

Platinum Ethyl Complexes with β -Agostic Pt–H–C Bonding†

Nicholas Carr,^a Laura Mole,^b A. Guy Orpen^a and John L. Spencer^{*,b}

^a Department of Inorganic Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

^b Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

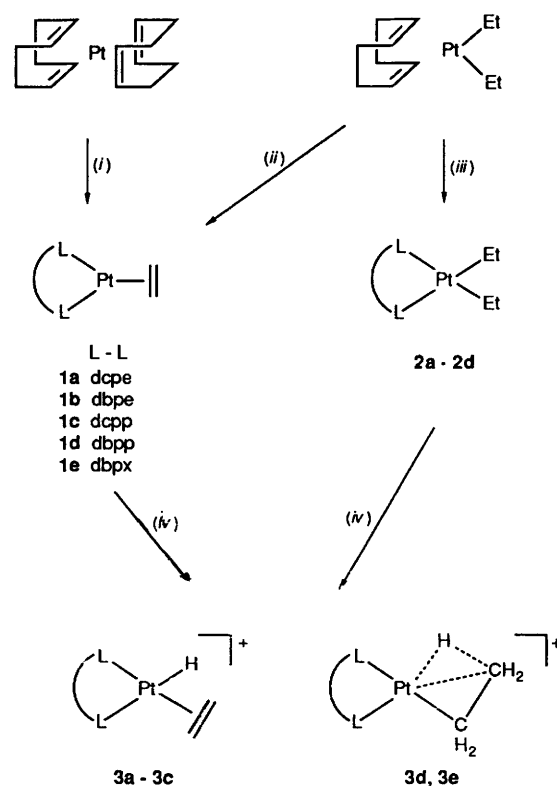
Protonation with non-co-ordinating acids of the complexes $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ [$\text{L-L} = (\text{H}_{11}\text{C}_6)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2$, **1a**, $\text{Bu}^t_2\text{P}(\text{CH}_2)_2\text{PBu}^t_2$, **1b**, $(\text{H}_{11}\text{C}_6)_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_{11})_2$, **1c**, $\text{Bu}^t_2\text{P}(\text{CH}_2)_3\text{PBu}^t_2$, **1d** or $o\text{-Bu}^t_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}^t_2$, **1e**] and $[\text{PtEt}_2(\text{L-L})]$ **2a–2d** affords a series of cationic platinum(II) complexes **3a–3e** which in the case of **3a–3c** adopt a *cis* ethene/hydride ground state whereas in **3d** and **3e** the otherwise electron-deficient metal centre is stabilized by a two-electron, three-centre agostic interaction with the β -CH bond of the ethyl ligand. Complexes **1–3** were characterized by ^1H , ^{13}C and ^{31}P NMR spectroscopy and for **2d** and **3d** by single-crystal X-ray crystallography. The influence of the chelating diphosphine ligand on the strength of the agostic bond was monitored by NMR spectroscopy. This revealed that the cations undergo two fluxional processes in solution: (a) agostic methyl rotation and (b) β -elimination/ethene rotation, a combination of which scrambles all five protons and both carbon atoms of the C_2H_5 moiety. The ^{31}P nuclei, however, remain inequivalent at temperatures up to 300 K. The agostic interaction was displaced by a small two-electron donor molecule L to form the series of adducts $[\text{PtEt}(\text{L})(\text{L-L})]^+$ (L = acetonitrile or pyridine) in which the 'normal' ethyl complex is the first formed species. The adducts are unstable to loss of C_2H_4 by β -elimination to form the series of cationic hydrides $[\text{PtH}(\text{L})(\text{L-L})]^+$. For comparison, the complex $[\text{PtH}(\text{O}_3\text{SCF}_3)\{\text{Bu}^t_2\text{P}(\text{CH}_2)_3\text{PBu}^t_2\}]$ was synthesised and characterized by ^1H and ^{31}P NMR spectroscopy and X-ray crystallography.

The pathway followed by the β -elimination/alkene insertion reaction can be modelled by complexes with three-centre, two-electron M–H–C $_{\beta}$ (β -agostic) interactions. Many complexes in which the agostic interaction is present in the ground state have been shown to exist and the area has recently been reviewed by Brookhart *et al.*¹ As part of our research into the factors which influence the position of the agostic alkyl *versus* the alkene/hydride equilibrium we have previously shown² that ancillary diphosphine ligands play a crucial role. In the series of complexes $[\text{Pt}(\text{C}_7\text{H}_{11})(\text{L-L})]^+$ (C_7H_{11} = norbornyl, L–L = chelating diphosphine) the diphosphine ligands with the more bulky substituents (Bu^t against cyclohexyl) and large chelate ring size result in weaker Pt–H–C agostic interactions. In all cases studied however the agostic isomer was always preferred over the alkene/hydride form.

We now report a series of platinum-diphosphine complexes of the general type $[\text{PtEt}(\text{L-L})]^+$ in which the preferred geometry of the complex is under the control of the associated diphosphine ligands. A preliminary report of this work has been published.³

Results and Discussion

The complexes $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ [$\text{L-L} = (\text{H}_{11}\text{C}_6)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2$ (dcpe) **1a**, $\text{Bu}^t_2\text{P}(\text{CH}_2)_2\text{PBu}^t_2$ (dbpe) **1b**, $(\text{H}_{11}\text{C}_6)_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_{11})_2$ (dcp) **1c**, $\text{Bu}^t_2\text{P}(\text{CH}_2)_3\text{PBu}^t_2$ (dbpp) **1d** or $o\text{-Bu}^t_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PBu}^t_2$ (dbpx) **1e**], prepared by the reaction of $[\text{Pt}(\text{cod})_2]$ (cod = cycloocta-1,5-diene) with diphosphines in the presence of C_2H_4 in hexane (Scheme 1), have been characterized by microanalysis and NMR (^1H , ^{13}C and ^{31}P) spectroscopy (Tables 1 and 2, and Experimental section). Compounds **1a** and **1c** have been prepared previously by a different method⁴ but no NMR data were published. The ethene protons of the compounds give rise to signals in the ^1H NMR spectra at δ 1.45–2.20 with $J(\text{PtH})$ of about 57 Hz; the



Scheme 1 (i) Diphosphine, 1 atm C_2H_4 (101 325 Pa), hexane, 273 K; (ii) dbpx, toluene, 373 K; (iii) diphosphine, diethyl ether at 293 K (**2a**, **2c**) or toluene at 363 K (**2b**, **2d**); (iv) HX, diethyl ether, 273 K

$^{13}\text{C}\{-^1\text{H}\}$ spectra show a characteristic signal for the carbons of the co-ordinated ethene at δ ca. 25, with coupling to ^{195}Pt [$J(\text{PtC})$ ca. 225 Hz]. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra all show a single resonance with coupling to ^{195}Pt of 3100–3550 Hz. As a

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

means of obtaining maximum information from NMR spectra, the synthesis of the doubly labelled [^{13}C]ethene analogue of **1b**

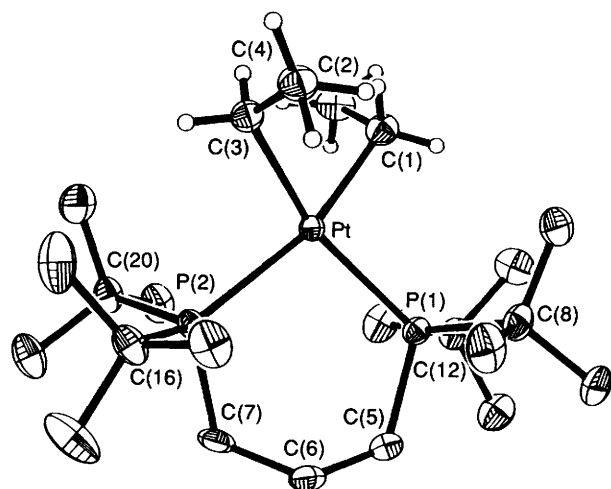


Fig. 1 Molecular structure of $[\text{PtEt}_2(\text{dbpp})]$ **2d**; all the dbpp hydrogen atoms have been omitted for clarity

Table 1 Analytical data^a and yields for the compounds $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ **1**, $[\text{PtEt}_2(\text{L-L})]$ **2**, $[\text{PtH}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]\text{BF}_4$ **3a–3c** and $[\text{PtEt}(\text{L-L})]\text{BF}_4$ **3d** and **3e**

| Complex | L-L | Analysis (%) | | Yield (%) |
|-----------------------|------|--------------|------------|-----------|
| | | C | H | |
| 1b | dbpe | 43.9 (44.4) | 8.1 (8.2) | 79 |
| 1d | dbpp | 45.3 (45.4) | 8.3 (8.35) | 82 |
| 1e | dbpx | 50.5 (50.6) | 7.9 (7.8) | 89 |
| 2a | dcpe | 53.3 (53.2) | 8.7 (8.6) | 96 |
| 2b | dbpe | 46.2 (46.2) | 8.7 (8.8) | 69 |
| 2c | dcpp | 53.9 (54.0) | 8.7 (8.8) | 69 |
| 2d | dbpp | 46.9 (47.2) | 9.0 (9.0) | 85 |
| 3a | dcpe | <i>b</i> | | 85 |
| 3b^c | dbpe | 36.3 (35.3) | 6.9 (6.7) | 87 |
| 3c | dcpp | <i>b</i> | | 85 |
| 3d | dbpp | 38.8 (39.2) | 7.4 (7.4) | 80 |
| 3e^d | dbpx | 43.8 (43.3) | 5.3 (5.4) | 80 |

^a Calculated figures in parentheses. ^b No accurate analyses were obtained because the salts are temperature sensitive. ^c As a CH_2Cl_2 solvate. ^d Analysis obtained for the $\text{CPh}(\text{CF}_3\text{SO}_2)_2^-$ salt.

was undertaken. The carbon atoms of the C_2H_4 ligand resonate in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum at the same chemical shift as for **1b** but the second-order AA'XX' spin system is apparent from which $^1J(\text{CC})$ 36 Hz is obtained. This value is substantially reduced from the value for unco-ordinated ethene (67 Hz)⁵ but is consistent with an η^2 -bound ethene complex.⁶ The proton-coupled ^{13}C NMR spectrum gives a value of $^1J(\text{CH})$ of 130 Hz.

The complexes $[\text{PtEt}_2(\text{L-L})]$ ($\text{L-L} = \text{dcpe}$ **2a**, **dbpe** **2b**, **dcpp** **2c** or **dbpp** **2d**), prepared by treatment of $[\text{Pt}(\text{cod})\text{Et}_2]$ with diphosphines in Et_2O or toluene, have been characterized by NMR (^1H , ^{13}C and ^{31}P), microanalysis (see Table 1 and Experimental section) and in the case of **2d** by an X-ray crystallographic study. It was noteworthy that the attempted synthesis by this method of the analogous platinum diethyl complex with dbpx resulted in the isolation of $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{dbpx})]$, formed presumably by β -elimination and subsequent reductive elimination of C_2H_6 from the intermediate $[\text{PtEt}_2(\text{dbpx})]$. The NMR spectra of the compounds **2a–2d** are consistent with their formulation as platinum(II) diethyl complexes (Table 3).

Protonation of the complexes $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ **1a–1e** and $[\text{PtEt}_2(\text{L-L})]$ **2a–2d** with $\text{HBF}_4\cdot\text{OEt}_2$ in diethyl ether at 273 K affords the off-white microcrystalline complexes **3a–3e** in 80–90% yield. The complexes **3d** and **3e** were also prepared as the PF_6^- , CF_3SO_3^- , $\text{CPh}(\text{CF}_3\text{SO}_2)_2^-$ and $\text{CB}_{11}\text{H}_{12}^-$ salts by protonation in the same way using the acids HPF_6 , $\text{CF}_3\text{SO}_3\text{H}$, $\text{CPh}(\text{CF}_3\text{SO}_2)_2$ and $\text{HCB}_{11}\text{H}_{12}$ respectively. The complex $[\text{PtH}(\text{O}_3\text{SCF}_3)(\text{dbpp})]$ **4**, which was isolated by treatment of **2d** with triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) in the absence of ethene, is readily converted into **3d** by treatment with ethene.

Variable-temperature NMR studies (see Tables 4–6) on the complexes **3b–3e** (**3a** is unstable above 240 K) show that at temperatures above 240 K facile scrambling within the C_2H_5 moiety results in the equivalence of all five protons and both carbon atoms (but not the phosphorus atoms) such that sharp averaged signals are observed in the ^1H and ^{13}C NMR spectra. For example, the ^{13}C NMR spectrum of **3e** at 298 K shows a single resonance at δ 16.5 coupled to only one phosphorus nucleus but five hydrogen nuclei [$J(\text{PC})$ 18, $J(\text{CH})$ 67 Hz]. These observations are consistent with rapid intramolecular processes involving both the alkyl isomer in which methyl rotation is rapid and the ethene hydride form for which ethene rotation is rapid. However, the observation that the phosphorus environments always remain distinct in the NMR spectra implies that either methyl-group rotation occurs in place *via* a double agostic bond thus maintaining the integrity of the quasi-square-planar geometry, or that no pivoting of the ethyl

Table 2 Selected room-temperature NMR data^a (^{31}P , ^1H and ^{13}C) for the complexes $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ **1a–1e**

| Complex | δP^b | $J(\text{PtP})$ | δH^c | $J(\text{PH})$ | $J(\text{PtH})$ | $\delta\text{C}^{c,d}$ | $J(\text{PC})$ | $J(\text{PtC})$ |
|-----------|--------------------|-----------------|--------------------|----------------|-----------------|------------------------|----------------|-----------------|
| 1a | 70.4 | 3135 | 1.45 | 2 | 58 | 21.9 | 31 | 231 |
| 1b | 101.6 | 3233 | 1.66 | 2 | 58 | 23.9 | 31 | 230 |
| 1c | 24.3 | 3256 | <i>e</i> | | | 23.6 | 27 | 220 |
| 1d | 47.2 | 3348 | 2.20 ^f | 2 | 56 | 26.6 | 27 | 219 |
| 1e | 49.6 | 3551 | 2.18 | 2 | 57 | 27.2 | 28 | 217 |

^a All data in CD_2Cl_2 unless otherwise stated. Chemical shifts in ppm, coupling constants in Hz. ^b Proton decoupled, chemical shifts are relative to $\text{P}(\text{OPh})_3$ (δ 126.5). ^c Refers to the protons and carbon atoms of the C_2H_4 ligand. ^d Proton decoupled, chemical shifts are positive to high frequency of SiMe_4 (δ 0.0). ^e Obscured by diphosphine signals. ^f Measured in C_6D_6 .

Table 3 Selected NMR data^a (^{31}P , ^1H and ^{13}C) recorded at 298 K for the complexes $[\text{PtEt}_2(\text{L-L})]$ **2a–2d**. All measurements in C_6D_6

| Complex | δP^b | $J(\text{PtP})$ | δH^c | $J(\text{PtH})$ | δC_α | $J(\text{C}_\alpha\text{P}_i)$ | $J(\text{C}_\alpha\text{P}_e)$ | $J(\text{PtC}_\alpha)$ | δC_β | $J(\text{PtC}_\beta)$ |
|-----------|--------------------|-----------------|--------------------|-----------------|-------------------------|--------------------------------|--------------------------------|------------------------|------------------------|-----------------------|
| 2a | 58.1 | 1641 | 1.95 | 72 | 10.9 | <i>d</i> | <i>d</i> | <i>d</i> | 16.9 | <i>d</i> |
| 2b | 74.1 | 1575 | 1.84 | 70 | 7.6 | 100 | 9 | 674 | 16.7 | 21 |
| 2c | 4.5 | 1700 | <i>e</i> | — | 11.0 | 98 | 11 | <i>d</i> | 16.8 | 23 |
| 2d | 18.3 | 1634 | 1.45 | 72 | 11.1 | 97 | 10 | 692 | 17.2 | 23 |

^a Chemical shifts in ppm, coupling constants in Hz. ^b Proton decoupled, chemical shifts are relative to $\text{P}(\text{OPh})_3$ (δ 126.5). ^c For the H_α protons on the ethyl moiety only. ^d Not observed. ^e Obscured by diphosphine signals.

Table 4 Selected NMR (^1H , ^{13}C and ^{31}P) data^a for complexes **3b–3e**

| Complex | δP^{1b} | $J(\text{PtP}^1)$ | δP^2 | $J(\text{PtP}^2)$ | δH^c | $J(\text{PH})$ | $J(\text{PtH})$ | δC^d | $J(\text{PC})$ | $J(\text{PtC})$ | $J(\text{CH})$ |
|-----------|-----------------------|-------------------|--------------------|-------------------|--------------------|----------------|-----------------|--------------------|----------------|-----------------|----------------|
| 3b | 104.8 | 2965 | 90.6 | 2980 | 1.70 | 22 | 63 | 47.8 | 13 | 54 | |
| 3c | 18.4 | 2833 | 12.8 | 3318 | ^e | | | 46.5 | 15 | 68 | 65 |
| 3d | 38.1 | 2707 | 48.4 | 4919 | 0.77 | 13 | 65 | 15.9 | 18 | 91 | 67 |
| 3e | 38.0 | 2800 | 53.2 | 5220 | 0.74 | 12 | ^f | 16.5 | 18 | 91 | 67 |

^a Chemical shifts in ppm, coupling constants in Hz. Recorded at ambient temperature in CD_2Cl_2 . No data available for complex **3a** which is unstable above -40°C . ^b Proton decoupled, chemical shifts are relative to $\text{P}(\text{OPh})_3$ (δ 126.5); P^1 is that phosphorus *cis* to the hydridic hydrogen, P^2 that *trans*. ^c Refers to the five protons of the ethyl moiety. ^d Proton decoupled; chemical shifts are positive to high frequency of SiMe_4 (δ 0.0). Refers to the two carbon atoms of the ethyl moiety. ^e Obscured by the diphosphine signals. ^f Not observed.

Table 5 Selected ^1H and ^{31}P NMR data^a for complexes **3a–3e** recorded in CD_2Cl_2 at the temperature shown

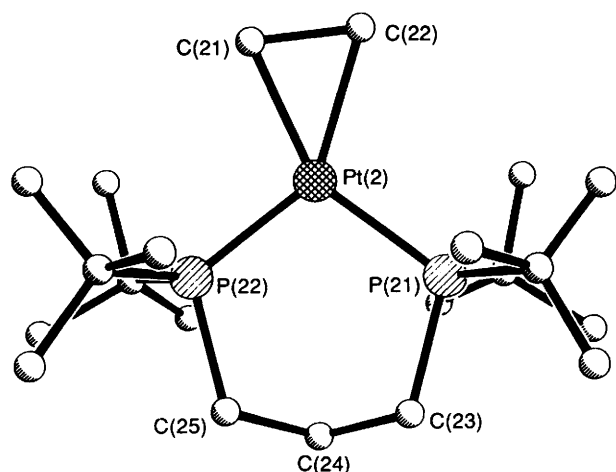
| Complex | T/K | δP^{1b} | $J(\text{PtP}^1)$ | δP^2 | $J(\text{PtP}^2)$ | δH^c | $J(\text{PH})$ | $J(\text{PtH})$ |
|-----------|--------------|-----------------------|-------------------|--------------------|-------------------|--------------------|----------------|-----------------|
| 3a | 193 | 81.6 | 2976 | 69.9 | 2076 | −3.2 | 115 | 690 |
| 3b | 186 | 106.3 | 2971 | 91.5 | 2645 | −4.6 | 109 | 508 |
| 3c | 180 | 13.8 | 2925 | 6.7 | 2988 | −4.2 | 94 | 423 |
| 3d | 186 | 36.8 | 2680 | 47.4 | 4923 | −2.6 ^d | ^e | |
| 3e | 203 | 34.5 | 2778 | 50.0 | 5123 | −2.8 | ^e | |

^a Chemical shifts in ppm, coupling constants in Hz. ^b Proton decoupled, chemical shifts are relative to $\text{P}(\text{OPh})_3$ (δ 126.5); P^1 is that phosphorus *cis* to the hydridic hydrogen; P^2 that *trans*. ^c Refers to the hydridic hydrogen or agostic hydrogen. ^d Recorded at 163 K in CD_2Cl_2 – $[\text{C}_4\text{H}_8]$ tetrahydrofuran. ^e Not observed.

Table 6 Low-temperature ^{13}C NMR data^a for the complexes $[\text{PtH}(\text{C}_2\text{H}_5)_2(\text{dbpe})]$ **3b**, $[\text{Pt}(\text{C}_2\text{H}_5)_2(\text{dbpp})]$ **3d** and $[\text{Pt}(\text{C}_2\text{H}_5)_2(\text{dbpx})]$ **3e**

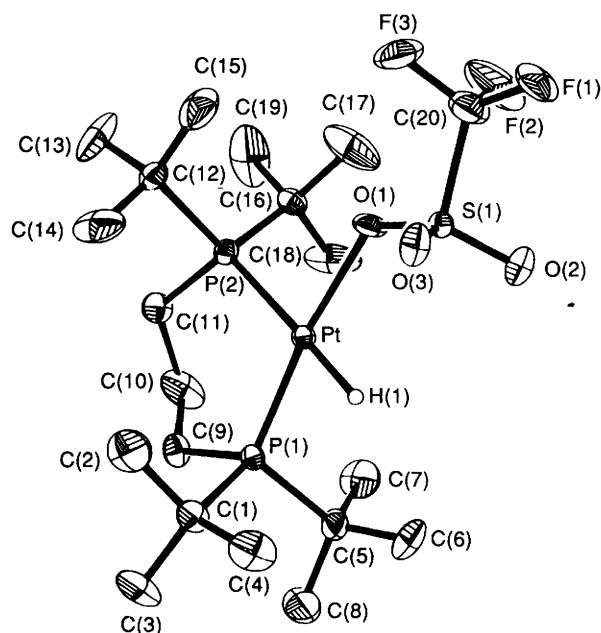
| Complex | T/K | δC_α | $J(\text{C}_\alpha\text{H})$ | $J(\text{C}_\alpha\text{C}_\beta)$ | $J(\text{PC}_\alpha)$ | $J(\text{PtC}_\alpha)$ | δC_β | $J(\text{C}_\beta\text{H}_{\text{agg}})$ | $J(\text{C}_\beta\text{H}_i)$ |
|-----------|--------------|-------------------------|------------------------------|------------------------------------|-----------------------|------------------------|------------------------|--|-------------------------------|
| 3b | 180 | 51.0 ^b | 160 | | | | | | |
| 3d | 145 | 22.0 | 158 | 26 | 41 | 200 | 8.2 | 60 | 153 |
| 3e | 145 | 22.0 | 155 | 29 | 39 | 218 | 9.0 | 75 | 155 |

^a In ppm with coupling constants in Hz; chemical shifts are positive to high frequency of SiMe_4 (δ 0.0). ^b One signal for both carbon nuclei.

**Fig. 2** Molecular structure of the major orientation of one of the two unique cations of $[\text{PtEt}(\text{dbpp})][\text{CB}_{11}\text{H}_{12}]$ **3d**. All hydrogen atoms of the dbpp have been omitted for clarity

group in a 14-electron species *via* a 'Y'-shaped intermediate occurs within the temperature range at which NMR spectra were recorded. The latter is contrary to the calculations of Thorn and Hoffmann⁷ in which a low activation energy was assigned to this process. However, the ^{31}P NMR spectrum of **3e** at 298 K shows that the signals are broad which may imply that the ethyl group pivoting is becoming rapid at this temperature.

Parameters derived from the limiting ^{13}C NMR spectra (at 145 K), in particular $^1J(\text{CH})$, show that for complexes **3d** and **3e** the evidence is consistent with the presence of ethyl ligands bound to platinum through both σ -alkyl and β -agostic C–H–Pt bonds. For example, in **3e**, C_α resonates at δ 22.0 as a triplet [$^1J(\text{CH})$ 155 Hz] whereas C_β at δ 9.0 has a triplet of doublets structure [$^1J(\text{CH})$ 155 and 75 Hz].

**Fig. 3** Molecular structure of $[\text{PtH}(\text{O}_3\text{SCF}_3)_3(\text{dbpp})]$ **4**

The NMR evidence was borne out by a low-temperature X-ray crystallographic study on the $\text{CB}_{11}\text{H}_{12}^-$ salt of **3d**, $[\text{PtEt}(\text{dbpp})][\text{CB}_{11}\text{H}_{12}]$; for comparison the structures of its diethyl precursor **2d** and the hydride complex $[\text{PtH}(\text{O}_3\text{SCF}_3)_3(\text{dbpp})]$ **4** were also determined. Selected bond lengths and angles for the three structures are given in Table 7, the molecular geometries are shown in Figs. 1, 2 and 3, and the crystallographic data are summarized in Table 8. In all three structures the molecular species present are well separated, without strong intermolecular interactions. For **3d** there are

Table 7 Selected bond lengths (Å) and angles (°) for [PtEt₂(dbpp)] **2d**, [PtEt(dbpp)] [CB₁₁H₁₂] **3d** and [PtH(O₃SCF₃)(dbpp)] **4**Compound **2d**

| | | | |
|-------------|-----------|-------------|-----------|
| Pt–P(1) | 2.329(2) | Pt–P(2) | 2.320(2) |
| Pt–C(1) | 2.103(10) | Pt–C(3) | 2.113(9) |
| P(1)–C(5) | 1.849(9) | P(1)–C(8) | 1.901(8) |
| P(1)–C(12) | 1.910(8) | P(2)–C(7) | 1.868(9) |
| P(2)–C(16) | 1.912(8) | P(2)–C(20) | 1.897(8) |
| C(1)–C(2) | 1.502(13) | C(5)–C(6) | 1.463(27) |
| C(3)–C(4) | 1.494(12) | C(6)–C(7) | 1.447(30) |
| C(5)–C(6) | 1.523(16) | C(8)–C(10) | 1.518(12) |
| C(6)–C(7) | 1.549(16) | C(12)–C(13) | 1.534(12) |
| C(8)–C(9) | 1.520(12) | C(12)–C(15) | 1.532(12) |
| C(8)–C(11) | 1.527(11) | C(16)–C(18) | 1.541(13) |
| C(12)–C(14) | 1.514(11) | C(20)–C(21) | 1.547(11) |
| C(16)–C(17) | 1.520(11) | C(20)–C(23) | 0.546(11) |
| C(16)–C(19) | 1.503(12) | | |
| C(20)–C(22) | 1.509(12) | | |

| | | | |
|-----------------|----------|------------------|----------|
| P(2)–Pt–P(1) | 97.9(1) | C(1)–Pt–P(1) | 93.0(3) |
| C(1)–Pt–P(2) | 160.0(2) | C(3)–Pt–P(1) | 159.5(2) |
| C(3)–Pt–P(2) | 94.0(3) | C(3)–Pt–C(1) | 80.9(4) |
| C(5)–P(1)–Pt | 116.6(3) | C(8)–P(1)–Pt | 106.7(3) |
| C(8)–P(1)–C(5) | 101.3(4) | C(12)–P(1)–Pt | 121.6(3) |
| C(12)–P(1)–C(5) | 98.7(4) | C(12)–P(1)–C(8) | 110.1(4) |
| C(7)–P(2)–Pt | 114.8(3) | C(16)–P(2)–Pt | 121.9(3) |
| C(16)–P(2)–C(7) | 100.2(4) | C(20)–P(2)–Pt | 106.8(3) |
| C(20)–P(2)–C(7) | 101.2(4) | C(20)–P(2)–C(16) | 110.2(4) |
| C(2)–C(1)–Pt | 110.0(7) | C(4)–C(3)–Pt | 110.6(6) |

Compound **3d**

| | | | |
|---------------|-----------|---------------|-----------|
| Pt(1)–P(11) | 2.295(4) | Pt(1)–P(12) | 2.274(4) |
| Pt(1)–C(11) | 2.068(25) | Pt(1)–C(12) | 2.257(19) |
| Pt(2)–P(21) | 2.257(6) | Pt(2)–P(22) | 2.194(6) |
| Pt(2)–C(21) | 2.092(25) | Pt(2)–C(22) | 2.282(21) |
| P(11)–C(13) | 1.811(14) | P(11)–C(16) | 1.904(19) |
| P(11)–C(110) | 1.897(16) | P(12)–C(15) | 1.813(15) |
| P(12)–C(114) | 1.824(20) | P(12)–C(118) | 1.898(21) |
| P(21)–C(23) | 1.953(18) | P(21)–C(26) | 1.925(18) |
| P(21)–C(210) | 1.859(20) | P(22)–C(25) | 1.933(16) |
| P(22)–C(214) | 1.855(21) | P(22)–C(218) | 1.871(20) |
| C(11)–C(12) | 1.469(43) | C(13)–C(14) | 1.524(20) |
| C(14)–C(15) | 1.511(20) | C(16)–C(17) | 1.552(34) |
| C(16)–C(18) | 1.580(27) | C(16)–C(19) | 1.521(34) |
| C(110)–C(111) | 1.436(25) | C(110)–C(112) | 1.515(29) |
| C(110)–C(113) | 1.545(24) | C(114)–C(115) | 1.584(26) |
| C(114)–C(116) | 1.596(28) | C(114)–C(117) | 1.587(26) |
| C(118)–C(119) | 1.548(30) | C(118)–C(120) | 1.539(29) |
| C(118)–C(121) | 1.473(26) | C(21)–C(22) | 1.563(36) |
| C(23)–C(24) | 1.538(21) | C(24)–C(25) | 1.510(21) |
| C(26)–C(27) | 1.429(26) | C(26)–C(28) | 1.449(31) |
| C(26)–C(29) | 1.522(24) | C(210)–C(211) | 1.573(28) |
| C(210)–C(212) | 1.516(30) | C(210)–C(213) | 1.547(27) |
| C(214)–C(217) | 1.565(27) | C(214)–C(216) | 1.536(29) |
| C(214)–C(217) | 1.591(36) | C(218)–C(219) | 1.532(26) |
| C(218)–C(220) | 1.514(25) | C(218)–C(221) | 1.581(33) |

| | | | |
|---------------------|----------|---------------------|----------|
| P(11)–Pt(1)–P(12) | 100.4(2) | P(11)–Pt(1)–C(11) | 156.4(7) |
| P(12)–Pt(1)–C(11) | 102.7(7) | P(11)–Pt(1)–C(12) | 117.3(9) |
| P(12)–Pt(1)–C(12) | 142.1(9) | C(11)–Pt(1)–C(12) | 39.4(12) |
| P(21)–Pt(2)–P(22) | 104.8(2) | P(21)–Pt(2)–C(21) | 151.3(7) |
| P(22)–Pt(2)–C(21) | 103.7(7) | P(21)–Pt(2)–C(22) | 109.7(6) |
| P(22)–Pt(2)–C(22) | 144.9(6) | C(21)–Pt(2)–C(22) | 41.6(9) |
| Pt(1)–P(11)–C(13) | 113.8(5) | Pt(1)–P(11)–C(16) | 109.4(7) |
| C(13)–P(11)–C(16) | 102.1(9) | Pt(1)–P(11)–C(110) | 113.9(6) |
| C(13)–P(11)–C(110) | 105.1(7) | C(16)–P(11)–C(110) | 111.9(8) |
| Pt(1)–P(12)–C(15) | 114.3(5) | P(1)–P(12)–C(114) | 110.2(7) |
| C(15)–P(12)–C(114) | 103.5(8) | Pt(1)–P(12)–C(118) | 112.1(7) |
| C(15)–P(12)–C(118) | 107.7(8) | C(114)–P(12)–C(118) | 108.6(9) |
| C(15)–P(21)–C(23) | 112.2(5) | Pt(2)–P(21)–C(26) | 113.3(6) |
| C(23)–P(21)–C(26) | 99.4(8) | Pt(2)–P(21)–C(210) | 116.3(7) |
| C(23)–P(21)–C(210) | 100.3(9) | C(26)–P(21)–C(210) | 113.2(9) |
| Pt(2)–P(22)–C(214) | 117.0(8) | Pt(2)–P(22)–C(25) | 114.2(5) |
| Pt(2)–P(22)–C(218) | 114.1(7) | C(25)–P(22)–C(214) | 99.7(10) |
| C(214)–P(22)–C(218) | 111.4(9) | C(25)–P(22)–C(218) | 97.9(9) |
| Pt(1)–C(12)–C(11) | 63.3(12) | Pt(1)–C(11)–C(12) | 77.2(14) |
| Pt(2)–C(22)–C(21) | 62.7(12) | Pt(2)–C(21)–C(22) | 75.7(13) |

Table 7 (continued)Compound **4**

| | | | |
|-------------|-----------|-------------|-----------|
| Pt–P(1) | 2.201(3) | Pt–P(2) | 2.374(3) |
| Pt–O(1) | 2.181(9) | Pt–H(1) | 1.64(10) |
| P(1)–C(1) | 1.881(13) | P(1)–C(5) | 1.908(13) |
| P(1)–C(9) | 1.826(13) | P(2)–C(11) | 1.852(14) |
| P(2)–C(12) | 1.900(12) | P(2)–C(16) | 1.904(13) |
| S–O(1) | 1.461(11) | S–O(2) | 1.409(8) |
| S–O(3) | 1.418(11) | S–C(20) | 1.788(17) |
| F(1)–C(20) | 1.329(23) | F(2)–C(20) | 1.311(24) |
| F(3)–C(20) | 1.333(24) | C(1)–C(2) | 1.530(20) |
| C(1)–C(3) | 1.512(18) | C(1)–C(4) | 1.539(21) |
| C(5)–C(6) | 1.505(26) | C(5)–C(7) | 1.508(25) |
| C(5)–C(8) | 1.528(22) | C(9)–C(10) | 1.448(20) |
| C(10)–C(11) | 1.531(23) | C(12)–C(13) | 1.525(23) |
| C(12)–C(14) | 1.495(22) | C(12)–C(15) | 1.468(22) |
| C(16)–C(17) | 1.490(28) | C(16)–C(18) | 1.443(27) |
| C(16)–C(19) | 1.509(27) | | |

| | | | |
|------------------|-----------|------------------|----------|
| P(1)–Pt–P(2) | 101.3(1) | P(1)–Pt–O(1) | 170.2(3) |
| P(2)–Pt–O(1) | 88.5(3) | P(1)–Pt–H(1) | 80.8(36) |
| P(2)–Pt–H(1) | 174.3(40) | O(1)–Pt–H(1) | 89.5(36) |
| Pt–P(1)–C(1) | 112.1(4) | Pt–P(1)–C(5) | 112.5(4) |
| C(1)–P(1)–C(5) | 110.5(6) | Pt–P(1)–C(9) | 114.6(4) |
| C(1)–P(1)–C(9) | 102.3(6) | C(5)–P(1)–C(9) | 104.1(7) |
| Pt–P(2)–C(11) | 112.1(4) | Pt–Pt(2)–C(12) | 112.2(4) |
| C(11)–P(2)–C(12) | 102.8(6) | Pt–P(2)–C(16) | 112.6(4) |
| C(11)–P(2)–C(16) | 104.0(6) | C(12)–P(2)–C(16) | 112.5(6) |

two independent cations in the crystal structure, which have similar geometries. The discussion below and the illustration in Fig. 2 refer to the major orientation of the better ordered of the two, that centred on Pt(2). The disorder present unfortunately limits the detail of the molecular geometry that may reliably be extracted for **3d**. In all three complexes the platinum is chelated by the dbpp ligand in the expected way. In **2d** the co-ordination of platinum is completed by two σ -ethyl ligands, in **3d** the platinum is bonded to just one ethyl ligand and does not interact with the anions (also disordered) which show the expected icosahedral shape. In **4** the platinum co-ordination is completed by a hydride ligand and an O-bonded trifluoromethanesulfonate ligand.

The solid-state structures of the cations of **3d**, although disordered, are similar to one another and consistent with the NMR spectra recorded at 145 K, in having the ethyl moiety bound asymmetrically to the platinum centre. The ethyl ligand bonds through a conventional σ -alkyl bond [Pt(2)–C(21) 2.09(3) Å] similar to those in the non-agostic ethyl ligands of **2d** [Pt–C 2.103(10), 2.113(9) Å], and a β -agostic interaction with the C–H bond of C _{β} [Pt(2)–C(22) 2.28(3) Å], although none of the ethyl hydrogen atoms could be located. The ethyl geometry is therefore similar to that observed in the agostic norbornyl complex ² [Pt(C₇H₁₁)(dbpe)]BPh₄ **5** [Pt–C _{α} 2.096(4) and Pt–C _{β} 2.309(5)]. The Pt–C _{α} –C _{β} angle in **3d** [75.7(13)°] is of course greatly reduced as compared with those of the non-agostic ethyls in **2d** [110.0(7), 110.6(6)°] but rather close to that [78.3(2)°] in **5**. While the C _{α} –C _{β} bond length in **3d** [1.56(4) Å] is poorly determined those of **2d** [1.494(12), 1.502(13) Å] provide a measure of the (librationally shortened) C–C distance prior to the distortions induced by the agostic interaction. The effect of such an interaction [as in **5**, C _{α} –C _{β} 1.480(6) Å] is typically to reduce the C–C bond length towards that expected for an η^2 -bonded alkene. The hydride complex **4** provides a measure of the Pt–H interaction that is the logical extension of the agostic distortion of an ethyl (*i.e.* the completion of the partial β -elimination reaction that the agostic interaction represents). Thus the Pt–H distance in **4** [1.64(10) Å] may be compared to the Pt–H(C _{β}) distance in **5** [1.90(7) Å] and those in the non-agostic case of **2d** (> 3.06 Å).

These structures also provide information on the co-

Table 8 Crystallographic data* for complexes **2d**, **3d** and **4**

| | 2d | 3d | 4 |
|--|---|---|--|
| Empirical formula | C ₂₃ H ₅₂ P ₂ Pt | C ₂₂ H ₅₉ B ₁₁ P ₂ Pt | C ₂₀ H ₄₃ F ₃ O ₃ P ₂ PtS |
| <i>M</i> | 585.7 | 699.7 | 677.7 |
| Crystal System | Monoclinic | Monoclinic | Orthorhombic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> 2 ₁ / <i>c</i> (no. 14) | <i>Pna</i> 2 ₁ (no. 33) |
| <i>a</i> /Å | 11.661(3) | 17.715(3) | 23.383(7) |
| <i>b</i> /Å | 15.394(3) | 22.576(4) | 8.663(1) |
| <i>c</i> /Å | 14.915(2) | 16.466(3) | 13.987(3) |
| β/° | 99.44(2) | 90.046(13) | 90 |
| <i>Z</i> (molecules per cell) | 4 | 8 | 4 |
| <i>U</i> /Å ³ | 2641(1) | 6584(2) | 4503(2) |
| <i>T</i> /K | 295 | 190 | 190 |
| <i>D_c</i> /g cm ⁻³ | 1.47 | 1.41 | 1.61 |
| μ(Mo-Kα)/cm ⁻¹ | 54.6 | 44.1 | 52.2 |
| Approximate crystal size/mm | 0.5 × 0.5 × 0.6 | 0.50 × 0.30 × 0.25 | 0.6 × 0.5 × 0.3 |
| 2θ range/° | 4–50 | 4–50 | 4–55 |
| <i>F</i> (000) | 1192 | 2832 | 1352 |
| No. of data collected | 5123 | 12 495 | 3115 |
| No. of unique data | 4677 | 11 665 | 2671 |
| No. with <i>I</i> > <i>nσ</i> (<i>I</i>), <i>N_o</i> | 3373 | 6241 | 2113 |
| <i>n</i> | 3 | 2 | 3 |
| Minimum, maximum transmission coefficients | 0.128, 0.233 | 0.618, 0.922 | 0.267, 0.345 |
| No. of variables, <i>N_v</i> | 286 | 669 | 271 |
| <i>R</i> | 0.033 | 0.048 | 0.031 |
| <i>R'</i> | 0.040 | 0.056 | 0.040 |
| <i>S</i> | 1.28 | 1.47 | 1.25 |

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

ordination geometry of the platinum atom under the small variations present. In each case the co-ordination may be loosely described as square planar, although there are significant deviations from planarity and the ligand set is not square (*i.e.* there is no *C*₄ axis of symmetry). This geometry is to be expected for the formal oxidation state of platinum present in each of complexes **2d**, **3d** and **4**. There are however some notable distortions present. Thus in **2d** the planes of the PtP₂ and PtC₂ units are twisted by 26.4° relative to one another (*cf.* a similar twist of 5.4° between the PtP₂ and PtHO planes in **4**). The P–Pt–P angles for the dbpp ligand are *ca.* 100° as judged from these structures [97.9(1), 104.8(2) and 101.3(1)° for **2d**, **3d** and **4** respectively] rather larger than for the dbpe ligand in **5** and the platinum(0) norbornene species [Pt(η²-C₇H₁₀)(dbpe)] [89.3(1) and 89.2(1)° respectively]. This confirms the expectation that the increased chelate ring size in these dbpp species is associated with a larger P–Pt–P angle. The Pt–P bond lengths in **2d**, **3d** and **4** show considerable variation which can be correlated with the *trans* ligand. Thus the Pt–P length *trans* to the weak ligand O₃SCF₃ in **4** is the shorter [2.201(3)], while the longer [2.374(3) Å] is *trans* to the hydride. The σ-alkyl carbons induce a Pt–P distance *ca.* 2.3 Å [2.320(2) and 2.329(2) in **2d**, 2.257(6) in **3d**, *cf.* 2.311(1) in **5**]. The Pt–P distance *trans* to the agostic interaction in **3d** is short [2.194(6), *cf.* 2.256(1) in **5**].

The strong dependence of both Pt–P bond length and *J*(Pt–P) on the *trans* ligand is clear. However there is an imperfect correlation between *J*(Pt–P) and the bond length, and clearly account must be taken of other factors (*cis* ligand, oxidation state, orbital effects, *etc.*). Similar comments apply to the Pt–C couplings and bond lengths. Interestingly the magnitudes of Pt–C_β couplings show very poor correlation with Pt...C_β distances, presumably because the factors dictating the coupling are complicated; for instance it is possible to envisage internuclear spin interaction by several routes.

The evidence from the NMR data (Tables 4–6) shows that the ground-state structures of complexes **3a–3c** are very different to those of **3d** and **3e**. For example, the ¹³C NMR spectrum of **3b** at 180 K shows that the signal for the C₂ moiety is a triplet due to proton coupling with ¹*J*(CH) *ca.* 160 Hz as compared with ¹*J*(CH) 130 Hz for [Pt(η²-¹³C₂H₄)(dbpe)] and 157 Hz for unco-ordinated C₂H₄. Moreover, in the ¹H NMR spectra of

3a–3c recorded at between 180 and 193 K (Table 5) there is a high-field signal in each case, typical of a hydride. For example in **3b** the hydride resonates at δ –4.6 with coupling to the *trans*-phosphorus atom and the platinum centre (109 and 508 Hz respectively). The IR spectrum of **3b** shows ν(PtH) at 2085 cm⁻¹. These observations are consistent with a *cis*-ethene/hydride ground-state structure for complexes **3a–3c** and may be compared with the similar hydride complex [PtH(O₃SCF₃)(dbpp)] **4** (see Experimental section) for which the hydride resonates at δ –6.6 with coupling to both *cis* and *trans* phosphorus nuclei [*J*(PH) 13 and 182 Hz respectively] and ¹⁹⁵Pt [*J*(PtH) 779 Hz].

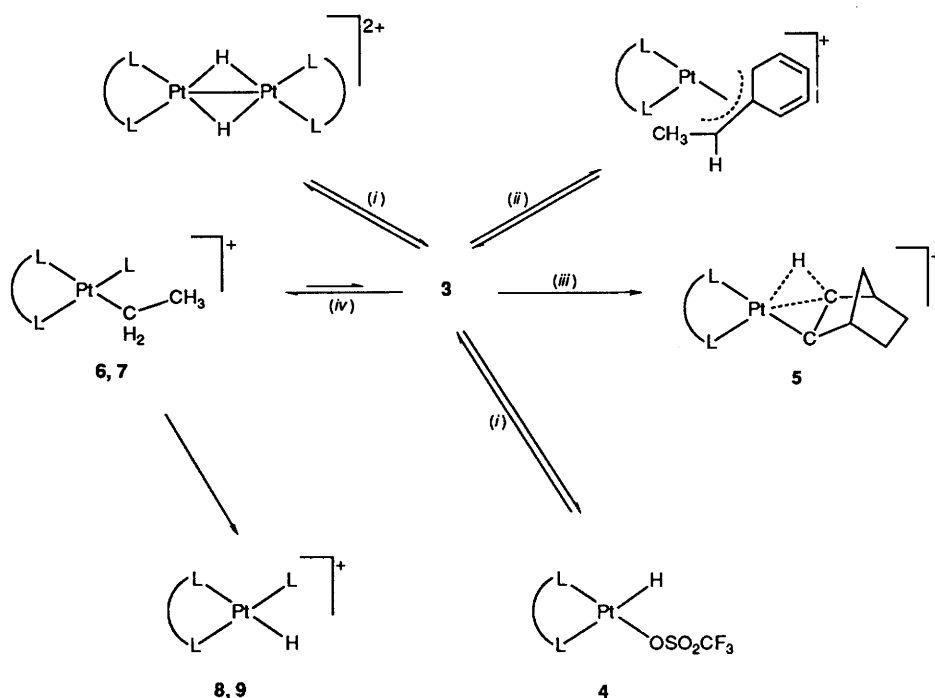
Furthermore, inspection of the variable-temperature ³¹P NMR data shows large differences in the values of ¹*J*(PtP) for the phosphorus nuclei *cis* and *trans* to the agostic bond in **3d** and **3e**, whereas for **3b** and **3c** at ambient temperatures the values for ¹*J*(PtP) are very similar to each other. The marked temperature dependence of ¹*J*(PtP) in **3b** and **3c** emphasizes the split in behaviour which occurs between **3b** and **3c** and the two agostic complexes **3d** and **3e**. Whereas both *cis*- and *trans*-¹*J*(PtP) for the latter vary little between the temperatures shown, the value of ¹*J*(PtP_{*trans*}) for **3b** and **3c** decreases sharply from 298 to 180 K whilst ¹*J*(PtP_{*cis*}) stays almost constant. One explanation of this behaviour is that at room temperature the values represent an average of contributions from each isomer in the equilibrium between agostic ethyl and ethene/hydride forms. At room temperature for **3a–3c** there may be present in solution significant concentrations of the agostic ethyl species which are in rapid equilibrium with the respective ethene/hydride isomers. As the temperature is lowered the thermodynamically preferred ethene/hydride complex dominates and is the only species present in observable concentration at the low-temperature limit.

For a series of cobalt complexes containing β-agostic interactions, Brookhart *et al.*⁸ considered the possibility that there might be a continuum of bonding involving progressive transfer of hydrogen from the metal to the β-carbon. However, in the platinum complexes reported here this appears not to be the case and the alkene/hydride and agostic forms apparently represent energy minima separated by a small barrier. The presence of such a barrier could indicate that the lowest-energy

Table 9 Selected ^1H , ^{13}C and ^{31}P NMR^a and IR data for the complexes $[\text{PtEt}(\text{L})(\text{L-L})]^+$ **6** ($\text{L} = \text{CD}_3\text{CN}$), **7** ($\text{L} = \text{C}_5\text{D}_5\text{N}$) and $[\text{PtH}(\text{L})(\text{L-L})]^+$ **8** ($\text{L} = \text{CD}_3\text{CN}$), **9** ($\text{L} = \text{C}_5\text{D}_5\text{N}$)

| Complex | L-L | δP^{1b} | $J(\text{PtP}^1)$ | δP^2 | $J(\text{PtP}^2)$ | δH^c | $J(\text{PtH})$ | $J(\text{P}^1\text{H})$ | $J(\text{P}^2\text{H})$ | δC_α^d | $J(\text{PtC}_\alpha)$ | $J(\text{PC}_\alpha)$ | $\nu(\text{PtH})^e$ |
|-----------------------|------|-----------------------|-------------------|--------------------|-------------------|--------------------|-----------------|-------------------------|-------------------------|---------------------------|------------------------|-----------------------|---------------------|
| 6b | dbpe | 87.7 | 1599 | 64.6 | 4415 | | | | | 6.8 | 453 | 81 | |
| 6d | dbpp | 27.6 | 1561 | 21.2 | 4447 | | | | | 6.8 | 438 | 76 | |
| 6e^f | dbpx | 23.6 | 1565 | 19.7 | 4578 | | | | | 8.3 | — | 66 | |
| 7b | dbpe | 79.1 | 1545 | 61.1 | 3839 | | | | | 9.5 | 490 | 83 | |
| 7d | dbpp | 20.3 | 1506 | 16.9 | 3933 | | | | | 8.1 | 477 | 79 | |
| 8b | dbpe | 91.5 | 1900 | 88.5 | 3945 | -4.23 | 915 | 180 | 21 | | | | |
| 8d | dbpp | 29.0 | 1898 | 42.5 | 3923 | -6.50 | 812 | 171 | 13 | | | | 2086 |
| 8e | dbpx | 28.1 | 2055 | 41.0 | 4103 | -7.74 | 756 | 173 | 16 | | | | 2128 |
| 9d | dbpp | 24.0 | 1833 | 37.6 | 3498 | -6.24 | 833 | 180 | 14 | | | | 2095 |
| 9e | dbpx | 26.3 | 2003 | 38.0 | 3670 | -7.50 | 815 | 177 | 15 | | | | 2119 |

^a Chemical shifts in ppm, coupling constants in Hz, measurements at ambient temperature unless otherwise stated. ^b ^1H decoupled, chemical shifts are relative to $\text{P}(\text{OPh})_3$ (δ 126.5 ppm). ^c Refers to the hydridic proton only. ^d ^1H decoupled; chemical shifts are positive to high frequency of SiMe_4 (δ 0.0 ppm). Refers to the C_α of the ethyl ligand. ^e Measured in CH_2Cl_2 . ^f Measured at 215 K.

**Scheme 2** (i) C_2H_4 ; (ii) styrene; (iii) norbornene; (iv) $\text{L} = \text{CD}_3\text{CN}$ or $\text{C}_5\text{D}_5\text{N}$

ethene/hydride structure might be one in which the alkene lies perpendicular to the co-ordination plane of the complex as is observed in Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$. Unfortunately the NMR data recorded at the lowest accessible temperatures indicate that the alkene is still rotating rapidly and it is not therefore possible to distinguish between in-plane and perpendicular co-ordination of the alkene.

Considerable progress has already been made in assessing the influence of the chelating diphosphine ligands on the nature of the bonding in the complexes $[\text{Pt}(\text{C}_7\text{H}_{11})(\text{L-L})]^+$,² for which it was clear that the agostic isomer was preferred for all the diphosphines used. In this series of diphosphine ethylplatinum(II) cations changes in the ancillary diphosphine ligands control the balance between the agostic ethyl and the ethene/hydride isomer. The control and understanding of this balance may prove critical in the chemistry of alkene polymerization and oligomerization reactions.

It is implicit in the results of our investigations that the smaller of the diphosphines favour the ethene/hydride isomer whilst the larger prefer the adoption of an agostic ethyl

structure. The calculation of reaction pathways by molecular orbital theory has shown that⁷ during the course of migration of a hydride to a co-ordinated ethene in a model complex $[\text{PtH}(\eta^2\text{-C}_2\text{H}_4)(\text{PH}_3)_2]^+$ the optimum ancillary ligands angle rises from 95° to 110° at the 'transition state' which would resemble a β -agostic species. Our results are consistent with this picture and demonstrate the crucial control which is exerted by the ancillary ligands on the degree of interaction between metal and the $\beta\text{-C-H}$ agostic bond.

The series of cationic platinum(II) complexes **3a–3d** are unstable in dichloromethane solution with respect to loss of ethene to form the dinuclear cations $[\text{Pt}_2(\mu\text{-H})_2(\text{L-L})_2]^{2+}$. The complex $[\text{PtEt}(\text{dbpx})]^+$ **3e** does not form a dinuclear cation by this pathway and it is of note that the diphosphine ligand in this complex has the largest bite angle of the diphosphines used which may render the corresponding dinuclear complex too sterically hindered to be stable. In the case of $\text{L-L} = \text{dbpp}$ the agostic ethyl complex **3d** can be regenerated from the reaction of the dinuclear complex $[\text{Pt}_2(\mu\text{-H})_2(\text{dbpp})_2]^{2+}$ with C_2H_4 . Loss of the C_2H_4 ligand from **3d** is facile in the presence of

norbornene or styrene to afford respectively $[\text{Pt}(\text{C}_7\text{H}_{11})\text{-(dbpp)}]^+$ and the known $\eta^3\text{-benzyl complex}^9 [\text{Pt}(\eta^3\text{-anti-1-MeCHPh})(\text{dbpp})]^+$ (Scheme 2).

The displacement of the agostic interactions *via* nucleophilic attack at the metal in complexes **3d** and **3e** by the small two-electron donor molecules CD_3CN and $\text{C}_5\text{D}_5\text{N}$ was investigated. The comparative reactivity of the ethene/hydride complex was also studied. NMR measurements of solutions of these complexes in CD_3CN and $\text{C}_5\text{D}_5\text{N}$ showed the presence of the ethyl complexes **6b**, **6d**, **6e** and **7b**, **7d** which, with the exception of **7b**, are unstable towards β -elimination of C_2H_4 to form the series of cationic hydrides **8b**, **8d**, **8e** and **9d**, **9e** (see Scheme 2 and Table 9). Similar reactivity leading to displacement of the agostic bond by small two-electron donor ligands has been observed in, for example,^{10,11} the compounds $[\text{CoEt}\{\text{P}(\text{OMe})_3\}(\eta\text{-C}_5\text{H}_5)]^+$ and $[\text{Co}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CHMe})\}(\eta\text{-C}_5\text{H}_5)]^+$.

Considerable progress has been achieved in assessing the influence of diphosphine ligand and alkyl on the position of the alkene/hydride *versus* agostic alkyl equilibrium, as monitored by NMR parameters. In particular it is clear that when the alkyl fragment is norbornyl the agostic isomer is always preferred (for all diphosphines used), whereas for 'ethyl' the less bulky, and smaller bite, diphosphines promote a predominance of the alkene/hydride isomer. The relief of ring strain in the norbornyl agostic isomer may be sufficient to favour this over the norbornene/hydride isomer with the smaller diphosphines. Alternatively the norbornene/hydride form may require more space than is offered even with the smallest phosphines used in this study. Within the norbornyl series the bulkier substituents (Bu^i *vs.* cyclohexyl) and larger chelate ring-size phosphines cause weaker agostic Pt–H–C interaction. The implications are that in platinum(II) diphosphine chemistry: (i) substituted alkyls (with β -hydrogens) are more easily accommodated in their agostic (η^2) form than as the corresponding alkene/hydrides; (ii) bulky, large chelate ring-size diphosphines promote the migration of hydride to alkene, increasingly favouring the alkyl over alkene/hydride form; and (iii) the degree of interaction between the $\beta\text{-C-H}$ bond and platinum in agostic complexes is very precisely controlled by the nature of the ancillary diphosphine ligand.

Experimental

All reactions were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques. Solvents were thoroughly dried over the appropriate reagents and freshly distilled prior to use. The compounds $[\text{Pt}(\text{cod})_2]$,¹² $[\text{Pt}(\text{cod})\text{-Et}_2]$,^{*,13} **dbpe**,¹⁴ **dcpp**,¹⁵ **dbpe**² and **dbpx**¹⁶ were prepared by published methods; the compound **dcpe** was purchased from Strem Chemicals, the gas $^{13}\text{C}_2\text{H}_4$ from MSD isotopes. Analytical and other data are given in Table 1. The NMR spectra were recorded on a Bruker AC300 and IR spectra with a Perkin Elmer FT1710 spectrophotometer. Although not reported, all ^1H and ^{13}C NMR data showed the expected signals arising from the diphosphine ligands.

Synthesis of the Complexes.— $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]$ ($\text{L-L} = \text{dcpe } \mathbf{1a}$, **dbpe } \mathbf{1b}, **dcpp } \mathbf{1c}, **dbpp } \mathbf{1d} or **dbpx } \mathbf{1e}). The method used was identical for each complex. To a stirred solution of the diphosphine (0.15 g, *ca.* 0.4 mmol) in ethene-saturated hexane (20 cm^3) at 273 K was added an equimolar amount of $[\text{Pt}(\text{cod})_2]$ over a period of *ca.* 10 min. After 30 min the solvent was removed *in vacuo* to afford the complexes as off-white microcrystals.********

$[\text{Pt}(\eta^2\text{-}^{13}\text{C}_2\text{H}_4)(\text{dbpe})]$. To a degassed frozen solution of

Table 10 Atomic coordinates ($\times 10^4$) for complex **2d**

| Atom | x | y | z |
|-------------------|------------|----------|-----------|
| Pt | 10 196(1) | 2 244(1) | 2 438(1) |
| P(1) | 11 716(2) | 1 308(1) | 2 270(1) |
| P(2) | 8 789(2) | 1 199(1) | 2 540(1) |
| C(1) | 11 026(9) | 3 324(7) | 1 965(6) |
| C(2) | 10 382(12) | 3 608(7) | 1 057(7) |
| C(3) | 9 270(8) | 3 246(6) | 2 975(6) |
| C(4) | 9 880(9) | 3 512(7) | 3 894(7) |
| C(5) | 11 442(8) | 134(6) | 2 388(7) |
| C(6) ^a | 10 433(12) | −182(8) | 2 834(10) |
| C(6) ^b | 10 273(25) | −88(13) | 1 927(21) |
| C(7) | 9 223(8) | 65(5) | 2 302(6) |
| C(8) | 12 909(7) | 1 506(6) | 3 281(5) |
| C(9) | 13 268(8) | 2 455(6) | 3 376(6) |
| C(10) | 12 409(8) | 1 269(7) | 4 127(6) |
| C(11) | 13 998(7) | 956(7) | 3 274(7) |
| C(12) | 12 361(7) | 1 272(6) | 1 173(5) |
| C(13) | 13 144(9) | 2 056(6) | 1 082(6) |
| C(14) | 11 344(8) | 1 298(7) | 399(5) |
| C(15) | 13 074(8) | 454(7) | 1 065(6) |
| C(16) | 8 171(8) | 1 016(6) | 3 636(6) |
| C(17) | 9 168(8) | 1 121(7) | 4 423(5) |
| C(18) | 7 260(8) | 1 711(8) | 3 764(6) |
| C(19) | 7 608(10) | 148(7) | 3 720(7) |
| C(20) | 7 566(7) | 1 396(6) | 1 554(5) |
| C(21) | 8 129(8) | 1 323(7) | 688(5) |
| C(22) | 7 051(8) | 2 296(7) | 1 545(7) |
| C(23) | 6 595(8) | 703(7) | 1 467(6) |

^a Occupancy 0.64(1). ^b Occupancy 0.36(1).

$[\text{Pt}(\text{cod})_2]$ (0.367 g, 0.9 mmol) and **dbpe** (0.298 g, 0.9 mmol) in hexane (25 cm^3) under vacuum at 77 K was condensed $^{13}\text{C}_2\text{H}_4$ (1.0 mmol, 92.1% by atom). After warming to ambient temperature and stirring for *ca.* 2 h the solvent was removed *in vacuo*. After purification by redissolving the reaction products in hexane (30 cm^3) and filtering off any undissolved material, the complex $[\text{Pt}(\eta^2\text{-}^{13}\text{C}_2\text{H}_4)(\text{dbpe})]$ was obtained as off-white crystals the purity of which was checked by ^1H , ^{13}C and ^{31}P NMR spectroscopy.

$[\text{PtEt}_2(\text{L-L})]$ ($\text{L-L} = \text{dcpe } \mathbf{2a}$ or **dcpp } \mathbf{2c}). The synthesis of the two compounds was identical. A solution of the diphosphine (*ca.* 0.25 g, 0.6 mmol) in diethyl ether (10 cm^3) was treated with $[\text{Pt}(\text{cod})\text{Et}_2]$ (*ca.* 0.21 g, 0.6 mmol). After 2 h the supernatant liquid was decanted and the precipitate dried *in vacuo* to reveal the complex as off-white microcrystals.**

$[\text{PtEt}_2(\text{L-L})]$ ($\text{L-L} = \text{dbpe } \mathbf{2b}$ or **dbpp } \mathbf{2d}). A solution of the diphosphine (*ca.* 0.25 g, 0.8 mmol) and $[\text{Pt}(\text{cod})\text{Et}_2]$ (*ca.* 0.29 g, 0.8 mmol) in toluene (5 cm^3) was heated to 363 K for 20 h. Reduction of the volume of solvent *in vacuo* to *ca.* 2 cm^3 and cooling to 250 K afforded colourless crystals of the complex.**

$[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{dbpx})]$ **1e** by an alternative method. A solution of **dbpx** (0.39 g, 1 mmol) and an equimolar amount of $[\text{Pt}(\text{cod})\text{Et}_2]$ in toluene (15 cm^3) was heated to 373 K for 20 h. The solvent was removed *in vacuo* to reveal complex **1e** as off-white microcrystals.

$[\text{PtH}(\eta^2\text{-C}_2\text{H}_4)(\text{L-L})]\text{X}$ ($\text{X} = \text{BF}_4$, $\text{L-L} = \text{dcpe } \mathbf{3a}$, **dbpe } \mathbf{3b}** or **dcpp } \mathbf{3c}) and $[\text{PtEt}(\text{L-L})]\text{X}$ ($\text{X} = \text{BF}_4$, PF_6 , CF_3SO_3 , $\text{CPh}(\text{CF}_3\text{SO}_2)_2$ or $\text{CB}_{11}\text{H}_{12}$; $\text{L-L} = \text{dbpp } \mathbf{3d}$ or **dbpx } \mathbf{3e}). The procedure was identical in each case. A solution of the diethyl or $\eta^2\text{-C}_2\text{H}_4$ complexes (*ca.* 0.3 g) in diethyl ether (10 cm^3) at 273 K was treated with an equimolar amount of $\text{HBF}_4\cdot\text{OEt}_2$ or $\text{HBF}_4\cdot\text{OMe}$ causing an immediate precipitate of a white solid. The supernatant liquid was decanted and the solid washed with diethyl ether (3 \times 5 cm^3 portions). The precipitate was dried *in vacuo* to reveal the complex as off-white microcrystals. Complexes **1e** and **2d** were also protonated with other acids *viz.* HPF_6 (60% aqueous solution), $\text{CF}_3\text{SO}_3\text{H}$, $\text{CHPh}(\text{CF}_3\text{SO}_2)_2$ ¹⁷ and $\text{HCB}_{11}\text{H}_{12}$.¹⁸ The method was identical to that for $\text{HBF}_4\cdot\text{OEt}_2$ using equimolar amounts of the appropriate acid.****

* The method in ref. 13 was considered unsatisfactory as $[\text{Pt}(\text{cod})\text{Et}(\text{Cl})]$ was produced as an impurity. It was modified by use of 2 equivalents of ZnEt_2 instead of MgEtBr and pure products were obtained consistently in good yield.

Table 11 Atomic coordinates ($\times 10^4$) for complex **3d**

| Atom | x | y | z | Atom | x | y | z |
|---------------------|----------|----------|----------|---------------------|-----------|----------|----------|
| Pt(1) ^a | 2542(1) | 6792(1) | 2425(1) | C(24') ^d | 2230 | 4822 | 7777 |
| Pt(2) ^b | 2491(1) | 4307(1) | 7551(1) | C(25') ^d | 2411 | 4709 | 6866 |
| Pt(1') ^c | 2544(2) | 5715(2) | 2590(3) | C(26) | 1906(9) | 3563(9) | 9304(11) |
| Pt(2') ^d | 2560(6) | 3232(4) | 7412(6) | C(27) | 2138(10) | 3983(8) | 9904(10) |
| P(11) | 2753(2) | 6274(2) | 3603(2) | C(28) | 1737(12) | 2975(10) | 9607(13) |
| P(12) | 2336(2) | 6033(2) | 1545(3) | C(29) | 1187(9) | 3773(11) | 8888(10) |
| P(21) | 2659(3) | 3572(3) | 8462(3) | C(210) | 3635(11) | 3471(10) | 8854(14) |
| P(22) | 2251(3) | 3854(3) | 6401(3) | C(211) | 3882(8) | 4106(8) | 9148(9) |
| C(11) ^a | 2527(13) | 7525(10) | 1673(16) | C(212) | 3722(10) | 3024(10) | 9534(10) |
| C(12) ^a | 2661(10) | 7787(8) | 2477(22) | C(213) | 4154(8) | 3320(10) | 8127(10) |
| C(13) ^a | 2782(8) | 5479(6) | 3464(9) | C(214) | 2986(11) | 3896(13) | 5600(13) |
| C(14) ^a | 2234(9) | 5213(8) | 2850(9) | C(215) | 2756(10) | 3655(9) | 4744(9) |
| C(15) ^a | 2478(9) | 5303(6) | 1979(9) | C(216) | 3705(10) | 3552(10) | 5821(11) |
| C(11') ^c | 2424 | 4862 | 2269 | C(217) | 3202(12) | 4571(10) | 5455(14) |
| C(12') ^c | 2576 | 4928 | 3329 | C(218) | 1291(11) | 4009(11) | 5978(12) |
| C(13') ^c | 2629 | 7234 | 3152 | C(219) | 965(8) | 3550(7) | 5390(8) |
| C(14') ^c | 2792 | 7294 | 2224 | C(220) | 743(9) | 4052(9) | 6680(9) |
| C(15') ^c | 2207 | 7078 | 1597 | C(221) | 1289(13) | 4630(10) | 5534(15) |
| C(16) | 3745(10) | 6439(12) | 3990(13) | B(11) | 5532(12) | 5380(12) | 7670(16) |
| C(17) | 4011(11) | 5906(11) | 4512(14) | B(12) | 5127(12) | 5594(9) | 6691(13) |
| C(18) | 4239(8) | 6492(10) | 3195(11) | B(13) | 4431(11) | 5483(11) | 7523(15) |
| C(19) | 3755(11) | 7028(11) | 4438(13) | B(14) | 4888(11) | 5630(8) | 8436(11) |
| C(110) | 2012(9) | 6404(8) | 4416(10) | B(15) | 5818(13) | 5936(12) | 8198(17) |
| C(111) | 2266(10) | 6222(9) | 5206(11) | B(16) | 5935(12) | 5978(13) | 7222(17) |
| C(112) | 1766(10) | 7046(10) | 4430(10) | B(17) | 5681(13) | 6588(9) | 7679(17) |
| C(113) | 1295(9) | 6068(10) | 4145(12) | B(18) | 5290(21) | 6434(14) | 6754(20) |
| C(114) | 3017(11) | 6059(10) | 716(12) | B(19) | 4379(14) | 6214(13) | 6972(13) |
| C(115) | 2851(9) | 6511(7) | 2(11) | B(110) | 4260(11) | 6193(9) | 7982(12) |
| C(116) | 3137(10) | 5436(8) | 279(10) | B(111) | 5080(15) | 6426(12) | 8451(16) |
| C(117) | 3833(9) | 6230(9) | 1040(11) | B(112) | 4741(15) | 6721(10) | 7496(14) |
| C(118) | 1349(11) | 6054(9) | 1097(15) | B(21) | — 79(14) | 6017(10) | 6863(13) |
| C(119) | 1218(12) | 5537(9) | 495(14) | B(22) | 321(12) | 5820(10) | 7852(14) |
| C(120) | 781(11) | 5896(10) | 1769(11) | B(23) | 755(15) | 6364(18) | 7216(15) |
| C(121) | 1082(9) | 6615(6) | 742(13) | B(24) | 43(12) | 6730(9) | 6721(11) |
| C(21) ^b | 2384(9) | 5202(11) | 7258(16) | B(25) | — 784(16) | 6480(13) | 6992(17) |
| C(22) ^b | 2501(11) | 5201(9) | 8199(15) | B(26) | — 636(12) | 5944(11) | 7713(13) |
| C(23) ^b | 2478(10) | 2791(8) | 7991(9) | B(27) | — 854(10) | 6656(8) | 8109(11) |
| C(24) ^b | 2676(9) | 2698(7) | 7091(9) | B(28) | — 178(9) | 6214(9) | 8573(12) |
| C(25) ^b | 2158(8) | 3003(7) | 6495(7) | B(29) | 712(11) | 6447(11) | 8261(12) |
| C(21') ^d | 2408 | 2632 | 6632 | B(210) | 486(14) | 7056(12) | 7601(13) |
| C(22') ^d | 2625 | 2314 | 7568 | B(211) | — 387(10) | 7160(11) | 7479(12) |
| C(23') ^d | 2836 | 4527 | 8360 | B(212) | 13(14) | 6860(18) | 8449(17) |

^a Site occupancy 0.802(4). ^b Site occupancy 0.859(4). ^c Site occupancy 0.198(4). ^d Site occupancy 0.141(4).

[Pt(¹³C₂H₅)(dbpp)]BF₄. A solution of complex **3d** (0.079 g, 0.9 mmol) in CD₂Cl₂ (0.4 cm³) in an NMR tube was frozen at 77 K and degassed; ¹³C₂H₄ (1 mmol) was condensed into the tube along with an estimated 0.2 cm³ Me₂O. The tube was then sealed and stored at ambient temperature for approximately 30 min to allow ethene exchange to take place. The ¹³C-labelled analogue of **3e** was prepared in an analogous way.

[PtH(O₃SCF₃)(dbpp)] **4**. Complex **4** formed on allowing a solution of [PtEt(dbpp)][CF₃SO₃] in CH₂Cl₂ to stand for 3 d at 293 K. NMR (CD₂Cl₂, 25 °C): ¹H (hydride moiety only) δ —6.6 [1 H, dd, *J*(PH) 13 and 182, *J*(PtH) 779]; ³¹P, δ 45.4 [*J*(PtP) 4496] and 34.0 [*J*(PtP) 1998 Hz].

Reactions of Complexes 3b, 3d and 3e with Acetonitrile and Pyridine.—Complexes **3b** and **3d** (ca. 0.150 g) were separately dissolved in CD₃CN or C₅D₅N (0.5 cm³) and the resulting solution transferred to an NMR tube so that the progress of the reaction could be monitored. Complex **3e** (ca. 0.15 g) was dissolved in CD₂Cl₂ (0.5 cm³) and kept at 195 K; CD₃CN (ca. 80 μ l) was added directly to the cooled sample which was then placed in the previously cooled probe of the NMR instrument.

Crystal Structure Determinations for Complexes 2d, 3d and 4.—Many of the details of the structure analyses carried out are listed in Table 8. Crystals of **2d**, **3d** and **4** were grown (colourless blocks, pale cream prisms and colourless cuboids respectively)

from Et₂O at ca. 0 °C and by the slow vapour diffusion of Et₂O into a CH₂Cl₂ solution of the complex for the last two. The crystal chosen for study was sealed under N₂ in a thin-walled glass capillary tube for diffractometry. Cell dimensions for each analysis were determined from the setting angle values of 42, 37 and 15 centred reflections respectively. Diffracted intensities (0–20 scans for **2d** and **4**, and Wyckoff ω scans for **3d**) were collected on Nicolet R3m four-circle diffractometers for a unique volume of reciprocal space using graphite-monochromated Mo-K α X-radiation (λ = 0.710 69 Å). Three check reflections remeasured after every 50 ordinary data showed no crystal decay but ± 4 and $\pm 5\%$ drifts for **3d** and **4**, and 15% decay for **2d**, 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 those with $F \geq n\sigma(F)$ (see Table 8) were used in the solution and refinement of the structures. Corrections for Lorentz, polarization, and X-ray absorption effects were applied. The latter correction was based on a semiempirical method using azimuthal scan data (294, 364 and 499 such data for **2d**, **3d** and **4** respectively).

The Laue group for the diffraction data for complex **3d** is rather close to *mmm*, and the metric symmetry likewise is very close to orthorhombic [refined angles were α = 90.005(14), β = 90.046(13), γ = 90.011(13)°]. Oscillation photographs taken

Table 12 Atomic coordinates ($\times 10^4$) for complex **4**

| Atom | x | y | z |
|-------|---------|-----------|-----------|
| Pt | 1944(1) | 2438(1) | 0 |
| P(1) | 2794(1) | 2328(3) | -675(3) |
| P(2) | 1400(1) | 841(3) | -1038(3) |
| S | 1154(1) | 3741(3) | 1714(3) |
| F(1) | 277(4) | 4285(13) | 2815(8) |
| F(2) | 79(4) | 4164(21) | 1334(11) |
| F(3) | 236(7) | 2126(16) | 2081(15) |
| O(1) | 1172(3) | 2813(10) | 842(7) |
| O(2) | 1236(4) | 5335(8) | 1570(7) |
| O(3) | 1449(4) | 3122(10) | 2513(8) |
| C(1) | 3339(4) | 1377(13) | 120(11) |
| C(2) | 3062(7) | -98(19) | 506(14) |
| C(3) | 3887(6) | 912(20) | -376(12) |
| C(4) | 3486(8) | 2326(17) | 1017(11) |
| C(5) | 3059(6) | 4304(14) | -1083(13) |
| C(6) | 3057(7) | 5451(16) | -275(18) |
| C(7) | 2643(7) | 4813(20) | -1845(15) |
| C(8) | 3665(7) | 4243(19) | -1491(18) |
| C(9) | 2827(6) | 1143(15) | -1753(9) |
| C(10) | 2335(7) | 1039(25) | -2378(11) |
| C(11) | 1839(6) | 38(17) | -2022(10) |
| C(12) | 1126(5) | -959(13) | -411(10) |
| C(13) | 879(10) | -2107(16) | -1127(15) |
| C(14) | 1630(6) | -1695(21) | 61(19) |
| C(15) | 692(8) | -606(18) | 315(13) |
| C(16) | 809(5) | 1944(15) | -1677(9) |
| C(17) | 399(10) | 2620(22) | -976(21) |
| C(18) | 1056(8) | 3187(27) | -2225(18) |
| C(19) | 466(9) | 1034(27) | -2396(18) |
| C(20) | 410(7) | 3586(23) | 2000(15) |

about each of the crystallographic axes showed minor deviation from mirror symmetry for the *a* and *c* axes but none for the *b* axis. Furthermore the merging *R* for the observed data under *mmm* symmetry is 0.123; this compares with 0.032 under 2/*m* symmetry. The crystal system was therefore assigned as monoclinic. The diffracted intensities show pronounced pseudo-C centring, only 2057 (out of 6257) reflections with $h + k = 2n + 1$ having $I > 3\sigma(I)$, and the mean $I/\sigma(I)$ for all such reflections being only 3.9. The space group was assigned on the rather ambiguous evidence of the systematic absences (there are very few violations of *a*, *c* or *n* glide conditions for reflections $h0l$), and confirmed by successful structure solution and refinement as below. Visual inspection of the data-collection crystal using a polarizing microscope showed no evidence for twinning, although this cannot be taken as proof positive that twinning is not present and responsible for the apparent disorder. We note that in other complexes containing the dbpp ligand similar disorder has been observed.

The structure of complex **3d** was solved by direct and Fourier methods and refined with the molecular cations and anions lying in general positions. There are two crystallographically independent cations and two independent anions in the structure. Both the cations are subject to a partial two-fold site disorder about a pseudo-centre of inversion near the geometric centre of the molecule. This disorder was modelled by assigning the platinum, $(\text{CH}_2)_3$, and ethyl carbon atoms occupancy *x* and including second positions for these atoms of occupancy $(1 - x)$, located in Fourier difference syntheses, related by the pseudo-inversion centre. The phosphorus and *tert*-butyl atoms were treated as full occupancy atoms, although each atom of these groups presumably occupies two very slightly separated sites. Occupancy parameters *x* refined to 0.802(4) and 0.859(4) for cations 1 and 2 respectively. The anions were also disordered in the sense that no carbon sites could be definitely located; all cage atoms of the anions were therefore assigned as boron. All full or high-occupancy non-hydrogen atoms, and the low-occupancy platinum atoms [Pt(1'), Pt(2')], were assigned anisotropic

displacement parameters and refined without positional constraints. The low-occupancy carbons [C(11')-C(15'), C(21')-C(25')] were placed in fixed positions and assigned fixed isotropic displacement parameters (0.05 \AA^2). All hydrogen atoms were constrained to idealized geometries (C-H 0.96 \AA , B-H 1.10 \AA) and assigned fixed isotropic displacement parameters (0.08 \AA^2). No hydrogens were assigned to the ethyl carbons or to the low-occupancy ethyl or $(\text{CH}_2)_3$ groups. At convergence this model resulted in ten carbon atoms having non-positive-definite anisotropic displacement parameters [C(12)-C(15), C(110), C(115), C(118), C(121), C(26), C(213)] as a consequence of the incomplete modelling of the disorder present in the structure. Although the final goodness of fit (*S*) and the agreement between independent molecules are satisfactory, the disorder affects the entire cation, and in particular the metal and ethyl atomic sites; as a result care should be taken not to overinterpret the bond lengths and angles reported.

The structures of complexes **2d** and **4** were solved by conventional heavy-atom methods, and successive Fourier difference syntheses were used to locate all non-hydrogen atoms, which were refined with anisotropic displacement parameters. The central atom of the dbpp ligand is disordered in **2d**, occupying two positions [C(6) and C(6')] in the ratio 0.64(1):0.36(1). The hydrogen atoms on the ethyl groups of **2d** and the of hydride ligand in **4** were directly located in Fourier difference syntheses and their positions were refined (with the C-H bonds for the ethyl groups forced to be close to 0.96 \AA). All other hydrogen atoms were included at calculated positions (C-H 0.96 \AA) with fixed isotropic thermal parameters (except for the ethyl hydrogens in **2d** whose *U* values were refined without constraints). The absolute structure given for **4** was assigned on the basis of an η refinement;¹⁹ the value of η refined to 0.29(6) which is consistent with the given structure although not unambiguously so.

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 and $g = 0.0005$] gave satisfactory analyses of variance and converged to the residuals listed in Table 8. The final electron-density difference syntheses showed no peaks ≥ 0.7 , 1.1, 1.0 or ≤ -1.1 , -0.2 , -0.9 e \AA^{-3} for **2d**, **3d** and **4** respectively. Calculations were performed using programs written by Sheldrick.²⁰ Complex neutral-atom scattering factors were taken from ref. 21. Tables 10-12 report the positional parameters for the non-hydrogen atoms of **2d**, **3d** and **4** respectively.

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

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