high frequency of triphenylphosphite (126.6) (external), coupling constants in Hz, solvent CD_2Cl_2; temperature in K. [b] $J(PP) = 5$ Hz. [c] $J(PP) = 7$ Hz.

temperature in the presence of 3,3-dimethylbut-1-ene, whilst solutions of **2d** in the presence of an excess of 2,3,3-trimethylbut-1-ene are stable for periods of several days at room temperature. However, in the absence of the alkene, complex **2a** decomposes within 2–4 h to the diplatinum species[5,8] $[Pt_2(\mu-H)_2(dbpe)_2][BF_4]_2$ and other unidentified products, whereas **2b** decomposes to form the complex $[Pt_2(\mu-H)_2(dbpp)_2][BF_4]_2$ within 0.5 h. The latter reaction is reversible and addition of excess 3,3-dimethylbut-1-ene to the dinuclear species $[Pt_2(\mu-H)_2(dbpp)_2][BF_4]_2$ regenerates complex **2b**. However no reaction was observed when excess 3,3-dimethylbut-1-ene was added to the dinuclear species $[Pt_2(\mu-H)_2(dbpe)_2][BF_4]_2$. Similar observations have been reported for the related complexes $[Pt(Et)(P-P)][BF_4]$ (P–P = dbpe or dbpp) although the rate of alkene displacement is slower for ethene.[5] Attempts to crystallize complex **2c** from dichloromethane by the slow vapour diffusion of diethyl ether into the solution resulted in the formation of the hydridochloride, [PtHCl(dbpx)]. Reactions between agostic complexes of Pt^{II} and chlorinated solvents are known; for example $[Pt(C_7H_{11})(dcpe)][BF_4]$ [dcpe = 1,2-bis(dicyclohexylphosphino)ethane] decomposes to the dinuclear complex $[Pt_2(\mu-H)(\mu-Cl)(dcpe)_2][BF_4]_2$ when crystallized from chlorinated solvents.[4] Dichloromethane solutions of **2a**–**2c** are stable for long periods of time at 195 K.

The complexes described in this paper differ from agostic complexes of Pt^{II} described previously[3–5] in that the β-carbon of the alkyl moiety possesses a bulky alkyl substituent. Although a dynamic equilibrium exists between the alkene–hydride and the alkyl forms, the α- and β-carbon atoms can be distinguished in the respective ^{13}C-{^1H} NMR spectra at room temperature. Tables 1 and 2 summarize some selected room- and low-temperature ^1H, ^{13}C and ^{31}P NMR data for the cationic complexes **2a**–**2d**.

Spectroscopy.—The IR spectrum (Nujol mull) of complex **2a** showed a medium absorption, ν_{max} 2100 cm^{-1}, which is assigned to the Pt–H bond. However, the proton NMR spectrum of **2a** at room temperature showed no resonance in the metal hydride region (δ < 0). A multiplet at δ 2.94 with an integral equivalent to two protons was assigned to the CH_2 protons of the alkene ligand. The protons of the phosphine Bu^t groups appear as two sharp doublets at room temperature indicating that the cation has a time-averaged plane of symmetry.

Cooling a solution of **2a** to 233 K resulted in the appearance of two broad signals, one doublet at δ −4.70 and the other a broad singlet at δ 4.45, each integrating as one proton. Further cooling to 203 K had little effect on the broad signal at δ 4.45. However, the hydride signal became a sharp doublet with ^{195}Pt satellites at δ −4.80, [J(PH) 107, J(PtH) 492 Hz]. Although ^1J(PtH) values are not an absolute measure of the Pt–H bond strength, they can be used to compare the degree of Pt–H interaction in related complexes because they are a measure of the degree of s character of the bond.[9] Thus, for complex **2a**, the chemical shift and ^1J(PtH) value indicate the presence of a hydride ligand *trans* to a soft donor atom. We have previously reported a similar value of ^1J(PtH) for a related *cis*-alkene–hydride complex, $[PtH(C_2H_4)(dbpe)][BF_4]$.[5] The changes in the spectrum were reversed as the temperature was raised towards room temperature. These results are interpreted in terms of a fluxional process which serves to exchange the terminal hydride ligand and one of the alkene hydrogens, coupled with at least partial rotation about the C_α–C_β bond (Scheme 3).

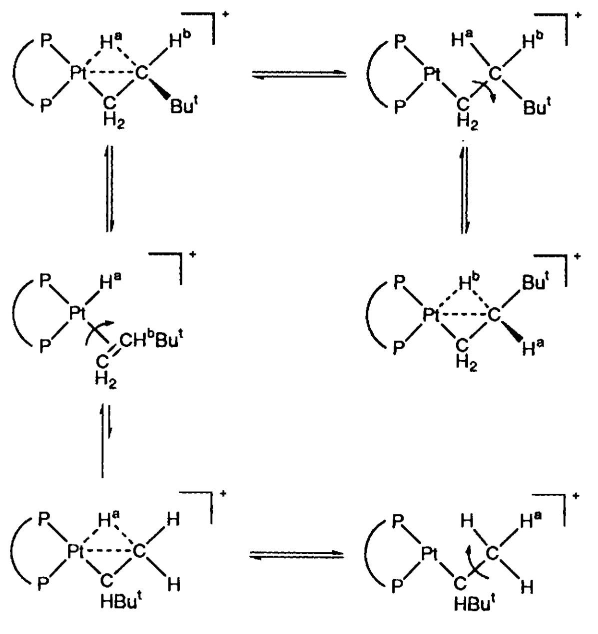
The ^{13}C NMR spectra of complex **2a** are also consistent with a *cis*-alkene–hydride ground-state structure. In the ^{13}C-{^1H} NMR spectrum at room temperature, one of the alkene carbons (CH_2=), resonates at δ 42.2 as a doublet with ^{195}Pt satellites, J(PC) 22, J(PtC) 112 Hz, and the other, (=CH–), is a broad singlet at 89.6 without obvious coupling to ^{195}Pt.

Although the Bu^t methyl carbon nuclei of the phosphine ligand are not resolved and appear as a broad singlet, the quaternary carbons are observed as two sharp doublets consistent with the cation possessing a time-averaged plane of symmetry. In order to understand further the nature of this complex, the proton-coupled ^{13}C NMR spectrum was recorded. The signal at δ 42.2 resonated as a 1 : 2 : 1 triplet, ^1J(CH) 158 Hz, which compares well with the ^1J(CH) values reported for other metal alkene–hydride cationic complexes.[5,8,10,11] However, the signal at δ 89.6 appears as a triplet, J(CH) 87 Hz, suggesting a rapid exchange of the alkene and hydrido protons at this carbon. A ^{13}C-{^1H} 135° distortionless enhancements by polarisation transfer (DEPT) NMR spectrum at room temperature showed a methylene signal at δ 42.2 which is assigned to the CH_2 carbon of the η^2-bound alkene. There was no signal corresponding to C_β at δ 89.6, presumably as a result of the exchange process. However, at 205 K the proton-coupled ^{13}C NMR spectrum revealed the C_β signal at δ 95.6 as a doublet, J(CH) 159 Hz. Clearly, at this temperature the exchange process is not evident on the NMR timescale and the large observed value of J(CH) is typical of a co-ordinated alkene. Interestingly at this temperature the quaternary carbons of the phosphine ligand appear as four doublets around δ 37.5 consistent with the proposed asymmetric static structure.

The $^{31}P-\{^1H\}$ NMR spectra of complex **2a** are also informative. At room temperature the two different phosphorus environments are observed, *viz.* δ 87.6, $J(PtP_t)$ 2997 and 101.4, $J(PtP_c)$ 2934 Hz. Cooling a solution of **2a** to 213 K had no major effect on the chemical shift or coupling constant of the phosphorus atom *cis* to the hydride ligand, which resonated at δ 100.0, $J(PtP_c)$ 2940 Hz (Table 2). However, for the *trans* phosphorus atom, a sharp decrease in the coupling constant was observed to $J(PtP_t)$ 2718 Hz (δ 86.9). This could be interpreted in terms of an equilibrium between alkene–hydride and agostic forms which shifts towards the alkene-hydride isomer as the temperature falls. However, if this is the case the concentration of the agostic form must be small at room temperature [values of $J(PtP_t)$ for an agostic structure are *ca.* 4500 Hz] and there is no evidence of the agostic isomer in the spectrum at 213 K which is sharp and shows only the peaks assigned to the alkene–hydride isomer.

Complexes **2b** and **2c** display similar NMR spectra (see Tables 1 and 2) and therefore only **2b** will be discussed in detail. The proton NMR spectrum of complex **2b** at room temperature exhibited a doublet resonance at δ −0.65, $J(PH)$ 27, $J(PtH)$ 42 Hz assigned to the two β-protons of an agostic 3,3-dimethylbutyl ligand which are exchanging rapidly at this temperature. The Bu^t protons of the phosphine ligand resonate as two doublets and the chelate-bridge protons appear as broad multiplets. A multiplet at δ 1.80 is assigned to the two α-protons of the alkyl ligand. Cooling a solution of **2b** to 233 K resulted in the collapse of the signal at δ −0.65 to the base line, whereas the signal for the Bu^t protons of the alkyl ligand remained sharp. Further cooling to 190 K resulted in the appearance of a broad doublet at δ −3.20, $J(PH)$ 48, $J(PtH)$ 77 Hz, and a new signal appeared at δ *ca.* 1.8, partly obscured by the signals of the methylene bridge protons. The room-temperature signal at δ −0.65, therefore, corresponds to the weighted average of the two signals at 190 K, *viz.* $[1.80 + (-3.20)]/2 = -0.70$. The resonances attributable to the Bu^t protons of the phosphine ligand appeared as a complex group of broad signals at this temperature. In contrast, throughout the temperature range studied (190–293 K), the signal for the Bu^t protons of the alkyl ligand remained sharp and distinct.

For complexes **2b** and **2c**, therefore, it appears that at room temperature there exists a dynamic process which results in exchange between the agostic hydrogen and the other non-agostic β-hydrogen of the alkyl ligand. Two alternative processes which could achieve this exchange can be envisaged; either *via* a 14-electron species (Scheme 3), involving the dissociation or detachment of the agostic hydrogen from the metal followed by rotation about the C_α–C_β bond, or an 'in-place' rotation about the C_α–C_β bond (Scheme 4) requiring an intermediate or transition state in which both β-hydrogens have significant interaction with the metal. Such an in-place rotation has been invoked by Green and Wong[12] to explain an apparently related dynamic process in the complex $[MoH(\eta^2\text{-}C_2H_4)_2(dppen)_2][CF_3SO_2]$ [dppen = bis(1,2-diphenylphosphino)ethylene].



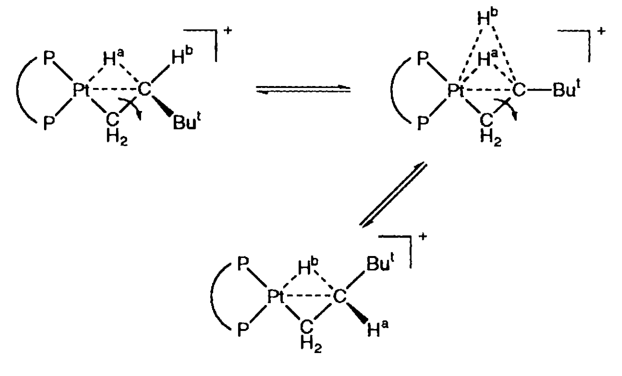
Scheme 3 P–P = dbpe **2a**, dbpp **2b** or dbpx **2c**

The high-field signals in the ^1H NMR spectra, δ −3.20 (**2b**) and −3.45 (**2c**) together with the coupling to both phosphorus and ^{195}Pt nuclei, compare well with the related norbornyl agostic complexes $[Pt(C_7H_{11})(P\text{–}P)][BF_4]$.[4] Likewise the agostic hydrogens in $[Pt(Et)(P\text{–}P)][BF_4]$ (P–P = dbpp or dbpx)[5] resonate as broad signals at δ −2.8 and −2.6 respectively.

The ^{13}C NMR spectra of complexes **2b** and **2c** are also consistent with agostic ground-state structures. In the $^{13}C-\{^1H\}$ NMR spectrum of **2b** at room temperature, the β-carbon resonates at δ 45.8, $J(PtC)$ 51 Hz, whilst the α-carbon signal appears as a doublet with ^{195}Pt satellites at δ 23.7 [$J(PtC)$ 217, $J(PC)$ 38 Hz]. The attachment of the Bu^t group in the alkyl ligand to the β-carbon was confirmed by a ^1H-coupled ^{13}C NMR spectrum at room temperature, which showed the β-carbon to resonate as a 1:2:1 triplet at δ 45.8, $J(CH)$ 103 Hz. This coupling constant represents a time-averaged value resulting from an agostic hydrogen and a terminal hydrogen attached to the β-carbon atom (see above). However, for the alkyl ligand to possess only two hydrogens at the β-carbon, implies that the Bu^t group must also be attached to the β-carbon. If the Bu^t group was attached to the α-carbon, then the β-carbon would have three hydrogens attached to it and would appear as a quartet in the ^1H-coupled ^{13}C NMR spectrum. Further support for the position of the Bu^t group was provided by a $^{13}C-\{^1H\}$ 135° DEPT NMR spectrum at room temperature, which displayed methylene signals for both the α-and β-carbons of the alkyl ligand.

The Bu^t carbons of the phosphine ligand resonated as two separate signals, at δ 30.0 and 30.5 in the $^{13}C-\{^1H\}$ NMR spectrum at room temperature. The quaternary carbon atoms also appeared as two separate signals with phosphorus couplings. These observations are consistent with the presence of a time-averaged plane of symmetry as suggested by the mechanisms of Schemes 3 and 4.

In order to provide a more complete characterization of these complexes, the low-temperature proton-coupled ^{13}C NMR spectrum of **2b** was recorded. Carbon-13 NMR spectroscopic parameters, particularly $^1J(CH)$, often provide an unambiguous characterization of agostic interactions.[2] The presence of an agostic bond would normally be reflected in a reduced carbon–hydrogen coupling constant, $^1J(CH)$, in the static spectrum. Indeed, at 194 K, the β-carbon of the alkyl group in complex **2b**



Scheme 4 P–P = dbpp **2b** or dbpx **2c**

resonates as a doublet of doublets at δ 47.6 with ^1J(CH) of 155 and 41 Hz respectively. Comparison of these values with those reported for the related ethyl[5] and norbornyl[4] analogues suggests substantial olefinic character for the β-carbon of complex **2b**. Thus, the chemical shift of the β-carbon of **2b** is further downfield and the coupling constant of 41 Hz is at the lower extremity of values expected (60–90 Hz) for an agostic bond.[2] However, this coupling constant is too large for a classical terminal metal hydride [the coupling constant ^2J(CH) for a *cis* alkene–hydride is *ca.* 0–10 Hz]. For example, the complex $[\mathrm{NbH(C_2H_4)(\eta\text{-}C_5Me_5)_2}]$ which is known to have an alkene–hydride structure has $^2J(\mathrm{CH}) = 6$ Hz.[13] The NMR data, therefore, confirm an agostic interaction for complex **2b** but one which possesses appreciable alkene–hydride character. An example of a similar low ^1J(CH) value for a β-agostic interaction has been reported for the complex $[\mathrm{Co(CH_2CH_2Me)\{P(OMe)_3\}(\eta\text{-}C_5Me_5)][BF_4]}$.[7]

At fast-exchange temperatures only average coupling constant values, $[^1J(\mathrm{CH})_{\mathrm{av}}]$ would be expected to be observed in the ^{1}H-coupled ^{13}C NMR spectrum of a fluxional complex. In fact, for complex **2b** this is the case and the value obtained at room temperature, ^1J(CH) 103 Hz, represents approximately an average of two couplings, *viz.* $[(155 + 41)/2] = 98$ Hz. Similar behaviour has been observed in other fluxional agostic systems. Thus, for example, the agostic methyl group in the complex $[\mathrm{MoPr^i(\eta^3\text{-}C_3H_5)_3}]$[14] resonates as a quartet at δ 7.3, ^1J(CH) 122 Hz at 213 K. However, at 158 K this signal appears as a triplet of doublets, ^1J(CH) 138 and 88 Hz respectively.

The ^{31}P-{^{1}H} NMR spectra of complex **2b** are also informative. In the spectrum of complex **2b** recorded at 293 K, two resonances were observed, δ 39.1, $J(\mathrm{PtP}_c)$ 2711 and 46.7, $J(\mathrm{PtP}_t)$ 4837 Hz, which were assigned to the phosphorus atoms *cis* and *trans* respectively to the agostic hydrogen. The large value of $J(\mathrm{PtP}_t)$ reflects the fact that this phosphorus nucleus is *trans* to a weakly interacting hydrogen, which exerts a weak *trans* influence. In contrast, the $J(\mathrm{PtP}_c)$ value is lower, which is consistent with the higher *trans* influence of the α-carbon atom which has some sp^3 character. Cooling a solution of **2b** to 193 K had no remarkable effect on the chemical shifts or coupling constant values [*viz.* δ 36.2, $J(\mathrm{PtP}_c)$ 2693 and 44.3, $J(\mathrm{PtP}_t)$ 4850 Hz] suggesting that the two phosphorus environments do not change within the temperature range 193–293 K.

The NMR data (Tables 1 and 2) show that complex **2c** undergoes the same fluxional behaviour in solution as **2b**, and strongly suggest that **2c** possesses the same ground-state structure as **2b**, namely that it includes a β-agostic interaction. Unfortunately, owing to the many signals and complex ^{31}P and ^{195}Pt couplings in the region of interest, direct observation of the ^1J(CH) values for the β-carbon at low temperature (slow exchange) for this complex has not been possible.

The IR spectra (Nujol mull) of complexes **2b** and **2c** showed weak absorptions at ν_{max} 2080 and 2110 cm^{-1} respectively. Infrared absorptions for M $\cdots$ H $\cdots$ C (agostic) interactions in transition-metal complexes are not normally observed[2] and the possibility that these complexes might exhibit a *cis*-alkene–hydride structure in the solid state cannot be ruled out. Solution NMR spectroscopy for complexes **2b** and **2c**, however, have unambiguously confirmed the presence of a β-agostic interaction in these complexes in solution and significantly IR studies of **2b** in dichloromethane solution show no stretch in the region of 2100 cm^{-1}. Unfortunately, the exact solid-state structure of these complexes could not be determined because attempts to obtain crystals suitable for X-ray crystallographic analysis proved unsuccessful.

The reaction between the red dinuclear complex $[\mathrm{Pt_2(\mu\text{-}H)_2(dbpp)_2][BF_4]_2}$ and 3,3-dimethylbut-1-ene resulted in the formation of the corresponding agostic cation (see above). In an attempt to explore the generality of this route, the diplatinum complex was reacted with 2,3,3-trimethylbut-1-ene. As expected, this reaction afforded the pale yellow agostic complex $[\mathrm{Pt(CH_2CHMeBu^t)(dbpp)][BF_4]}$ **2d** (Scheme 2) within 6–12 h.

The ^{1}H NMR spectrum of complex **2d** at room temperature exhibited a high-field doublet signal at δ −3.90, J(PH) 62, J(PtH) 142 Hz, which is assigned to a β-agostic hydrogen. This signal is at higher field compared to the average signal observed for complexes **2b** and **2c** at room temperature. The coupling constants [J(PH) and J(PtH)] are also higher. This observation can be readily explained by the fact that complex **2d** possesses one hydrogen only at the β-carbon. As such, no exchange process similar to that in **2b** or **2c** is occurring, and the observed high-field signal corresponds to the interaction of the single hydrogen on the β-carbon with the platinum atom. The Bu^t protons of the phosphine ligand appear as a complicated group of signals as expected from the low symmetry of the complex. A singlet signal at δ 1.19 is assigned to the Bu^t protons of the alkyl ligand, whilst the methyl group protons also resonate as a doublet at δ 1.58. Cooling a solution of **2d** to 203 K had no significant effect on the chemical shift or coupling constant values. Thus, throughout the temperature range 203–298 K the ^{1}H NMR spectrum of complex **2d** exhibited a high field signal at δ *ca.* −3.8, with coupling to both ^{31}P and ^{195}Pt although some change in the parameters was observed. For example, at 203 K, the agostic hydrogen resonates at δ −3.75, J(PH) 58, J(PtH) 117 Hz.

The ^{13}C NMR spectra of complex **2d** are also consistent with an agostic ground-state structure. In the ^{13}C-{^{1}H} NMR spectrum of **2d** at room temperature, the α-carbon resonates at δ 34.3, J(PC) 35, J(PtC) 208 Hz, whilst the β-carbon appears at δ 65.7, J(PtC) 43 Hz. These assignments were confirmed by a ^{13}C-{^{1}H} 135° DEPT NMR spectrum at room temperature. A negative signal for the resonance at δ 34.3 confirmed it to be a CH$_2$ group, whilst a positive resonance for the signal at δ 65.7 confirmed it as a CH group. In order to provide an unambiguous structural characterization, a ^{1}H-coupled ^{13}C NMR spectrum of this complex was recorded at room temperature. Consistent with a β-agostic interaction, the signal at δ 65.7 appeared as a broad doublet, J(CH) 52 Hz. This coupling constant compares well with the $^1J(\mathrm{CH})_{\mathrm{agostic}}$ value obtained for complex **2b** at the slow exchange limit (194 K).

The ^{31}P-{^{1}H} NMR spectrum of **2d** at room temperature reveals two different phosphorus environments, *viz.* δ 44.2, [J(PP) 7, $J(\mathrm{PtP}_c)$ 2757] and 45.4, [J(PP) 7, $J(\mathrm{PtP}_t)$ 4513 Hz]. Cooling **2d** to 203 K had no significant effect on the chemical shifts or coupling constant values, which are consistent with an agostic ground-state structure.

Several ethyl agostic complexes of the type $[\mathrm{M(C_2H_5)L}_n]^+$ have been reported in the literature.[2] The energy difference between agostic and alkene–hydride forms is often small, and closely related complexes have been shown to possess different ground-state structures. This work was concerned with the effects of introducing bulky alkyl groups on the stability of the agostic bond. Some interesting points emerge:

(*a*) In the agostic isomers of these platinum(II) complexes the alkyl substituent is placed on the β-carbon, in line with previous observations on cobalt systems.[7] The energetic difference between α- and β-substitution appears to be relatively high. Thus, although previous work[3–5] shows that the barrier to hydride transfer to the metal is very low, as is the barrier to alkene rotation in the alkene–hydride isomer, there is no rapid exchange of protons between the α- and β-carbon atoms which should occur if there were any substantial concentration of the α-isomer (Scheme 3).

(*b*) The energetic balance between agostic and alkene–hydride isomers does not appear to be particularly sensitive to the presence of the Bu^t group. Considering the steric interaction between the alkyl (or alkene) ligand and the rest of the complex would suggest that the Bu^t substituent on the alkene should favour the agostic form. However, the behaviour of the system described in this paper is generally similar to the ethyl/ethene complexes which we have described previously, *i.e* the dbpe complex has an alkene–hydride structure whereas the larger chelates promote the agostic alkyl isomer. It seems probable that this arises from a fortuitous balance of opposing factors. The tendency of alkyl substituents to favour the alkene–hydride extreme, noted above for the cobalt complex[7] is offset by the steric influence of the substituent.

(*c*) Alkyl substituents destabilize the complex with respect to alkene dissociation. Although we have not quantified the tendency to lose alkene our qualitative observations suggest that the bulky alkyl complexes are significantly less stable than their ethyl counterparts.

Experimental

All the solvents were dried prior to use by refluxing over the appropriate drying agent: tetrahydrofuran (thf) and diethyl ether over Na–benzophenone, toluene over Na, hexane and CH$_2$Cl$_2$ over CaH$_2$. All compounds were assumed to be air sensitive, unless stated otherwise. All operations were carried out on a vacuum/nitrogen manifold using conventional Schlenk-type vessels and techniques. The NMR solvents were degassed by the freeze–thaw method. Microanalyses were performed by Butterworth Laboratories Ltd., Middlesex, UK.

Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrometer and NMR spectra on either a Bruker AC300 (^{1}H 300, ^{13}C 75 and ^{31}P 121 MHz) or a JEOL JNM-EX90 (^{1}H 90 and ^{31}P 36.2 MHz) spectrometer. All spectra were run at room temperature (*ca.* 293 K) unless stated otherwise. The terms ^{13}C and ^{31}P NMR refer to proton decoupled spectra unless stated otherwise, and ^{1}H and ^{13}C NMR chemical shifts are expressed in ppm with positive values to high frequency of SiMe$_4$ (δ 0.00); proton-coupled spectra were measured using the gated-decoupling pulse sequence; ^{31}P NMR chemical shifts are relative to triphenyl phosphite (δ 126.6). Coupling constants (J) are measured in Hz. For low temperature work, the temperatures at which the spectra were recorded were estimated by the variation of the proton chemical shift of a 4% methanol in [^{2}H$_4$]methanol sample at a given temperature, measured immediately prior to the recording of the spectrum. The estimated error in the temperature is ± 5 K.

The chelating diphosphines dbpe,[15] dbpp[8] and dbpx,[16] and the complexes [PtCl$_2$(dbpe)][17] and [PtCl$_2$(dbpp)][8] were prepared by published methods. The olefins 3,3-dimethylbut-1-ene and 2,3,3-trimethylbut-1-ene were used as purchased from Aldrich.

Preparation of [Pt(CH$_2$=CHBu^t)(P–P)] (P–P = dbpe **1a**, dbpp **1b** *or* dbpx **1c**). *General Method.*—A Schlenk tube was charged with 10–13 g of 1% Na–Hg amalgam, and thf (25 cm^3) was added followed by 3,3-dimethylbut-1-ene (*ca.* 15–20 mol equivalents of the dichloride compound to be added). To the rapidly stirred suspension the corresponding dichloride [PtCl$_2$(P–P)] (P–P = dbpe, dbpp or dbpx) (typically 0.4 g), was added and stirring was continued for 45–120 min. The amalgam was then allowed to settle. The supernatant liquid was decanted and the residue extracted with thf (2 × 15 cm^3; 0.5 cm^3 of the alkene was added to each extraction to stabilize the product). The solvent was removed *in vacuo* and the residue extracted with diethyl ether (1 × 25 cm^3 and then 2 × 10 cm^3) (0.5 cm^3 of the alkene was added to each extraction). Evaporation of the diethyl ether *in vacuo* afforded the product.

[Pt(CH$_2$=CHBu^t)(dbpe)] **1a**. The reduction of [PtCl$_2$(dbpe)] (0.420 g, 0.72 mmol) in the presence of 3,3-dimethylbut-1-ene (1.4 cm^3) (reaction time 120 min) afforded a pale yellow solid, which was extracted with hexane to give **1a** as an off-white solid, yield 0.32 g, 74% (Found: C, 47.4; H, 8.3. C$_{24}$H$_{52}$P$_2$Pt requires C, 48.2; H, 8.8%); δ_H(C$_6$D$_6$) 1.07–1.32 [36 H, m, C(CH$_3$)$_3$ phosphine], 1.43 [9 H, s, C(CH$_3$)$_3$ alkene, J(PtH) 4], 2.25 (1 H, m, CH$_2$ alkene), 2.34 (1 H, m, CH$_2$ alkene) and 2.85 [1 H, m, CH alkene, J(PtH) 66]; δ_C(C$_6$D$_6$) 24.7 (m, CH$_2$ phosphine), 26.9 [d, CH$_2$=, J(PC)$_{trans}$ 37, J(PtC) 196], 27.8 [apparent t, CH$_2$ phosphine, |J(PC) + J(P′C)| 23], 29.9–30.8 [br m, C(CH$_3$)$_3$ phosphine], 34.1 [d, C(CH$_3$)$_3$ alkene, J(PC) 4, J(PtC) 37], 34.0–36.5 [m, C(CH$_3$)$_3$ phosphine and alkene] and 60.4 [d, =CHBu^t, J(PC)$_{trans}$ 45, J(PtC) 324]; δ_P(C$_6$D$_6$) 95.7 [J(P$_A$P$_B$) 77, J(PtP$_A$) 3154], 98.5 [J(P$_B$P$_A$) 77 and J(PtP$_B$) 3140].

[Pt(CH$_2$=CHBu^t)(dbpp)] **1b**. The reduction of [PtCl$_2$(dbpp)] (0.380 g, 0.63 mmol) in the presence of 3,3-dimethylbut-1-ene (1.63 cm^3) (reaction time 90–120 min) afforded **1b** as a pale yellow solid, yield 0.27 g, 60% (Found: C, 48.7; H, 8.2. C$_{25}$H$_{54}$P$_2$Pt requires C, 49.1; H, 8.9%); δ_H(C$_6$D$_6$) 1.10, 1.13, 1.18 and 1.28 [36 H, 4 × d, C(CH$_3$)$_3$ phosphine, J(PH) 12], 1.41 [9 H, s, C(CH$_3$)$_3$ alkene, J(PtH) 4], 1.35–1.80 (6 H, br m, CH$_2$ bridge of phosphine), 2.00 (1 H, m, CH$_2$ alkene), 2.35 (1 H, m, CH$_2$ alkene) and 2.75 [1 H, m, CH alkene, J(PtH) 67]; δ_C(C$_6$D$_6$) 21.8 [m, PCH$_2$, J(PC) 10], 22.4 (d, PCH$_2$), 26.5 [s, PCH$_2$$CH_2CH_2$P, J(PtC) 25], 29.2–31.8 [m, C(CH$_3$)$_3$ phosphine], 34.0 [d, C(CH$_3$)$_3$ alkene, J(PC) 3, J(PtC) 38], 35.0–37.2 [m, C(CH$_3$)$_3$ phosphine and alkene] and 58.8 [dd, =CH–, J(PH)$_{cis}$ 8, J(PC)$_{trans}$ 43, J(PtC) 314]. The CH$_2$ olefinic carbon is presumed to be obscured by the Bu^t carbons of the phosphine; δ_P(C$_6$D$_6$) 42.6 [J(P$_A$P$_B$) 46, J(PtP$_A$) 3028], 48.4 [J(P$_B$P$_A$) 46 and J(PtP$_B$) 3453].

[Pt(CH$_2$=CHBu^t)(dbpx)] **1c**. The reaction between [PtCl$_2$(dbpx)] (0.450 g, 0.68 mmol) and 3,3-dimethylbut-1-ene (1.5 cm^3) (reaction time 45 min) afforded **1c** as a pale yellow microcrystalline solid, yield 0.33 g, 71% (Found: C, 53.0; H, 8.0. C$_{30}$H$_{56}$P$_2$Pt requires C, 53.5; H, 8.4%); δ_H(C$_6$D$_6$) 1.17–1.32 [36 H, C(CH$_3$)$_3$ phosphine], 1.34 [9 H, s, C(CH$_3$)$_3$ alkene], 1.93 (1 H, m, CH$_2$ alkene), 2.35 (1 H, m, CH$_2$ alkene), 2.60 (1 H, m, CH alkene), 3.50 (4 H, m, CH$_2$ phosphine), 6.94 and 7.20 (4 H, br m, C$_6$H$_4$); δ_C(C$_6$D$_6$) 21.1 [s, CH$_2$ phosphine, J(PtC) 12], 28.8 (s, CH$_2$ phosphine), 30.4 [br d, C(CH$_3$)$_3$ phosphine, J(PC) 4], 32.7 [d, CH$_2$=, J(PC) 35, J(PtC) obscured], 37.5 [br m, C(CH$_3$)$_3$ phosphine and alkene], 51.4 [d, =CH–, J(PC) 28, J(PtC) 226], 125.8 [d, C$_6$H$_4$, J(PC) 6], 133.3 [d, C$_6$H$_4$, J(PC) 19] and 138.7 [s, C$_6$H$_4$, J(PtC) 59]; δ_P(C$_6$D$_6$) 42.1 [J(P$_A$P$_B$) 46, J(PtP$_A$) 3151], 51.2 [J(P$_B$P$_A$) 46 and J(PtP$_B$) 3631].

Protonation of the Complexes [Pt(CH$_2$=CHBu^t)(P–P)] **1a–1c.** *General Method.*—To a stirred solution of **1a**, **1b** or **1c** (typically 0.25 g) in diethyl ether (20 cm^3) at 273 K was added HBF$_4$·OMe$_2$ (*ca.* 10% mol excess). A pale yellow precipitate was formed immediately and stirring was continued for 15 min. The reaction mixture was allowed to settle and then filtered. The product was washed with diethyl ether (3 × 10 cm^3) and then extracted with CH$_2$Cl$_2$ (2 × 5 cm^3) (*ca.* 200 μl of 3,3-dimethylbut-1-ene was added to each extraction). Evaporation of the solvent *in vacuo* afforded the product.

[PtH(CH$_2$=CHBu^t)(dbpe)][BF$_4$] **2a**. The reaction of [Pt(CH$_2$=CHBu^t)(dbpe)] **1a** with HBF$_4$·OMe$_2$ afforded complex **2a** as a pale yellow solid in *ca.* 90% yield. The sample for analysis was crystallized from CH$_2$Cl$_2$–hexane at 195 K (Found: C, 38.3; H, 7.3. C$_{24}$H$_{53}$BF$_4$P$_2$Pt·CH$_2$Cl$_2$ requires C, 39.0; H, 7.2%); IR (Nujol mull): 2100 m (Pt–H); δ_H(CD$_2$Cl$_2$) 1.19 [9 H, s, C(CH$_3$)$_3$ alkene], 1.30 [18 H, d, C(CH$_3$)$_3$ phosphine, J(PH) 14], 1.35 [18 H, d, C(CH$_3$)$_3$ phosphine, J(PH) 13], 2.20 (4 H, m, CH$_2$ phosphine) and 2.94 (2 H, m, $C$$H_2$CHBu^t). Coalescence temperature: 253 K for β-protons. δ_H(CD$_2$Cl$_2$, 203 K) (only signals which have moved are quoted) −4.80 [1 H, d, Pt–H, J(PH) 107, J(PtH) 492] and 4.45 (1 H, br s, CH$_2$=CHBu^t); δ_C(CD$_2$Cl$_2$) 24.5 [dd, CH$_2$ phosphine, J(PC) 11 and 26], 26.0 [dd, CH$_2$ phosphine, J(PC) 11 and 26], 30.2 [m, C(CH$_3$)$_3$ phosphine], 32.0 [s, C(CH$_3$)$_3$ alkene, J(PtC) 24], 34.8 [s, C(CH$_3$)$_3$ alkene], 37.0 [d, C(CH$_3$)$_3$ phosphine, J(PC) 25], 37.9 [d, C(CH$_3$)$_3$ phosphine, J(PC) 19] and 42.2 [d, =CH$_2$ alkene, J(PC) 22, J(PtC) 112], 89.6 (br s, CHBu^t); δ_C(CD$_2$Cl$_2$, proton-coupled, alkene carbons), 42.2 [td, J(PC) 23, J(CH) 158], 89.6 [br t, J(CH) 87]; (205 K) 44.8 [dt, J(PC) 22, J(CH) 154], 95.6 [d, J(CH) 159]; δ_P(CH$_2$Cl$_2$) 87.6 [J(PtP$_t$) 2997] and 101.4 [J(PtP$_c$) 2934]; δ_P(CD$_2$Cl$_2$, 213 K) 86.9 [J(PtP$_t$) 2718], 100.0 [J(PtP$_c$) 2940].

$[Pt(C_6H_{13})(dbpp)][BF_4]$ **2b**. This complex was prepared by three different methods.

Method 1. Protonation of $[Pt(CH_2{=}CHBu^t)(dbpp)]$ **1b** with $HBF_4{\cdot}OMe_2$. The reaction of complex **1b** with $HBF_4{\cdot}OMe_2$ afforded complex **2b** as a pale yellow solid in *ca.* 80% yield.

Method 2. To a red solution of $[Pt_2(\mu\text{-}H)_2(dbpp)_2][BF_4]_2$ (0.060 g, 0.049 mmol) in CD_2Cl_2 (0.5 cm^3) was added 3,3-dimethylbut-1-ene (50 μl, *ca.* 8 mol equivalents). After 8 h the solution changed from red to pale yellow and ^1H, ^{13}C and ^{31}P NMR spectra recorded after 12 h indicated the formation of complex **2b**.

Method 3. To a solution of $[Pt(\eta^3\text{-}CH_3CHPh)(dbpp)]$-$[BF_4]$[18] (0.120 g, 0.167 mmol) in CH_2Cl_2 (0.5 cm^3) was added 3,3-dimethylbut-1-ene (86 μl, *ca.* 4 mol equivalents). After 0.5 h the solvent was evaporated *in vacuo*, affording the product as a pale yellow solid, yield 0.107 g, 92% (Found: C, 42.6; H, 7.0. $C_{25}H_{55}BF_4P_2Pt$ requires C, 42.9; H, 7.9%); IR (Nujol mull): 2080w; $\delta_H(CD_2Cl_2)$ −0.65 [2 H, d, $\text{–}CH_2Bu^t$, $J(PH)$ 27, $J(PtH)$ 42], 1.17 [9 H, s, $C(CH_3)_3$ alkyl], 1.29 [18 H, d, $C(CH_3)_3$ phosphine, $J(PH)$ 14], 1.34 [18 H, d, $C(CH_3)_3$ phosphine, $J(PH)$ 14], 1.80 (2 H, m, $PtCH_2$) and 2.00–2.38 (6 H, m, CH_2 phosphine). Coalescence temperature: 233 K for β-protons. $\delta_H(CD_2Cl_2$, 190 K) −3.20 [1 H, br d, H_{ag}, $J(PH)$ 48, $J(PtH)$ 77, H_{ag} = agostic H]. The signal for the other hydrogen on the β-carbon could not be positively identified. $\delta_C(CD_2Cl_2)$ 19.1 [d, PCH_2, $J(PC)$ 23], 19.3 [dd, PCH_2, $J(PC)$ 30 and 7], 23.7 [d, $PtCH_2$, $J(PC)$ 38, $J(PtC)$ 217], 24.1 [s, CH_2 phosphine, $J(PtC)$ 56], 30.0 [s, $C(CH_3)_3$ phosphine], 30.5 [s, $C(CH_3)_3$ phosphine, $J(PtC)$ 27], 30.8 [s, $C(CH_3)_3$ alkyl], 32.9 [$C(CH_3)_3$ alkyl], 36.0 [d, $C(CH_3)_3$ phosphine, $J(PC)$ 36], 38.9 [d, $C(CH_3)_3$ phosphine, $J(PC)$ 29] and 45.8 [s, $PtCH_2CH_2Bu^t$, $J(PtC)$ 51]; $\delta_C(CD_2Cl_2$, ^1H-coupled, β-carbon) 45.5 [t, $PtCH_2CH_2Bu^t$, $J(CH)$ 103]; $\delta_C(CD_2Cl_2$, 194 K, ^1H-coupled, β-carbon) 47.6 [dd, $PtCH_2CH_2$, $J(CH)$ 41 and 155]; $\delta_P(CD_2Cl_2)$ 39.1, $J(PtP_c)$ 2711; 46.7, $J(PtP_t)$ 4837; $\delta_P(CD_2Cl_2$, 193 K) 36.2 [$J(P_tP_c)$ 5.5, $J(PtP_c)$ 2693], 44.3 [$J(P_cP_t)$ 5.5, $J(PtP_t)$ 4850].

$[Pt(C_6H_{13})(dbpx)][BF_4]$ **2c**. The reaction of $[Pt(CH_2{=}CHBu^t)(dbpx)]$ **1c** with $HBF_4{\cdot}OMe_2$ afforded complex **2c** as a pale yellow solid, yield 80%. The sample for analysis was crystallized from CH_2Cl_2–hexane at 195 K. The complex crystallizes with one mole of CH_2Cl_2 (Found: C, 43.75; H, 6.8. $C_{30}H_{57}BF_4P_2Pt{\cdot}CH_2Cl_2$ requires C, 44.0; H, 7.0%). IR (Nujol mull): 2110m; $\delta_H(CD_2Cl_2)$ −0.85 (2 H, br m, $PtCH_2CH_2$), 1.16 [9 H, s, $C(CH_3)_3$ alkyl], 1.28 [18 H, d, $C(CH_3)_3$ phosphine, $J(PH)$ 14], 1.43 [18 H, d, $C(CH_3)_3$ phosphine, $J(PH)$ 14.5], 2.31 [2 H, d, $PtCH_2$, $J(PH)$ 10], 3.80 (4 H, m, CH_2 phosphine), 7.26 [2 H, d, C_6H_4, $J(PH)$ 3] and 7.44 [2 H, d, C_6H_4, $J(PH)$ 17]. Coalescence temperature for β-protons: 214 K. $\delta_H(CD_2Cl_2$, 194 K) (only signals which are different are described) −3.45 [1 H, br s, H_{ag}, $J(PtH)$ not resolved], 1.76 (1 H, br s, $PtCH_2CHH_{ag}$), 2.25 [1 H, d, $PtCH_2$, $J(PH)$ 9, $J(PtH)$ not observed] and 2.28 [1 H, d, $PtCH_2$, $J(PH)$ 9, $J(PtH)$ not observed]; $\delta_C(CD_2Cl_2)$ 26.0 (s, CH_2 phosphine), 28.5 (m, CH_2 phosphine), 29.8–30.8 [br m, $C(CH_3)_3$ phosphine], 31.1 [s, $C(CH_3)_3$ alkyl], 31.7 [s, $C(CH_3)_3$ alkyl], 33.7 [d, $PtCH_2$, $J(PC)$ 38, $J(PtC)$ 187], 36.8 [br m, $C(CH_3)_3$ phosphine], 40.5 [br m, $C(CH_3)_3$ phosphine], 43.4 [s, $PtCH_2CH_2$, $J(PtC)$ 60], 127.9 (m, C_6H_4), 133.2 (s, C_6H_4) and 133.4 (s, C_6H_4); $\delta_C(CD_2Cl_2$, ^1H-coupled) (only the β-carbon is described) 43.5 [t, $PtCH_2CH_2$, $J(CH)$ 101]; $\delta_P(CD_2Cl_2)$ 43.1 [$J(PtP_c)$ 3268], 53.1 [$J(PtP_t)$ 4865]; $\delta_P(CD_2Cl_2$, 213 K) 41.1 [$J(PtP_c)$ 3275], 49.0 [$J(PtP_t)$ 4789].

$[Pt(C_7H_{15})(dbpp)][BF_4]$ **2d**. To a red solution of $[Pt_2(\mu\text{-}H)_2(dbpp)_2][BF_4]_2$ (0.095 g, 0.078 mmol) in CD_2Cl_2 (0.4 cm^3) was added 2,3,3-trimethylbut-1-ene (110 μl, *ca.* 10 mol equivalent). After *ca.* 8 h the solution changed from red to pale yellow and ^1H, ^{13}C and ^{31}P NMR spectra recorded after 12 h indicated the formation of complex **2d**. This complex decomposes in solution at room temperature without the presence of the alkene (2,3,3-trimethylbut-1-ene). In the solid state it decomposes within 2–3 h to a red solid, and for this reason elemental analysis could not be performed. $\delta_H(CD_2Cl_2)$ −3.90 [1 H, d, H_{ag}, $J(PH)$ 62, $J(PtH)$ 142], 1.19 [9 H, s, $C(CH_3)_3$ alkyl], 1.27–1.40 [36 H, $C(CH_3)_3$ phosphine], 1.90–2.55 (6 H, CH_2 phosphine) and 1.58 [3 H, d, $\text{–}CH(CH_3)Bu^t$, $J(PH)$ 5, $J(PtH)$ 36]; $\delta_H(CD_2Cl_2$, 203 K) no substantial change from the room-temperature spectrum was observed: only the agostic hydrogen is quoted, −3.75 [$J(PH)$ 58, $J(PtH)$ 117]; $\delta_C(CD_2Cl_2)$ 19.5 (m, 2 × CH_2 phosphine), 21.8 [s, $CH(CH_3)$-Bu^t alkyl], 24.2 [s, CH_2 phosphine, $J(PtC)$ 50], 27.7 [s, $C(CH_3)_3$ alkyl], 29.9–31.0 [$C(CH_3)_3$ phosphine], 30.8 [s, $C(CH_3)_3$ alkyl], 34.3 [d, $PtCH_2$, $J(PC)$ 35, $J(PtC)$ 208], 35.1, 35.8, 38.6, 38.9 [4 × d, $C(CH_3)_3$ phosphine, $J(PC)$ 24, 33, 27, 27 respectively] and 65.7 [s, $PtCH_2CH$, $J(PtC)$ 43]; $\delta_C(CD_2Cl_2$, ^1H-coupled) only the β-carbon is described: 65.7 [d, $J(CH)$ 55]; $\delta_P(CD_2Cl_2)$ 44.2 [$J(P_cP_t)$ 7, $J(PtP_c)$ 2757], 45.4 [$J(P_tP_c)$ 7, $J(PtP_t)$ 4513]; $\delta_P(CD_2Cl_2$, 203 K) 40.0 [$J(P_tP_c)$ 5.5, $J(PtP_c)$ 2707], 43.6 [$J(P_cP_t)$ 5.5, $J(PtP_t)$ 4655].

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