Reactions of Co-ordinated Ligands. Part 57.[1] Synthesis, Structure and Interrelationship of 2-σ-Butadienyl and Cationic (1,2,3-η)-*trans*-Butadienyl-platinum and -palladium Complexes; Crystal Structures of *cis*-[PtCl{σ-C(CH_2)C(Et)=CH_2}(dppf)] and [Pt{(1,2,3-η)-*trans*-CH_2C(Et)C=CH_2}(PPh_3)$_2$][PF_6] [dppf = 1,1′-bis(diphenylphosphino)ferrocene] *

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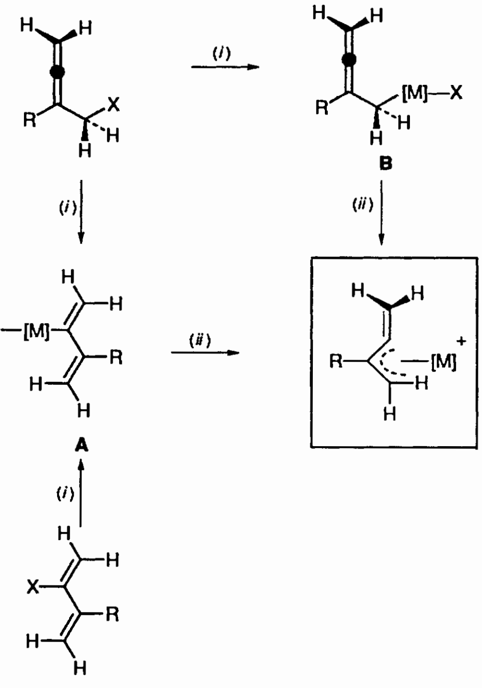
Reaction of the platinum(0) complexes [Pt(C_2H_4)(PPh_3)$_2$], [Pt(C_2H_4)(dppf)] [dppf = 1,1-bis(diphenylphosphino)ferrocene], [Pt(cod)$_2$] (cod = cycloocta-1,5-diene) and the palladium(0) complex [Pd(PPh_3)$_4$] with the 4-chlorobuta-1,2-dienes CH_2=C=C(R)CH_2Cl (R = Me or Et) affords *trans* or *cis* 2-σ-butadienyl complexes of the general formula [MCl{σ-C(CH_2)C(R)=CH_2}L_2]; the structural identity of *cis*-[PtCl{σ-C(CH_2)C(Et)=CH_2}(dppf)] was confirmed by single-crystal X-ray diffraction. Treatment of [Pt(C_2H_4)(PPh_3)$_2$] or [Pt(C_2H_4)(dppf)] with an excess of 2-chlorobuta-1,3-diene leads to the formation of the corresponding unsubstituted 2-σ-butadienyl platinum complexes. Addition of thallium hexafluorophosphate to these 2-σ-butadienyl complexes results in elimination of TlCl and formation in high yield of a range of cationic (1,2,3-η)-*trans*-butadienyl complexes characterised by NMR spectroscopy, and in the case of [Pt{1,2,3-η)-*trans*-CH_2C(Et)C=CH_2}(PPh_3)$_2$][PF_6] by single crystal X-ray diffraction.

As part of a developing interest [2,3] in the chemistry of transition-metal complexes containing the (1,2,3-η)-*trans*-butadienyl ligand our attention focused on the X-ray crystallographically identified cationic complex [Pt{(1,2,3-η)-*trans*-CH(Ph)C(Ph)-C=CH_2}(PPh_3)$_2$][BF_4] reported[4] to be formed on reaction of [Pt(C_2H_4)(PPh_3)$_2$] with the cyclopropenium cation [C_3(Me)-Ph_2][BF_4]. The reactivity of such a cationic complex towards nucleophilic reagents and the site of attack was clearly of interest; however, before such studies could be undertaken it was obviously important to try to develop a more versatile synthetic approach to such species. The report[5] that certain metal carbonyl anions react with the allene (CF_3)$_2$C=C=C-(CF_3)$_2$, to give initially a 2-σ-bonded butadienyl species, which can then be transformed *via* CO loss into (1,2,3-η)-*trans*-C(CF_3)$_2$C(CF_3)C=CF_2-substituted complexes, suggested that it might be possible to access the sought for (1,2,3-η)-*trans*-butadienyl-substituted platinum cations by halide abstraction from 2-σ-butadienyl species such as *cis*- or *trans*-[PtCl{σ-C(CH_2)C(R)=CH_2}L_2]. An alternative approach to cationic (1,2,3-η)-*trans*-butadienyl complexes was to attempt a similar halide abstraction from a σ-bonded allenyl complex, for example, *trans*-[PtCl{σ-CH_2C(R)=C=CH_2}L_2]. This paper describes our detailed[3] exploration of these ideas.



Scheme 1 X = Halogen. (*i*) + [M^0]; (*ii*) $AgBF_4$ or Tl[PF_6]

Results and Discussion

These two alternative synthetic pathways are summarised in Scheme 1. A literature search for 2-σ-bonded butadienyl platinum(II) complexes revealed that the complex *trans*-[PtCl-{σ-C(CH_2)C(Me)=CH_2}(PPh_3)$_2$] is reported[6] to be one of the products of the reaction of *cis*-[PtCl_2(PPh_3)$_2$] with hydrazine hydrate and isopropenylacetylene. However, the reaction is not selective and only moderate yields are reported. We therefore began to explore the reaction of zerovalent platinum complexes

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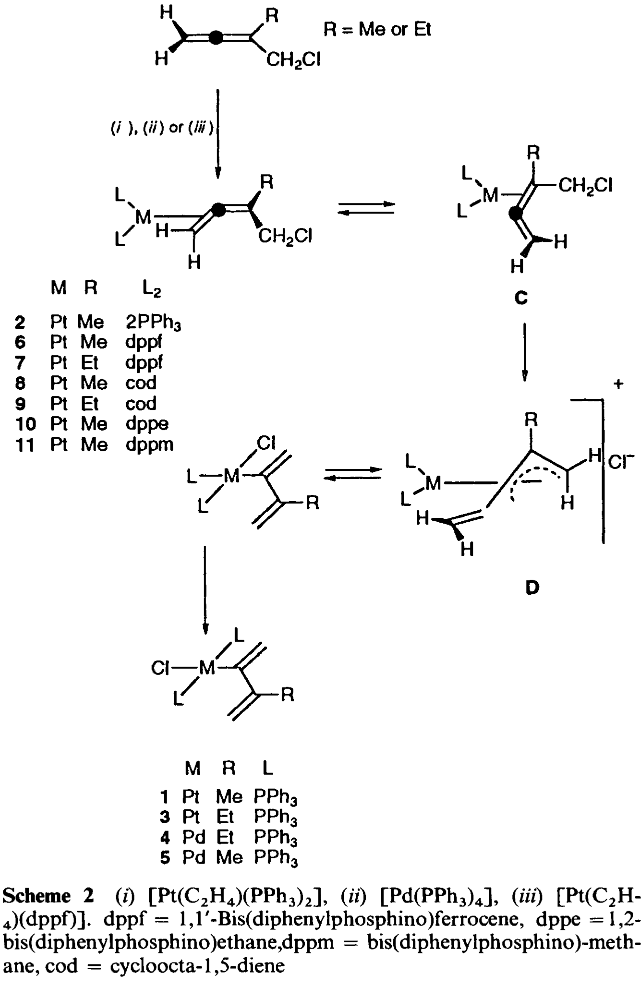
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, Issue 1, pp. xxiii–xxviii.

with allenyl halides as a possible route to either 2-σ-bonded butadienyl or σ-allenyl complexes, *i.e.* **A** and **B** in Scheme 1. Additions of [Pt(C_2H_4)(PPh_3)$_2$] to a solution of CH_2=C=C-(Me)CH_2Cl[7] in tetrahydrofuran (thf) resulted in a rapid reaction at room temperature and the formation in high yield (89%) of the colourless crystalline complex *trans*-[PtCl{σ-C(CH_2)C(Me)=CH_2}(PPh_3)$_2$] **1** (Scheme 2). Elemental analysis, ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR spectroscopy confirmed the structural identity of the complex. When the reaction was conducted at low temperature (−78 °C ⟶ −30 °C) in an NMR tube, ^1H resonances attributable to *cis*-[PtCl{σ-C-(CH_2)C(Me)=CH_2}(PPh_3)$_2$] **2** were observed, and on warming to room temperature these were replaced by resonances corresponding to the isolated *trans* isomer **1**. A plausible rationale for these observations is illustrated in Scheme 2 and requires that the unsubstituted end of the allene is initially co-ordinated onto the Pt^0 centre with displacement of ethylene. This is followed by an intramolecular movement of the Pt(PPh_3)$_2$ fragment onto the substituted allenic double bond, thus accessing the thermodynamically less stable but more reactive η^2-allene complex **C**. Backside intramolecular nucleophilic attack by the Pt^0 centre on the carbon–chlorine bond would then afford the cation **D**, which apparently collapses to give initially a *cis*-2-σ-butadienyl complex isomerising to the thermodynamically more stable isolated *trans*-2-σ-butadienyl complexes. Although, in principle **D** could alternatively collapse to give a σ-bonded allenyl species, *i.e.* **B** in Scheme 1, this was not observed.

The synthetic pathway to **1** proved to be capable of generalisation. Thus, reaction of [Pt(C_2H_4)(PPh_3)$_2$] with CH_2=C=C(Et)CH_2Cl[8] gave **3**, and it was found that the palladium analogues **4** and **5** could also be formed in good yield by treating the corresponding allenyl halide with [Pd(PPh_3)$_4$].



	M	R	L_2
2	Pt	Me	2PPh$_3$
6	Pt	Me	dppf
7	Pt	Et	dppf
8	Pt	Me	cod
9	Pt	Et	cod
10	Pt	Me	dppe
11	Pt	Me	dppm

	M	R	L
1	Pt	Me	PPh$_3$
3	Pt	Et	PPh$_3$
4	Pd	Et	PPh$_3$
5	Pd	Me	PPh$_3$

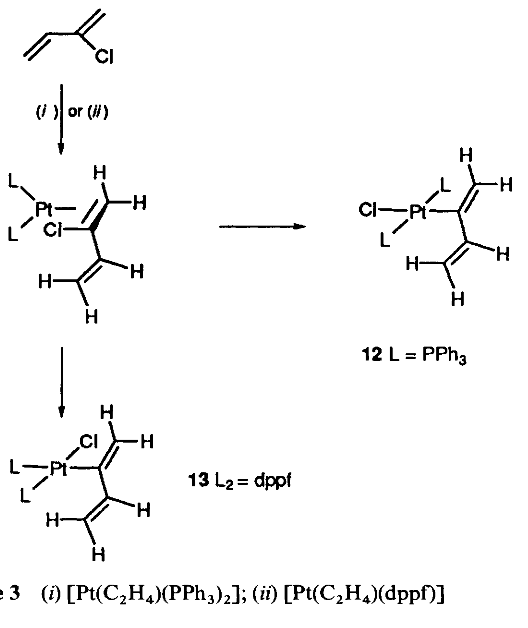
Scheme 2 (*i*) [Pt(C_2H_4)(PPh_3)$_2$], (*ii*) [Pd(PPh_3)$_4$], (*iii*) [Pt(C_2H_4)(dppf)]. dppf = 1,1′-Bis(diphenylphosphino)ferrocene, dppe = 1,2-bis(diphenylphosphino)ethane,dppm = bis(diphenylphosphino)-methane, cod = cycloocta-1,5-diene

Similarly, reaction of [Pt(C_2H_4)(dppf)][9] with CH_2=C=C-(Me)CH_2Cl or CH_2=C=C(Et)CH_2Cl afforded excellent yields of the stable *cis*-σ-butadienylplatinum complexes **6** and **7** respectively. Alternatively, it was found that *cis*-2-σ-butadienyl complexes could be prepared by treating [Pt(cod)$_2$][10] with allenyl halides. Thus, reactions with CH_2=C=C(Me)CH_2Cl or CH_2=C=C(Et)CH_2Cl in pentane gave good yields of the cream coloured crystalline complexes **8** and **9** (Scheme 2). Unlike the related σ-allyl complexes[11] prepared by reacting allyl halides with [Pt(cod)$_2$], the 2-σ-butadienyl complexes showed no fluxional behaviour in solution at room temperature. As might be expected the cycloocta-1,5-diene ligand was labile and reaction of **8** with 2 molar equivalents of triphenylphosphine gave **1**. In a similar way treatment of **8** with the chelating ligands dppe and dppm afforded the complexes **10** and **11**, again in good yield.

A potential alternative route to 2-σ-butadienylplatinum(II) complexes is to react a 2-halogenobuta-1,3-diene with a Pt^0 complex (see Schemes 1 and 3). This idea is based on the well known[9,12] ability of vinyl halides to react with, for example, [Pt(C_2H_4)(PPh_3)$_2$] to give initially η^2-vinylhalide substituted Pt^0 moieties, which then readily rearrange to form σ-vinylhaloplatinum(II) complexes. Treatment of [Pt(C_2H_4)(PPh_3)$_2$] with an excess of 2-chlorobuta-1,3-diene in chloroform led to the formation of the unsubstituted 2-σ-butadienyl *trans*-complex **12** in good yield. A similar reaction between [Pt(C_2H_4)(dppf)] and 2-chlorobuta-1,3-diene gave an excellent yield of **13**.

Thus, two new synthetic pathways to 2-σ-butadienyl complexes have been established. All of these new compounds were obtained as colourless or pale yellow crystalline, air-stable materials and they were characterised by elemental analysis, ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR spectroscopy (see Experimental section for details).

In order to establish firmly the structural identity of the complexes **1–13** it was thought important to carry out a single crystal X-ray diffraction study with a representative example. Since the previous X-ray studies[6] with 2-σ-butadienylplatinum(II) complexes were with the *trans* species [PtCl{σ-C(CH_2)C-(Me)=CH_2}(PPh_3)$_2$] and [Pt{σ-C_2C(Me)=CH_2}{σ-C(CH_2)C-(Me)=CH_2}(PPh_3)$_2$], crystals of the *cis*-2-σ-butadienylplatinum complex **7** were chosen for detailed study. A suitable crystal of **7** was obtained by slow solvent diffusion using dichloromethane and diethyl ether. The overall structure converged well (R = R' = 0.0587), with final shift/estimated standard deviation ratios averaging 0.001. However, the errors associated with the positional parameters of the carbon atoms in the 2-σ-butadienyl moiety remained disappointingly high. As a consequence, errors in the lengths and angles were also large.



12 L = PPh$_3$

13 L_2 = dppf

Scheme 3 (*i*) [Pt(C_2H_4)(PPh_3)$_2$]; (*ii*) [Pt(C_2H_4)(dppf)]

Fig. 1 shows the geometry of the molecule and the atomic numbering scheme used and Table 1 lists selected bond lengths, angles and important dihedral angles. The complex is monomeric with the chelating dppf ligand ensuring a *cis* configuration of the other two co-ordination sites, which are occupied by a chlorine atom, and a σ-bonded carbon atom from the butadienyl ligand to give an overall co-ordination that is nearly square planar, in agreement with the NMR spectral data.

The Pt–Cl distance of 2.374(5) Å, is comparable with those found[13] in [PtCl$_2$(dppf)] and other *cis*-platinum(II) complexes. The Pt–P(1) and Pt–P(2) bond distances are 2.326(5) and 2.224(5) Å respectively, which compare well with those reported for the dichloroplatinum(II) system. The P(1)–Pt–P(2) angle of 100.3(2)° is the most striking feature of the bidentate ligand. The large angle is due to the bulk of the dppf moiety, where the two cyclopentadienyl rings can be seen to be staggered. This has the effect of forcing C(35) and the C(1) atom closer together, which can be seen from the C(35)–Pt–Cl bond angle of 85.2(8)°. The butadienyl ligand lies essentially perpendicular to the co-ordination plane as evidenced by a dihedral angle for C(37)–C(35)–Pt–P(1) of 89.22°. The dihedral angle for C(36)–C(35)–C(37)–C(38) of 174.19° shows that there is also slight twisting of the butadienyl possibly because the ethyl substituent is almost at right angles [C(40)–C(39)–C(37)–C(35) 85.47°] to the butadienyl plane. However, the most interesting feature, which is difficult to explain, is the bond lengths C(35)–C(36) 1.55(4), C(35)–C(37) 1.27(4) and C(37)–C(38) 1.27(4) Å, implying that despite the larger than desirable errors, there is a considerable shortening of the central C–C bond of the butadienyl ligand.

Table 1 Selected bond lengths (Å), and selected interbond and dihedral angles (°) for complex 7

Pt–Cl	2.374(5)	C(35)–C(37)	1.27(4)
Pt–P(1)	2.326(5)	C(37)–C(38)	1.27(4)
Pt–P(2)	2.224(5)	C(37)–C(39)	1.69(4)
Pt–C(35)	2.08(3)	C(39)–C(40)	1.57(4)
C(35)–C(36)	1.55(4)		
P(1)–Pt–Cl	85.2(2)	C(39)–C(37)–C(38)	126(3)
P(2)–Pt–Cl	174.5(2)	C(40)–C(39)–C(37)	108(2)
P(2)–Pt–P(1)	100.3(2)	C(36)–C(35)–Pt–P(1)	78.05
C(35)–Pt–Cl	85.2(8)	C(37)–C(35)–Pt–P(1)	89.22
C(35)–Pt–P(1)	170.3(8)	C(36)–C(35)–Pt–P(2)	87.98
C(35)–Pt–P(2)	89.3(8)	C(37)–C(35)–Pt–P(2)	104.75
C(36)–C(35)–Pt	113(2)	C(36)–C(35)–Pt–Cl	91.72
C(37)–C(35)–Pt	122(3)	C(37)–C(35)–Pt–Cl	75.55
C(37)–C(35)–C(36)	123(3)	C(36)–C(35)–C(37)–C(39)	0.23
C(38)–C(37)–C(35)	120(3)	C(36)–C(35)–C(37)–C(38)	174.19
C(39)–C(37)–C(35)	113(3)	C(40)–C(39)–C(37)–C(35)	85.47

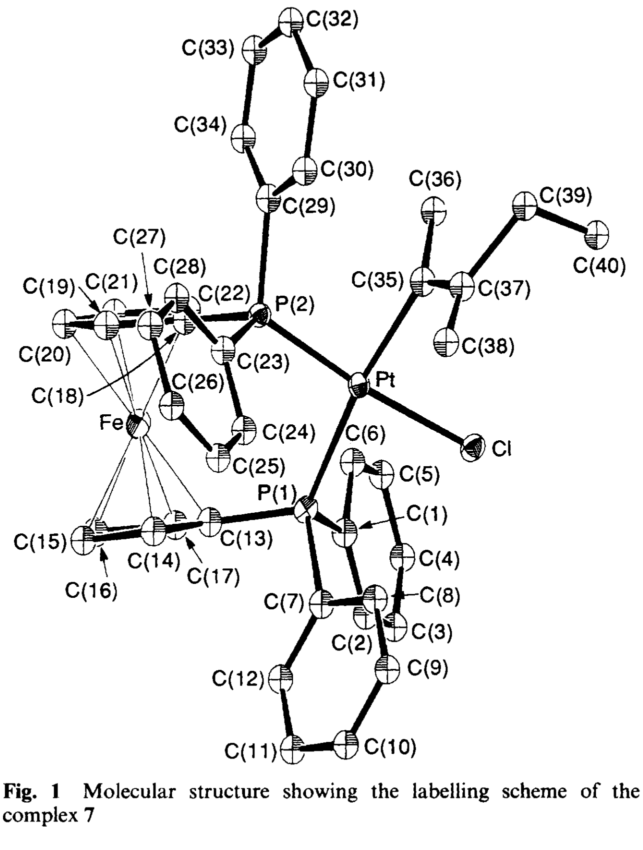
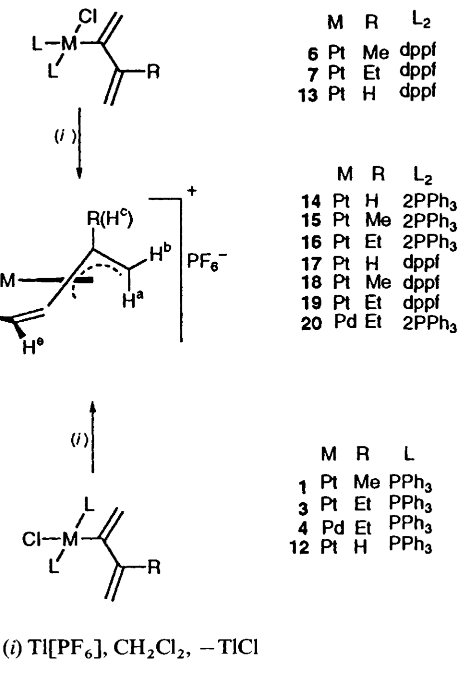


Fig. 1 Molecular structure showing the labelling scheme of the complex 7

With the establishment of a satisfactory synthetic route to 2-σ-butadienyl complexes attention was then turned to their transformation into cationic (1,2,3-η)-*trans*-butadienyl complexes. In our preliminary investigations[3] it was observed that reaction of **1** and **12** with AgPF$_6$ led to precipitation of AgCl and formation of cationic platinum complexes in reasonable yield; however, further work showed that the use of thallium hexafluorophosphate as a halide abstracting agent led to higher and more reproducible yields. Thus, as summarised in Scheme 4 high yields of the cationic (1,2,3-η)-*trans*-butadienyl platinum and palladium complexes **14–20** were obtained by treating the corresponding 2-σ-butadienyl complex with Tl[PF$_6$] in dichloromethane as solvent. These cations were obtained as white to colourless air-stable crystalline materials soluble in dichloromethane. They were all characterised by elemental analysis, ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectroscopy (see Experimental section), and in one case by single-crystal X-ray crystallography.

The ^{31}P NMR spectra were the simplest to interpret and all showed the presence of two inequivalent phosphorus atoms in the form of two doublets with their respective ^{195}Pt satellites. The complexes containing the dppf ligand showed larger *J*(PP) and *J*(PPt) coupling constants than those species containing PPh$_3$ ligands. The ^{1}H NMR spectra of these complexes were complicated, since splitting patterns for two inequivalent ^{31}P ligands accompanied by ^{1}H couplings and respective ^{195}Pt satellites were observed. The olefinic protons H^d and H^e resonated between δ 5.67 and 3.93 with their respective ^{31}P and ^{195}Pt couplings. The proton H^d, being *trans* to a ^{31}P atom, experiences a larger *J*(HP) coupling than H^e, allowing these two protons to be differentiated. The *anti*- and *syn*-protons (H^a and



Scheme 4 (*i*) Tl[PF$_6$], CH$_2$Cl$_2$, –TlCl

H^b) of the allyl function of the butadienyl moiety were assigned assuming that the *anti* H^a proton would appear further upfield than the *syn* H^b proton, due to the shielding effect of the platinum fragment on the *anti* proton. Signals due to H^a and H^b appear between δ 4.36 and 3.26. Proton H^c in complex **17** resonated at δ 5.32 as a broad singlet. The presence of the dppf ligand in complexes **17**–**19** further complicated the ^1H NMR spectra. The phenyl protons resonated in the aromatic region between δ 8.11 and 7.02, and the cyclopentadienyl protons appeared between δ 4.61 and 4.00. The ^{13}C NMR spectra were also complicated, but the assignment of the carbon atoms C^1, C^2, C^3 and C^4 of the butadienyl moiety was possible. The ^{31}P splittings in conjunction with the ^{195}Pt couplings lead to a considerable signal-to-noise ratio. This had the two-fold effect of making *J*(CP) and *J*(CPt) couplings difficult to elucidate and detect. Distortionless enhancement polarisation transfer (DEPT) experiments proved very useful in characterising these complexes. The CH_2 groups could be differentiated from other carbon groups, for instance, C^1 of complex **18** could be detected by DEPT. This carbon atom resonated in the cyclopentadienyl region and could not otherwise have been identified. The DEPT experiments also confirmed the presence of the quaternary carbons, C^2 and C^3, and the other CH_2 group of the butadienyl ligand, C^4. The C^3 resonances occurred at relatively low field and the possible significance of this is discussed later in relationship to the X-ray crystal structure of **16**. The ethyl substituents in complexes **16** and **19** also exhibited interesting ^{13}C NMR spectra, the *J*(CPt) couplings for the CH_3 carbon atoms being considerably larger than the *J*(CPt) couplings for the CH_2 carbon atoms.

As mentioned previously a single-crystal X-ray diffraction study with **16** was also carried out with the objective of defining the stereochemistry of the (1,2,3-η)-*trans*-butadienyl ligand and to provide a basis for a theoretical extended-Huckel molecular orbital (EHMO) study of the reactivity of these cations towards nucleophilic reagents. Fig. 2 shows the geometry of the molecule and the atomic numbering scheme used, while Fig. 3 shows an alternative view of **16** omitting the phenyl rings. Selected bond lengths and angles are given in Table 2 with various dihedral angles.

Complex **16** is monomeric and four-co-ordinate around the platinum atom. Two triphenylphosphine ligands are co-ordinated *cis* to the metal centre which is in agreement with the NMR spectral data. The other two co-ordination sites are occupied by the butadienyl ligand. The butadienyl ligand is bonded *via* C(37), C(38) and C(39) to the platinum, with C(40) bent away from the platinum at a non-bonding distance of 3.19 Å with a C(38)–C(39)–C(40) angle of 141(2)°. The allylic double bond distance in **16** and the complex [Pt{(1,2,3-η)-*trans*-CH(Ph)C(Ph)C=CH_2}$(PPh_3)_2$][BF_4] **21**, prepared by Hughes *et al.*,[4] are 1.26(4) and 1.31(2) Å respectively, which are in the range expected for the terminal C–C bond length in free buta-1,3-diene[14] and the unco-ordinated C=CH_2 bond of ligated allene complexes.[15–17] It is these two features which suggest a significant contribution from formalism **E** (Scheme 5) to the bonding in **16** and also in **21**. Scheme 5 shows the corresponding data for co-ordinated allene complexes, which can be seen to exhibit close similarities. The allyl function of the butadienyl ligand in **16** has a C(37)–C(38)–C(39) angle of 117(2) °, which is *ca.* 8° less than in cationic platinum η^3-allyl complexes,[18] but is

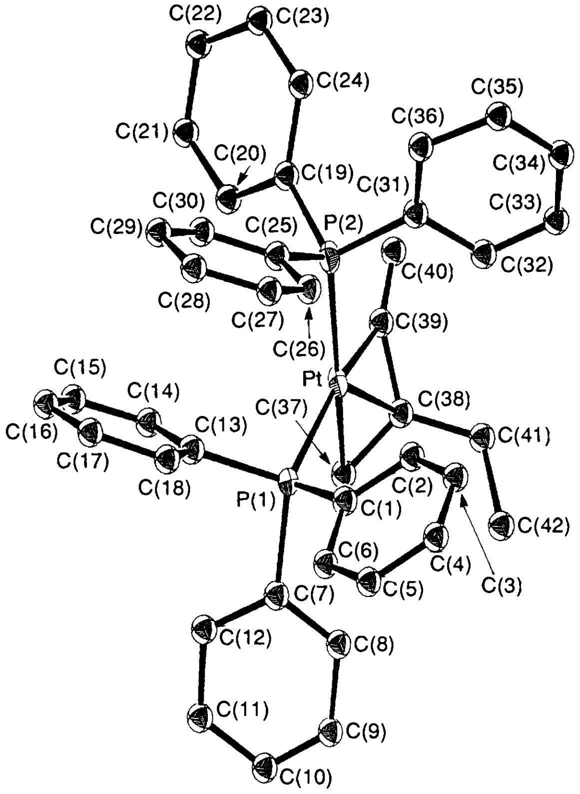


Fig. 2 Molecular structure showing the labelling scheme of the cation contained within the complex **16**

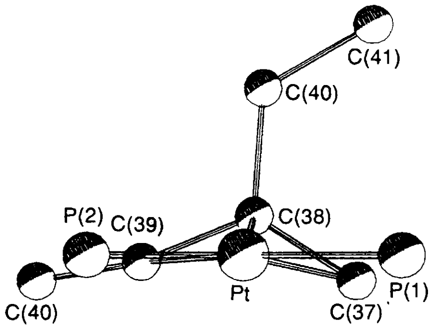
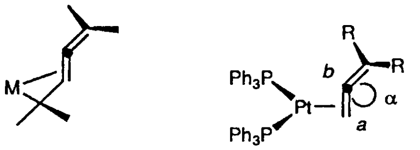


Fig. 3 Alternative simplified view of the cation contained within the complex **16**



E

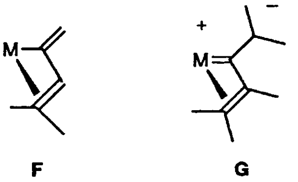
R	*a* /Å	*b* /Å	α°
Me	1.430(11)	1.316(11)	140.8(8)
H	1.48(5)	1.31(5)	142(3)

Scheme 5

Table 2 Selected bond lengths (Å), and selected interbond and dihedral angles (°) for complex **16**

Pt–P(1)	2.299(5)	C(37)–C(38)	1.42(3)
Pt–P(2)	2.294(5)	C(38)–C(39)	1.44(3)
Pt–C(37)	2.20(2)	C(39)–C(40)	1.26(4)
Pt–C(38)	2.20(2)	C(38)–C(41)	1.56(3)
Pt–C(39)	2.09(2)	C(41)–C(42)	1.45(5)
Pt–C(40)	3.19(2)		
P(1)–Pt–P(2)	100.3(2)	C(37)–C(38)–C(39)	117(2)
C(37)–Pt–P(1)	94.2(6)	C(38)–C(39)–C(40)	141(2)
C(37)–Pt–P(2)	163.6(6)	C(41)–C(38)–C(37)	122(2)
C(38)–Pt–P(1)	125.8(6)	C(41)–C(38)–C(39)	120(2)
C(38)–Pt–P(2)	131.9(6)	C(37)–C(38)–C(39)–C(40)	137.06
C(38)–Pt–C(37)	37.5(7)	C(37)–C(38)–C(41)–C(42)	22.72
C(39)–Pt–C(38)	39.1(9)	C(41)–C(38)–C(39)–C(40)	53.75
C(37)–Pt–C(39)	69.1(8)	C(39)–C(38)–C(41)–C(42)	145.63

similar to the equivalent angle in **21** [115(1) Å]. The carbon–carbon interatomic distances C(37)–C(38) and C(38)–C(39) are 1.42(3) and 1.44(3) Å respectively, which are slightly unsymmetrical. The equivalent bond distances in **21** are 1.40(2) and 1.46(2) Å respectively, which can be seen to be even more unsymmetrical. This coupled with the metal–carbon separations of 2.20(2), 2.20(2) and 2.10(2) Å in **16** and 2.29(1), 2.20(1), 2.07(1) Å in **21**, implies some degree of localised bonding from the platinum to C(39) in **16** and to the equivalent carbon atom in **21**, as shown in formalism **F** in Scheme 6.



Scheme 6

Examination of Fig. 3 shows that the geometry about the platinum atom is essentially square planar. There is a maximum deviation for C(37) of 0.086 Å from the least squares plane containing Pt(1), P(1), P(2), C(37) and C(39). The tilt angle (τ) and bow angle (β) are 122.85 and 93.17 ° respectively. These values are comparable with the tilt and bow angles for the cationic species $[Pt(\eta^3\text{-}C_3H_5)\{P(C_6H_{11})_3\}_2]^+$, which are 118.8 and 92.3 ° respectively.[18] The allyl function of the butadienyl moiety is essentially planar. The methyl group of the ethyl substituent is bent out of the allyl plane [dihedral angle C(37)–C(38)–C(41)–C(42) 22.72 °] onto the opposite side to the olefinic functional group. This olefinic group is also bent away from the allyl plane and away from the metal [dihedral angle C(37)–C(38)–C(39)–C(40) 137.06 °].

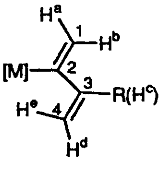
These same structural features as exhibited by **16** and **21** are also found in other (1,2,3-η)-*trans*-butadienyl complexes.[2] All have shorter metal–carbon bonds consistent with formalism **F**, but a significant contribution from **E** (Scheme 5) is also implied upon examination of the carbon–carbon interatomic distances (Table 2). It has been suggested[19] that, since the quaternary carbon in the butadienyl moiety has a low field chemical shift and a short metal–carbon bond distance, a small degree of carbenoid character for C(39) in **16** is implied, indicating a contribution from the zwitterionic formalism **G** (Scheme 6). Obviously the relative contribution from **E**, **F** and **G** in different complexes will be dependent on the metal, the butadienyl substituents and the other ligands.

In summary, a new synthetic pathway to cationic (1,2,3-η)-*trans*-butadienyl palladium and platinum complexes has been established, and their structural identity confirmed by NMR spectroscopy and single-crystal X-ray crystallography.

Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and further degassed before use where necessary. Reagents were obtained from commercial sources unless otherwise indicated. The ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded on Bruker AM360, JEOL GX270 and GX400 MHz FT spectrometers, as appropriate. Chemical shifts are referenced relative to tetramethylsilane and external H_3PO_4 respectively, with coupling constants in Hz. Data given are for room-temperature measurements unless otherwise stated. Infrared spectra were measured using a Perkin Elmer 983G spectrometer. Mass spectra (AEI MS902) and analytical data were obtained courtesy of the University of London and Bath Services.

Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ *with* $CH_2{=}C{=}C(Me)CH_2Cl$.—(*a*) *At room temperature*. A solution of $[Pt(C_2H_4)(PPh_3)_2]$ (0.20 g, 0.27 mmol) in tetrahydrofuran (thf) (10 cm^3) was stirred at room temperature for 15 min in the presence of a slight excess of the 4-chloro-3-methylbuta-1,2-diene, $CH_2{=}C{=}C(Me)CH_2Cl$ (0.032 g, 0.32 mmol). Volatile material was removed *in vacuo*, the residue dissolved in toluene (2 cm^3) and filtered through Celite. The solvent was removed *in vacuo* and the residue washed with diethyl ether–pentane (1:1) to give colourless microcrystals of *trans*-$[PtCl\{\sigma\text{-}C(CH_2)C(Me){=}CH_2\}(PPh_3)_2]$ **1** (0.195 g, 89%) (Found: C, 59.5; H, 4.6. $C_{41}H_{37}ClP_2Pt$ requires C, 59.9; H, 4.5%). NMR (CD_2Cl_2): ^1H, δ 7.77–7.36 (m, 30 H, C_6H_5), 5.99 [br d, 1 H, H^c, $J(H^cH^d)$ 3.2], 5.18 [s, 1 H, H^b, J(HPt) 125.0], 4.77 [br s, 1 H, H^a, J(HPt) 72.0], 4.60 (br s, 1 H, H^d) and 1.01 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 150.0 (br s, C^3), 148.2 [t, C^2, J(CP) 8.9], 135.5–128.0 (C_6H_5), 118.9 [s, C^1, J(CPt) 62.3], 117.3 (br s, C^4) and 19.6 (s, Me); $^{31}P\text{-}\{^1H\}$ δ 24.9 [s, PPh_3, J(PPt) 3227.5].



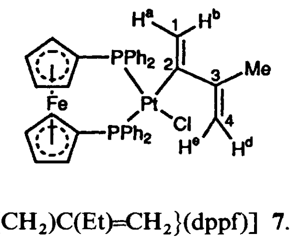
(*b*) *At low temperature*. A cooled (−78 °C) solution of $[Pt(C_2H_4)(PPh_3)_2]$ (0.03 g, 0.04 mmol) in CD_2Cl_2 (0.5 cm^3) contained in a 5 mm NMR tube was treated with $CH_2{=}C{=}C(Me)CH_2Cl$ (0.005 g, 0.05 mmol). The tube and contents was allowed to warm to −30 °C over a period of 30 min. Examination of the NMR spectra revealed resonances attributable to *cis*-$[PtCl\{\sigma\text{-}C(CH_2)C(Me){=}CH_2\}(PPh_3)_2]$ **2**. NMR (CD_2Cl_2): ^1H, δ 7.51–7.13 (m, 30 H, C_6H_5), 6.01 [br d, 1 H, H^c, $J(H^cH^d)$ 3.6], 5.47 [br d, 1 H, H^b, J(HP) 25.2], 5.06 [br d, 1 H, H^a, J(HP) 10.8], 4.97 (br s, 1 H, H^d) and 1.33 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 164.8 [dd, C^2, J(CP) 110.3, J(CP), 9.1], 149.6 (s, C^3), 134–129.7 (m, C_6H_5), 118.0 (C^4), 115.8 (C^1) and 20.7 (Me). On warming to room temperature the signals due to **2** were clearly replaced by resonances corresponding to the *trans*-isomer **1**.

Preparations of Other 2-σ-Bonded 3-Alkylbutadienyl Complexes.—*trans*-$[PtCl\{\sigma\text{-}C(CH_2)C(Et){=}CH_2\}(PPh_3)_2]$ **3**. Similarly, reaction (room temperature) of $[Pt(C_2H_4)(PPh_3)_2]$ (0.463 g, 0.62 mmol) with $CH_2{=}C{=}C(Et)CH_2Cl$ (0.075 g, 0.64 mmol) in thf (10 cm^3) gave white *crystals* of **3** (0.42 g, 81%) (Found: C, 60.0; H, 4.7. $C_{42}H_{39}ClP_2Pt$ requires C, 60.3; H, 4.7%). NMR (CD_2Cl_2): ^1H, δ 7.86–7.41 (m, 30 H, C_6H_5), 6.20 [br d, 1 H, H^c, $J(H^cH^d)$ 2.38], 5.36 [s, 1 H,H^b, J(HPt) 75.1], 4.88 [s, 1 H, H^a, J(HPt), 70.3], 4.71 (br s, 1 H, H^d), 1.31 [q, 2 H, CH_2CH_3, J(HH) 7.33] and 0.63 [t, 3 H, CH_2CH_3, J(HH) 7.33]; $^{13}C\text{-}\{^1H\}$, δ 154.8 [C^3, J(CPt) 30.9], 148.3 [t, C^2, J(CP) 8.8], 135.3–127.7 (C_6H_5), 116.6 [C^1, J(CPt) 62.7], 115.9 [br t, C^4 J(CP) 8.8], 24.9 [CH_2CH_3, J(CPt) 27.5] and 12.4 (CH_2CH_3); $^{31}P\text{-}\{^1H\}$, δ 24.2 [J (PPt) 3234.1].

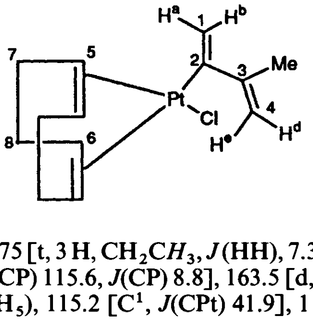
trans-$[PdCl\{\sigma\text{-}C(CH_2)C(Et){=}CH_2\}(PPh_3)_2]$ **4**. To a suspension of $[Pd(PPh_3)_4]$ (0.726 g, 0.62 mmol) in thf (20 cm^3) was slowly added $CH_2{=}C{=}C(Et)CH_2Cl$ (0. 10 g, 0.85 mmol). After 40 min stirring at room temperature the volatile material was removed *in vacuo* from the resulting dark grey suspension. The residue was dissolved in toluene and filtered through Celite. Removal of the solvent afforded an off-white solid which was washed with diethyl ether (4 x 30 cm^3) to give on drying *in vacuo* white *microcrystals* of **4** (0.35 g, 72%) (Found: C, 67.5; H, 4.6. $C_{42}H_{39}ClP_2Pd$ requires C, 67.5; H 5.3%). NMR (CD_2Cl_2): ^1H, δ 7.71–7.30 (m, 30 H, C_6H_5), 6.06 (br s, 1 H, H^c), 4.77 (br s, 1 H, H^b), 4.68 (br s, 2 H, H^a and H^d), 1.20 [br q, 2 H, CH_2CH_3, J(HH) 7.32] and 0.5 [t, 3 H, CH_2CH_3, J(HH) 7.32]; $^{13}C\text{-}\{^1H\}$, δ 163.2 (C^3), 153.7 (C^2), 135.1–127.9 (C_6H_5), 117.1 (C^1), 115.9 (C^4), 25.3 (CH_2CH_3) and 12.0 (CH_2CH_3); $^{31}P\text{-}\{^1H\}$, δ 24.4 (s, PPh_3).

trans-[PdCl{σ-C(CH$_2$)C(Me)=CH$_2$}(PPh$_3$)$_2$] **5**. A similar reaction between [Pd(PPh$_3$)$_4$] (0.03 g, 0.2 mmol) and CH$_2$=C=C(Me)CH$_2$Cl (0.032 g, 0.032 mmol) in thf (10 cm^3) afforded colourless *crystals* of **5** (0.17 g, 90%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.76–7.35 (m, 30 H, C$_6$H$_5$), 5.85 [br d, 1 H, H^e, *J*(HP) 2.6], 4.70 (s, 1 H, H^b) 4.65 (br s, 2 H, H^3) and 0.98 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 163.2(C^3), 149.0(C^2), 135.4–128.2 (C$_6$H$_5$), 119.6 (C^1), 117.4 (C^4) and 19.9 (Me); ^{31}P-{^{1}H}, δ 25.0 (s, PPh$_3$).

cis-[PtCl{σ-C(CH$_2$)C(Me)=CH$_2$}(dppf)] **6**. To a solution of [Pt(C$_2$H$_4$)(dppf)] (0.40 g, 0.52 mmol) in thf (10 cm^3) was added slowly CH$_2$=C=C(Me)CH$_2$Cl (0.06, 0.58 mmol). The colour changed from orange to pale orange. After 1 h at room temperature the volatiles were removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$ and filtered through Celite. Reduction of the volume of the solvent and addition of diethyl ether gave a yellow solid. This was collected and recrystallised from CH$_2$Cl$_2$–Et$_2$O to give yellow-orange *crystals* of **6** (0.36 g, 81%) (Found: C, 54.7; H, 4.3; C$_{39}$H$_{35}$ClFeP$_2$Pt requires C, 55.0; H, 4.1%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 8.05–7.05 (m, 20 H, Ph), 5.79 [br d, 1 H, H^e, *J* (H^{e}H^d) 3.11], 5.45 [d, 1 H, H^b, *J*(HP) 21.6, *J*(HPt) 51.3], 4.91 [d, 1 H, H^a, *J* (HP) 10.62, *J* (HPt) 43.18], 4.81 (br s, 2 H, C$_5$H$_4$), 4.76 (br s, 1 H, H^d), 4.52 (br s, 2 H, C$_5$H$_4$), 4.13 (br s, 2 H, C$_5$H$_4$), 4.13 (br s, 2 H, C$_5$H$_4$), 3.54 (br s, 2 H, C$_5$H$_4$) and 1.35 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 164.3 [dd, C^2, *J*(CP) 114.5, *J*(CP) 8.8], 149.3 [d, C^3, *J*(CP) 4.4], 135.5–127.1 (m, C$_6$H$_5$), 117.7 [C^1, *J*(CPt) 41.8], 115.7 (C^4), 76.6–52.8 (C$_5$H$_4$) and 20.8 [d, Me, *J*(CP) 6.7]; ^{31}P-{^{1}H}, δ 15.9 [d, *J*(PP) 15.8, *J*(PPt) 4573.7] and 14.5 [d, *J* (PP) 15.8, *J*(PPt) 1630.9].



cis-[PtCl{σ-C(CH$_2$)C(Et)=CH$_2$}(dppf)] **7**. Similarly, reaction of [Pt(C$_2$H$_4$)(dppf)] (0.30 g, 0.38 mmol) with CH$_2$=C=C(Et)CH$_2$Cl (0.06 g, 0.51 mmol) in thf (10 cm^3) gave on recrystallisation from CH$_2$Cl$_2$–Et$_2$O yellow-orange *crystals* of **7** (0.308 g, 92%) (Found: C, 55.5; H, 4.5. C$_{40}$H$_{37}$ClFeP$_2$Pt requires C, 55.5; H, 4.3%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 8.03–7.14 (m, 20 H, C$_6$H$_5$), 5.80 [d, 1 H, H^e, *J* (H^{e}H^d) 2.57], 5.49 [d, 1 H, H^b, *J* (HP) 22.17, *J*(HPt) 73.64], 4.88 [d, 1 H, H^a, *J*(HP) 10.8, *J*(HPt) 41.4], 4.75 (m, 3 H, 2 × C$_5$H$_4$, H^d), 4.50 (br s, 2 H, C$_5$H$_4$), 4.15 (br s, 2 H, C$_5$H$_4$), 3.43 (br s, 2 H, C$_5$H$_4$), 1.88 (br m, 1 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$) and 0.75 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$, *J* (HH), 7.33]; ^{13}C-{^{1}H}, δ 164.4 [dd, C^2, *J*(CP) 115.6, *J*(CP) 8.8], 163.5 [d, C^3, *J*(CP) 4.4], 135.6–127.0 (C$_6$H$_5$), 115.2 [C^1, *J*(CPt) 41.9], 114.2 [C^4, *J*(CP) 3.3], 76.6–71.9 (C$_5$H$_4$), 26.0 [$\mathit{C}\mathrm{H}_2\mathrm{CH}_3$, *J*(CP) 5.5] and 12.5 ($\mathrm{CH}_2\mathit{C}\mathrm{H}_3$); ^{31}P-{^{1}H} δ 15.8 [d, *J*(PP) 15.8, *J*(PPt) 29.3] and 14.6 [d, *J*(PP) 15.8, *J*(PPt) 3293.5].



[PtCl{σ-C(CH$_2$)C(Me)=CH$_2$}(cod)] **8**. An excess of CH$_2$=C=C(Me)CH$_2$Cl (0.199 g, 1.94 mmol) was added dropwise to a stirred solution of [Pt(cod)$_2$] (0.40 g, 0.97 mmol) in pentane (10 cm^3). After 10 min the supernatant liquid was removed, and the precipitate washed with pentane (3 × 5 cm^3) and dried *in vacuo* to give cream coloured *crystals* of **8** (0.304 g, 77%) (Found: C, 38.0; H, 4.4 C$_{13}$H$_{19}$ClPt requires C, 38.5; H 4.7%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 5.82 [s, 1 H, H^b, *J*(HPt) 81.0], 5.64 [m, 2 H, CH=CH of cod, *J*(HPt) 79.0], 5.46 [br d, 1 H, H^e, *J*(H^{e}H^d) 2.6], 5.01 [br d, 1 H, H^d, *J*(H^{d}H^e) 2.6], 4.87 [s, 1H, H^a, *J*(HPt) 41.1], 4.53 [m, 2 H, CH=CH of cod, *J*(HPt) 76.6], 2.44 (m, 8 H, CH$_2$CH$_2$ of cod) and 1.93 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 153.6 (C^2), 149.1 (C^3), 117.1 [C^1, *J*(HPt) 40.5], 115.7 (C^4), 100.7 [C^6, *J*(CPt) 153.5], 87.4 [C^5, *J*(CPt) 211.7], 32.0 [C^8, *J*(CPt) 25.0], 27.9 [C^7, *J*(CPt) 24.5] and 22.1 (Me). Mass spectrum: *m*/*z* 406 [*M*]$^+$ and 371 [*M* − Cl]$^+$.

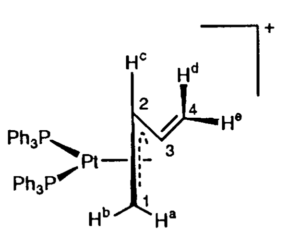
[PtCl{σ-C(CH$_2$)C(Et)=CH$_2$}(cod)] **9**. Similarly, reaction of an excess of CH$_2$=C=C(Et)CH$_2$Cl (0.096 g, 0.82 mmol) with [Pt(cod)$_2$] (0.170 g, 0.41 mmol) in pentane (5 cm^3) gave cream coloured *crystals* of **9** (0.094 g, 54%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 5.79 [s, 1 H, H^b, *J*(HPt) 84.7], 5.67 [br d, 1 H, H^e, *J*(H^{e}H^d) 2.8], 5.58 [m, 2 H, CH=CH of cod, *J*(HPt) 68.8], 4.92 [br d, 1 H, H^d, *J*(H^{d}H^c) 2.8], 4.83 [s, 1 H, H^a, *J*(HPt) 42.5], 4.53 (m, 2 H, CH=CH of cod, *J*(HPt) 78.9], 2.45 (m, 8 H, CH$_2$CH$_2$ of cod), 2.19 [q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$, *J*(HH) 7.3] and 1.05 [t, 3 H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_3$) 7.3]; ^{13}C-{^{1}H}, δ 156.0 (C^2), 148.9 (C^3), 115.6 [C^1, *J*(CPt) 42.5], 113.4 (C^4), 100.7 [C^6, *J*(CPt) 152.0], 87.5 [C^5, *J*(CPt) 213.7], 32.0 [C^8, *J*(CPt) 28.7], 27.9 [C^7, *J*(CPt) 25.8], 26.2 ($\mathit{C}\mathrm{H}_2\mathrm{CH}_3$) and 13.3 ($\mathrm{CH}_2\mathit{C}\mathrm{H}_3$).

Reactions of Complex **8**.—*With triphenylphosphine*. To a solution of **8** (0.15 g, 0.37 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added PPh$_3$ (0.194 g, 0.74 mmol). After stirring for 30 min at room temperature the volatiles were removed *in vacuo*, and the residue redissolved in toluene (5 cm^3) and filtered through Celite. Removal of the solvent under reduced pressure and washing the residue with diethyl ether–pentane (1:1) (3 × 10 cm^3) afforded colourless crystals of **1** (0.243 g, 80%), identical (^{1}H and ^{31}P-{^{1}H} NMR) with an authentic sample.

With 1,2-*bis*(*diphenylphosphino*)*ethane*. A similar reaction between **8** (0.14 g, 0.34 mmol) and (dppe) (0.147 g, 0.37 mmol) in CH$_2$Cl$_2$ (10 cm^3) afforded pale yellow *microcrystals* of [PtCl{σ-C(CH$_2$)C(Me)=CH$_2$} (dppe)] **10** (0.192 g, 80%) (Found: C, 53.1; H, 4.4. C$_{30}$H$_{31}$ClP$_2$Pt requires C, 53.5; H, 4.4%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.90–7.46 (m, 20 H, Ph), 5.86 [br d, 1 H, H^b, *J*(HP) 21.3, *J* (HPt) 80.6], 5.21 [br d, 1 H, H^e, *J*(H^{e}H^d) 3.5], 4.96 [br d, 1 H, H^a, *J*(HP) 14.8, *J*(HPt) 45.3], 4.53 (br s, 1 H, H^d), 2.18 (m, 4 H, $\mathrm{Ph}_2\mathrm{PC}\mathit{H}_2\mathrm{CH}_2$) and 1.58 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 167.3 [dd, C^2, *J*(CP) 108.4, *J*(CP) 7.3], 150.4 (C^3), 134.1–128.4 (m, C$_6$H$_5$), 118.6 [C^1, *J*(CPt) 45.0], 116.2 (C^4), 28.79 ($\mathrm{Ph}_2\mathrm{P}\mathit{C}\mathrm{H}_2$) and 22.0 [d, Me, *J*(CP) 4.4]; ^{31}P-{^{1}H}, δ 38.7 [*J*(PPt) 1661] and 35.7 [*J*(PPt) 4219].

With bis(*diphenylphosphino*)*methane*. Similarly, reaction of **8** (0.13 g, 0.32 mmol) with dppm (0.135 g, 0.35 mmol) in CH$_2$Cl$_2$ (10 cm^3) gave yellow *microcrystals* of [PtCl{σ-C(CH$_2$)C(Me)=CH$_2$}(dppm)] **11** (0.166 g, 76%) (Found: C, 52.9; H, 4.4. C$_{29}$H$_{29}$ClP$_2$Pt requires C, 52.8; H, 4.3%). NMR: ^{1}H (CDCl$_3$), δ 8.01–6.95 (m, 20 H, Ph), 5.73 [br d, 1 H^b, *J*(HP) 24.8, *J*(HPt) 79.3], 5.51 [br d, 1 H, H^e, *J*(H^{e}H^d) 3.5], 4.93 [br d, 1 H, H^a, *J*(HP) 17.5, *J*(HPt) 41.6], 47.9 (br s, 1 H, H^d), 4.26 (m, 2 H, $\mathrm{Ph}_2\mathrm{PC}\mathit{H}_2$), and 1.83 (s, 3 H, Me); ^{13}C-{^{1}H} (CDCl$_3$), δ 165.8 [dd, C^2, *J*(CP) 106.9, *J*(CP) 7.7], 149.0 (C^3), 135.3–129.6 (C$_6$H$_5$), 117.9 [C^1, *J*(CPt), 43.6], 115.8 (C^4), 43.2 ($\mathrm{Ph}_2\ \mathrm{P}\mathit{C}\mathrm{H}_2$) and 21.8 [d, Me, *J*(CP), 5.1]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ 43.2 [d, *J*(PP), 40.1, *J*(PPt) 1222] and 44.1 [d, *J*(PP) 40.1, *J*(PPt) 3799].

Preparation of 2-σ-*Bonded Butadienyl Complexes*.—*trans*-[PtCl{σ-C(CH$_2$)CH=CH$_2$}(PPh$_3$)$_2$] **12**. An excess of 2-chlorobuta-1,3-diene (0.04 g, 0.45 mmol) was added to a solution of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (0.14 g, 0.19 mmol) in chloroform (10 cm^3). The resulting mixture was stirred at room temperature for 2 h. The volatile material was removed *in vacuo*, and the residue extracted into CH$_2$Cl$_2$. Filtration through Celite, reduction of the volume of the solvent, followed by addition of diethyl ether gave a colourless solid. This was recrystallised from CH$_2$Cl$_2$–diethyl ether to give colourless *crystals* of **12** (0.091 g, 60%) (Found: C, 59.5; H, 4.3. C$_{40}$H$_{35}$ClP$_2$Pt requires C, 59.4; H, 4.4%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.80–7.35 (m, 30 H, C$_6$H$_5$), 5.67 [dd, 1 H, H^e, *J*(H^{e}H^c) 16.9, *J*(H^{e}H^d) 2.4], 5.33 [dd, 1 H, H^c,



J(H^{c}H^e) 16.9, *J*(H^{c}H^d) 10.0, *J*(HPt) 64.8], 5.11 [br s, 1 H, H^b, *J*(HPt) 126.2], 4.69 [br s, 1 H, H^a, *J*(HPt) 67.1] and 4.39 [dd, 1 H, H^d, *J*(H^{d}H^c) 10.0, *J* (H^{d}H^e) 2.1]; ^{13}C-{^{1}H}, δ 148.6 [t, C^2, *J*(CP) 8.4], 147.6 [C^3, *J*(CPt) 40.4], 135.8–127.8 (C_6H_5), 121.8 (C^4) and 116.6 [C^1, *J*(CPt) 61.0]; ^{31}P-{^{1}H}, δ 25.1 [*J*(PPt) 3166].

cis-[PtCl{σ-C(CH$_2$)CH=CH$_2$}(dppf)] **13**. In a similar way reaction of [Pt(C_2H_4)(dppf)] (0.29 g, 0.37 mmol) with 2-chlorobuta-1,3-diene (0.04 g, 0.45 mmol) in chloroform (10 cm^3) gave on recrystallisation from CH_2Cl_2–diethyl ether yellow-orange *crystals* of **13** (0.29 g, 93%) (Found: C, 53.8; H, 4.0. $C_{38}H_{33}ClFeP_2Pt$ requires C, 54.5; H, 4.0%). NMR: ^{1}H (CDCl$_3$), δ 8.08–7.12 (m, 20 H, C_6H_5), 6.09 (br m, 1 H, H^c), 5.66 [dd, 1 H, H^e, *J* (H^{e}H^c) 17.0, *J*(H^{e}H^d) 2.83], 5.41 [d, 1 H, H^b, *J*(HP) 20.33, *J*(HPt) 75.6], 4.85 [d, 1 H, H^a, *J*(HP) 10.7, *J*(HPt) 37.8], 4.78 (br s, 2 H, C_5H_4), 4.48 (br s, 2 H, C_5H_4), 4.09 (br s, 2 H, C_5H_4), 3.96 [dd, 1 H, H^d, *J* (H^{d}H^c) 10.16, *J*(H^{d}H^e) 2.83] and 3.47 (br s, 2 H, C_5H_4); ^{13}C-{^{1}H} (CD_2Cl_2), δ 164,3 [dd, C^2, *J*(CP) 123.4, *J*(CP) 8.9], 146.3 [d, C^3, *J*(CP) 4.5], 135.3–127.6 (C_6H_5), 119.9 (C^4), 116.0 [d, C^1, *J*(CP) 0.4, *J*(CPt) 39.6] and 76.3–72.4 (C_5H_4); ^{31}P-{^{1}H} (CD_2Cl_2), δ 16.3 [d, *J*(PP) 15.9, *J*(PPt) 4487.4] and 14.2 [d, *J*(PP) 15.9, *J*(PPt) 1668.6].

Preparation of (1,2,3-η)-trans *Butadienyl Complexes*.—[Pt{1,2,3-η)-*trans*-CH$_2$CHC=CH$_2$}(PPh$_3$)$_2$][PF$_6$] **14**. Thallium hexafluorophosphate (0.173 g, 0.50 mmol) was added to a stirred (room-temperature) solution of **12** (0.40 g, 0.50 mmol) in CH_2Cl_2 (10 cm^3). After 1 h the reaction mixture was filtered through Celite, the volume of the solvent reduced (*ca*. 5 cm^3) *in vacuo*, and diethyl ether added. The resultant precipitate was collected and recrystallised from CH_2Cl_2–diethyl ether to give white *crystals* of **14** (0.388 g, 85%) (Found: C, 52.6; H, 3.9. $C_{40}H_{35}F_6P_3Pt$ requires C, 52.4; H, 3.8%. NMR (CD_2Cl_2): ^{1}H, δ 7.53–7.14 (m, 30 H, C_6H_5), 5.70 [dd, 1 H, H^d, *J* (HP) 16.5, *J*(HP) 7.2, *J*(HPt) 4.2], 5.33 [br m, 1 H, H^c, *J*(HPt) 64.8], 4.14 [dq, 1 H, H^b, *J* (H^{b}H^c) 10.0, *J* (HP) = *J*(H^{b}H^a) 3.2], 3.95 [br d, 1 H, H^e, *J*(HP) 8.1, *J*(HP) 4.0] and 3.23 [dd, 1 H, H^a, *J*(H^{a}H^c) 14.3, *J*(HP) 7.8, *J*(HPt) 46.8]; ^{13}C-{^{1}H}, δ 168.6 [d, C^3, *J*(CP) 52.3], 134.7–129.0 (C_6H_5), 99.6 (C^4), 97.0 [C^2, *J*(CPt) 16.0] and 75.9 [d, C^1, *J*(CP) 23.5]; ^{31}P-{^{1}H}, δ 21.6 [d, *J*(PP) 10.2, *J*(PPt) 10.2, *J*(PPt) 4267], 13.6 [d, *J*(PP) 10.2, *J*(PPt) 3447] and −144.4 [spt, PF$_6$, *J*(PF) 711].

[Pt{(1,2,3-η)-*trans*-CH$_2$C(Me)C=CH$_2$}(PPh$_3$)$_2$][PF$_6$] **15**. Similarly, reaction of Tl[PF$_6$] (0.173 g, 0.50 mmol) with **1** (0.50 g, 0.50 mmol) in CH_2Cl_2 (10 cm^3) afforded colourless *crystals* of **15** (0.45 g, 86%) (Found: C, 52.4; H, 3.9. $C_{41}H_{37}F_6P_3Pt$ requires C, 52.9; H, 4.0%). NMR (CD_2Cl_2): ^{1}H, δ 7.47–7.20 (m, 30 H, C_6H_5), 5.61 [ddd, 1 H, H^d, *J*(HP) 17.4, *J*(HP) 7.3, *J*(H^{d}H^e) 3.2], 4.09 [br d, 1 H, H^b, *J*(HP) 10.5, *J*(HPt) 37.5], 3.70 [br s, 1 H, H^e), 3.35 [br d, 1 H, H^a, *J*(HP) 7.4, *J*(HPt) 32.4] and 2.13 [s, 3 H, Me, *J*(HPt) 66.4]; ^{13}C-{^{1}H}, δ 168.2 [d, C^3, *J*(CP) 54.5], 134.7–129.0 (C_6H_5), 116.7 (C^2), 99.6 (C^4), 75.8 [d, C^1, *J*(CP) 24.2, *J*(CPt) 75.0] and 23.8 [Me, *J*(CPt) 30.5]; ^{31}P-{^{1}H}, δ 23.4 [d, *J*(PP) 10.7, *J*(PPt) 4169], 15.8 [d, *J*(PP) 10.7, *J*(PPt) 3287] and −143.7 [spt, PF$_6$, *J*(PF) 711].

[Pt{(1,2,3-η)-*trans*-CH$_2$C(Et)C=CH$_2$}(PPh$_3$)$_2$][PF$_6$] **16**. In a similar way reaction of **3** (0.286 g, 0.34 mmol) with Tl[PF$_6$] (0.119 g, 0.34 mmol) in CH_2Cl_2 (10 cm^3) afforded on recrystallisation from CH_2Cl_2–diethyl ether white translucent *crystals* of **16** (0.22 g, 68%) (Found: 52.8; H, 4.2. $C_{42}H_{39}F_6P_3Pt$ requires C, 53.3; H, 4.2%). NMR (CD_2Cl_2): ^{1}H, δ 7.48–7.19 (m, 30 H, Ph), 5.60 [ddd, 1 H, H^d, *J*(HP) 17.76, *J*(HP) 7.32, *J*(H^{d}H^e) 2.57], 4.10 [dt, 1 H, H^e, *J*(HP) 10.62, *J*(HP) = *J*(H^{e}H^d) 2.57, *J*(HPt) 22.62], 3.69 (br s, 1 H, H^b), 3.34 [d, 1 H, H^a, *J*(HP) 7.69, *J*(HPt) 31.87], 2.39 (m, 2 H, C*H*$_2$CH$_3$) and 1.08 [t, 3 H, CH$_2$C*H*$_3$, *J*(HH) 7.51]; ^{13}C-{^{1}H}, δ 167.2 [dd, C^3, *J*(CP) 55.1, *J*(CP) 2.2, *J*(CPt) 304.6], 134.6–128.8 (C_6H_5), 120.8 [C^2, *J*(CPt) 33.1], 99.7 [d, C^4, *J*(CP) 3.3], 74.1 [d, C^1, *J* (CP) 24.2, *J*(CPt) 49.05], 29.9 [*C*H$_2$CH$_3$, *J*(CPt) 26.4] and 11.5 [CH$_2$*C*H$_3$, *J*(CPt) 41.9]; ^{31}P-{^{1}H}, δ 21.2 [d, *J*(PP) 11.8, *J*(PPt) 4168.5], 13.8 [d, *J*(PP) 11.8, *J*(PPt) 3281.4] and −145.3 [spt, PF$_6$, *J*(PF) 711].

[Pt{(1,2,3-η)-*trans*-CH$_2$CHC=CH$_2$}(dppf)][PF$_6$] **17**. Using an analogous procedure **13** (0.206 g, 0.25 mmol) was treated with Tl[PF$_6$] (0.086 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3). Crystallisation from CH_2Cl_2–diethyl ether yielded yellow-orange *crystals* of **17** (0.23 g, 96%) (C, 48.6; H, 3.5. $C_{38}H_{33}F_6FeP_3Pt$ requires C, 48.2; H, 3.5%). NMR [$(CD_3)_2CO$]: ^{1}H, δ 8.11–7.02 (m, 20 H, Ph), 5.67 (br s, 1 H, H^d), 5.32 (br s, 1 H, H^c), 4.61–4.44 (m, 6 H, C_5H_4), 4.39 (br s, 1 H, H^e), 4.36 (br s, 1 H, H^b), 4.05 (br s, 2 H, C_5H_4) and 3.86 (br s, 1 H, H^a); ^{13}C-{^{1}H}, δ 169.5 [d, C^3, *J*(CP) 52.9], 136.8–129.0 (C_6H_5, C^2), 99.9 (C^4), 99.0 [C^1, *J*(CPt) 33.0] and 78.3–74.6 (C_5H_4); ^{31}P-{^{1}H}, δ 22.5 [d, *J*(PP) 18.0, *J*(PPt) 4356], 14.8 [d, *J*(PP) 18.0, *J*(PPt) 3496] and −145.3 [spt, PF$_6$, *J*(PF) 711].

[Pt{(1,2,3-η)-*trans*-CH$_2$C(Me)C=CH$_2$}(dppf)][PF$_6$] **18**. Similarly, reaction of **6** (0.084 g, 0.09 mmol) with Tl[PF$_6$] (0.034 g, 0.09 mmol) in CH_2Cl_2 (5 cm^3) afforded on recrystallisation from CH_2Cl_2–diethyl ether yellow-orange *crystals* of **18** (0.087 g, 92%) (Found: C, 49.1; H, 3.7. $C_{39}H_{35}F_6FeP_3Pt$ requires C, 48.7; H, 3.7%). NMR (CD_2Cl_2): ^{1}H, δ 7.64–7.42 (m, 20 H, Ph), 5.62 (m, 1 H, H^d), 4.61 (br m, 3 H, C_5H_4), 4.47 (br m, 3 H, C_5H_4), 4.13 (br s, 1 H, H^e), 4.07 (br s, 1 H, C_5H_4), 4.02 (br s, 1 H, C_5H_4), 3.66 (br s, 1 H, H^b), 3.26 [d, 1 H, H^a, *J* (H^{a}H^b) 8.24, *J* (HPt) 41.6] and 2.08 [s, 3 H, Me, *J*(HPt) 65.92]; ^{13}C-{^{1}H}, δ 167.7 [d, C^3, *J*(CP) 57.0, *J*(CPt) 307.4], 134.8–129.0 (C_6H_5), 116.5 [C^2, *J*(CPt) 41.0], 99.4 (C^4), 76.6–75.3 (C_5H_4), 75.1 (C^1), 74.7–73.6 (C_5H_4) and 23.7 [Me, *J*(CPt) 29.0].

[Pt{(1,2,3-η)-*trans*-CH$_2$C(Et)C=CH$_2$}(dppf)][PF$_6$] **19**. In a similar way reaction of **7** (0.146 g, 0.17 mmol) with Tl[PF$_6$] in CH_2Cl_2 (10 cm^3) gave on crystallisation from CH_2Cl_2–diethyl ether yellow-orange *crystals* of **19** (0.138 g, 84%) (Found: C, 49.4; H, 3.8. $C_{40}H_{37}F_6FeP_3Pt$ requires C, 49.2; H, 3.8%). NMR (CD_2Cl_2): ^{1}H, δ 7.66–7.43 (m, 20 H, C_6H_5), 5.59 [ddd, 1 H, H^d, *J*(HP) 17.95, *J*(HP) 7.14, *J*(H^{d}H^e) 2.79, *J*(HPt) 74.37], 4.60–4.42 (m, 6 H, C_5H_4), 4.11 [dt, 1 H, H^e, *J*(HP) 10.8, *J*(HP) = *J*(H^{e}H^d) 2.79], 4.06–4.00 (m, 2 H, C_5H_4), 3.65 (br s, 1 H, H^b), 3.29 [d, 1 H, H^a, *J*(HP) 7.87, *J*(HPt) 31.33], 2.30 (m, 2 H, C*H*$_2$CH$_3$) and 0.97 [t, 3 H, CH$_2$C*H*$_3$, *J*(HH) 7.51]; ^{13}C-{^{1}H}, δ 167.0 [dd, C^3, *J*(CP) 57.3, *J*(CP), 2.2, *J* (CPt) 306.3], 135.0–128.8 (C_6H_5), 121.1 [C^2, *J*(CPt) 33.0], 99.8 [d, C^4, *J*(CP) 3.3], 76.5–72.2 (C_5H_4, C^1), 29.9 [*C*H$_2$CH$_3$, *J*(CPt) 26.4] and 11.3 [CH$_2$*C*H$_3$, *J*(CPt) 39.7]; ^{31}P-{^{1}H}, δ 21.8 [d, *J*(PP) 16.9, *J*(PPt) 4269.4], 14.9 [d, *J*(PP) 16.9, *J*(PPt) 3338.1] and −144.0 [spt, PF$_6$, *J*(PF) 7.11].

[Pd{(1,2,3-η)-*trans*-CH$_2$C(Et)C=CH$_2$}(PPh$_3$)$_2$][PF$_6$] **20**. To a solution of **4** (0.404 g, 0.54 mmol) in thf (10 cm^3) was added Tl[PF$_6$] (0.189 g, 0.54 mmol). Thallium(I) chloride precipitated from the reaction mixture which was stirred for 45 min at room temperature, and then filtered through Celite. The volume of the solvent was reduced *in vacuo* and diethyl ether added. The resultant yellow solid was washed with diethyl ether, until the washings were colourless, this procedure affording white *crystals* of **20** (0.322 g, 70%) (Found: C, 58.9; H, 4.6. $C_{43}H_{39}F_6P_3Pd$ requires C, 58.9; H, 4.5%). Storage of this complex in a dry oxygen-free nitrogen atmosphere at −30 °C protected from light, retarded slow decomposition of this compound. NMR (CD_2Cl_2): ^{1}H, δ 7.47–7.18 (m, 30 H, C_6H_5), 5.35 [ddd, 1 H, H^d, *J*(HP) 22.90, *J*(HP) 16.49, *J*(H^{d}H^e) 5.68], 3.93 [br d, 1 H, H^e, *J*(HP) 5.13], 3.91 (m. 1 H, H^b), 3.61 [br d, 1 H, H^a, *J*(HP) 8.42], 2.32 [dq, 2H, C*H*$_2$CH$_3$, *J*(HP) 1.92, *J*(HH) 7.51] and 1.10 [t, 3 H, CH$_2$C*H*$_3$, *J*(HH) 7.51]; ^{13}C-

Table 3 Fractional atomic coordinates for complex **7**

Atom	*x*	*y*	*z*
Pt	0.359 76(6)	0.175 42(9)	0.136 55(3)
Fe	0.012 4(2)	0.299 4(3)	0.114 6(1)
Cl	0 521 4(4)	0.234 9(5)	0.099 7(2)
P(1)	0 255 4(4)	0.257 4(5)	0.064 5(2)
P(2)	0.219 8(4)	0.114 2(6)	0.177 4(2)
C(2)	0.327 4(12)	0.448 8(14)	0.003 0(4)
C(3)	0.369 4(12)	0.566 8(14)	−0.004 2(4)
C(4)	0.394 5(12)	0.646 8(14)	0.036 4(4)
C(5)	0.377 6(12)	0.608 7(14)	0.084 3(4)
C(6)	0.335 6(12)	0.490 7(14)	0.091 4(4)
C(1)	0.310 5(12)	0.410 7(14)	0.050 8(4)
C(8)	0.344 7(10)	0.063 5(13)	0.012 0(4)
C(9)	0.350 4(10)	−0.013 8(13)	−0.028 9(4)
C(10)	0.273 3(10)	0.000 9(13)	−0.072 6(4)
C(11)	0.190 6(10)	0.093 0(13)	−0.075 3(4)
C(12)	0.184 9(10)	0.170 3(13)	−0.034 4(4)
C(7)	0.261 9(10)	0.155 5(13)	0.009 3(4)
C(13)	0.103 7(16)	0.286 1(20)	0.057 3(7)
C(14)	0.049 7(17)	0 406 8(22)	0.055 7(8)
C(15)	−0 072 2(18)	0.381 3(24)	0.051 8(8)
C(16)	−0.091 7(19)	0.256 9(25)	0.047 2(9)
C(17)	0.015 5(16)	0.193 7(23)	0.052 2(7)
C(18)	0.102 3(15)	0.218 0(20)	0.174 8(7)
C(19)	−0.017 2(16)	0.182 9(24)	0.172 0(7)
C(20)	−0.079 9(19)	0.302 3(25)	0.173 1(9)
C(21)	−0.003 3(21)	0.395 5(28)	0.178 7(10)
C(22)	0.109 8(16)	0.352 9(22)	0.180 3(7)
C(24)	0.174 2(12)	−0.082 5(14)	0.110 5(5)
C(25)	0.129 0(12)	−0.197 0(14)	0.094 5(5)
C(26)	0.066 3(12)	−0.264 8(14)	0.125 0(5)
C(27)	0.048 9(12)	−0.218 0(14)	0.171 5(5)
C(28)	0.094 1(12)	−0.103 4(14)	0.187 5(5)
C(23)	0.156 8(12)	−0.035 7(14)	0.157 0(5)
C(30)	0.316 9(12)	−0.016 9(12)	0.261 2(5)
C(31)	0.350 8(12)	−0.037 2(12)	0.312 2(5)
C(32)	0.323 4(12)	0.048 5(12)	0.347 3(5)
C(33)	0.262 1(12)	0.154 6(12)	0.331 3(5)
C(34)	0.228 2(12)	0.174 9(12)	0.280 2(5)
C(29)	0.255 6(12)	0.089 2(12)	0.245 2(5)
C(35)	0.476 6(22)	0.114 9(30)	0.196 2(10)
C(36)	0.506 6(20)	0.214 5(26)	0.237 1(9)
C(37)	0 535 0(30)	0.017 1(41)	0.193 3(14)
C(38)	0 500 9(22)	−0.066 0(29)	0.161 2(10)
C(39)	0.645 7(25)	0.005 5(33)	0.240 1(11)
C(40)	0 750 2(24)	0.073 7(31)	0 222 9(11)

Table 4 Fractional atomic coordinates for complex **16**

Atom	*x*	*y*	*z*
Pt	0.150 84(7)	0.169 28(4)	0.249 29(5)
P(1)	0.090 3(5)	0.097 4(2)	0.341 9(3)
P(2)	0.326 0(4)	0.198 9(3)	0.310 8(3)
P(3)	0.164 1(5)	0.666 8(4)	0.660 9(4)
F(1)	0.251 6(16)	0.666 3(10)	0.735 7(10)
F(2)	0.078 3(16)	0.667 7(10)	0.586 5(10)
F(3)	0.087 8(16)	0.619 2(9)	0.706 5(11)
F(4)	0.242 5(17)	0.714 3(9)	0.615 7(11)
F(5)	0.242 2(18)	0.617 5(9)	0.617 1(10)
F(6)	0.085 0(18)	0.714 4(9)	0.704 2(13)
C(1)	0.186 2(17)	0.032 3(9)	0.340 7(12)
C(2)	0.286 3(19)	0.029 5(10)	0.286 8(14)
C(3)	0.354 6(24)	−0.021 8(13)	0.285 3(17)
C(4)	0.327 5(22)	−0.069 6(12)	0.331 7(15)
C(5)	0.229 3(22)	−0.068 4(12)	0.387 2(15)
C(6)	0.159 5(19)	−0.016 1(10)	0.389 3(13)
C(7)	−0.053 3(19)	0.060 9(10)	0.325 3(13)
C(8)	−0.065 0(22)	0.023 7(12)	0.255 9(16)
C(9)	−0.176 9(25)	−0.004 0(13)	0.241 6(18)
C(10)	−0.270 9(28)	0.004 4(15)	0.292 3(19)
C(11)	−0.260 4(29)	0.044 5(15)	0.360 8(20)
C(12)	−0.151 1(22)	0.072 3(11)	0.378 2(15)
C(13)	0.076 2(16)	0.128 2(9)	0.449 2(11)
C(14)	0.020 4(18)	0.180 8(10)	0.452 2(12)
C(15)	−0.001 2(21)	0.205 8(11)	0.530 3(14)
C(16)	−0.038 6(21)	−0.176 2(12)	0.398 4(15)
C(17)	0.092 1(22)	0.126 4(12)	0.594 2(15)
C(18)	0.114 5(18)	0.096 4(10)	0.518 5(13)
C(19)	0.327 9(17)	0.275 8(9)	0.324 6(12)
C(20)	0.219 0(23)	0.306 5(12)	0.342 9(16)
C(21)	0.218 8(25)	0.366 8(14)	0.361 5(17)
C(22)	0.325 0(25)	0.399 3(13)	0.364 0(17)
C(23)	0.433 4(23)	0.371 2(13)	0.342 4(16)
C(24)	0.436 1(20)	0.311 3(10)	0.324 0(14)
C(25)	0.363 0(17)	0.173 6(11)	0.414 6(12)
C(26)	0.415 5(18)	0.118 6(10)	0.427 7(13)
C(27)	0.443 0(21)	0.099 2(11)	0.507 5(15)
C(28)	0.409 9(21)	0.130 6(12)	0.575 8(15)
C(29)	0.360 6(20)	0.188 4(11)	0.566 9(14)
C(30)	0.331 4(20)	0.209 7(10)	0.483 8(14)
C(31)	0.458 1(18)	0.181 0(10)	0.252 0(12)
C(32)	0.437 7(21)	0.158 1(11)	0.165 0(15)
C(33)	0.538 0(24)	0.144 5(12)	0.114 0(16)
C(34)	0.651 1(24)	0.150 9(12)	0.148 6(17)
C(35)	0.674 1(25)	0.171 1(15)	0.229 5(18)
C(36)	0.570 9(20)	0.184 8(11)	0.285 0(14)
C(37)	−0.016 6(17)	0.167 1(11)	0.177 2(12)
C(38)	0.078 8(18)	0.183 2(10)	0.123 1(13)
C(39)	0.156 6(20)	0.229 8(11)	0.150 8(14)
C(40)	0.206 7(23)	0.276 1(12)	0.125 1(16)
C(41)	0.116 4(24)	0.144 2(12)	0.047 3(16)
C(42)	0.078 5(31)	0.082 8(17)	0.049 0(22)

{^{1}H}, δ 173.2 [dd, C^3, *J*(CP) 52.9, *J*(CP) 4.4], 134.3–129.0 (C_6H_5), 120.8 (C^2), 99.3 (C^4), 81.9 [d, C^1, *J*(CP) 24.2], 29.4 ($\mathit{C}H_2CH_3$) and 12.0 ($CH_2\mathit{C}H_3$).

Structure Determination of Complexes 7 *and* **16**.—Both data sets were measured at room temperature on a Hilger and Watts Y290 four-circle diffractometer. A crystal of **7** of approximate dimensions 0.25 × 0.25 × 0.25 mm was used for data collection.

Crystal data: $C_{40}H_{37}ClFeP_2Pt$, *M* = 865.99, monoclinic, *a* = 11.896(1), *b* = 10.821(3), *c* = 26.959(4) Å, β = 98.17(2) °, *U* = 3435.1 Å^3, space group $P2_1/c$, *Z* = 4, D_c = 1.67 g cm^{-3}, μ(Mo-Kα) = 44.84 cm^{-1}, *F*(000) = 1712. Data were measured in the range 2 ⩽ θ ⩽ 22°. 4718 Reflections were collected of which 2501 were unique with $I \geqslant 3\sigma(I)$. Data were corrected for Lorentz and polarization effects and also for absorption.[20] The structure was solved by Patterson methods and refined using the SHELX[21,22] suite of programs. In the final least-squares cycles the platinum, iron, chlorine and phosphorus atoms were allowed to vibrate anisotropically. All other atoms were treated isotropically. Hydrogen atoms were not included. Final residuals after 14 cycles of least squares were *R* = *R′* = 0.0587, for unit weights. Maximum final shift/e.s.d. was 0.007. The maximum and minimum residual densities were 0.52 and −0.54 e Å^{-3} respectively. Selected bond lengths and angles are given in Table 1 and fractional atomic coordinates in Table 3.

A crystal of **16** of approximate dimensions 0.25 × 0.25 × 0.25 mm was used for data collection.

Crystal data: $C_{42}H_{39}F_6P_3Pt$, $M = 945.66$, monoclinic, $a = 11.174(2)$, $b = 22.611(6)$, $c = 16.003(2)$ Å, $\beta = 89.76(2)°$, $U = 4043.2$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.55$ g cm^{-3}, μ(Mo-Kα) = 34.75 cm^{-1}, $F(000) = 1872$. Data were measured in the range $2 \leqslant \theta \leqslant 22°$. 5790 Reflections were collected of which 3308 were unique with $I \geqslant 3\sigma(I)$. Data were corrected for Lorentz and polarization effects and also for absorption.[20] The structure was solved by Patterson methods and refined using the SHELX[21,22] suite of programs. In the final least-squares cycles the platinum, phosphorus and fluorine atoms were allowed to vibrate anisotropically. All other atoms were treated isotropically. Hydrogen atoms were not included. The cationic and anionic moieties were treated as separate blocks in the latter stages of convergence. Final residuals after 14 cycles of blocked-matrix least squares were $R = R' = 0.0690$, for unit weights. Maximum final shift/e.s.d. was 0.010. The maximum and minimum residual densities were 0.81 and -0.71 e Å^{-3} respectively in the region of the platinum, and as such have no chemical significance. Selected bond lengths and angles are given in Table 2 and fractional atomic coordinates are given in Table 4.

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

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