Ligand-substitution Reactions of Neutral and Cationic Allyl(cyclo-octa-1,5-diene)platinum Complexes

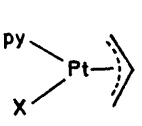
By **Neil M. Boag, Michael Green, John L. Spencer,** and **F. Gordon A. Stone,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Treatment of the compound $[PtX(\sigma\text{-}C_3H_5)(cod)]$ (X = Cl or Br; cod = cyclo-octa-1,5-diene) with pyridine (py) affords $[PtX(\eta^3\text{-}C_3H_5)(py)]$. In solution these complexes dimerise to form allyl-bridged binuclear species. Reaction of the complex $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ with allyl halides, or reaction of $[PtX(\sigma\text{-allyl})(cod)]$ (X = Cl, allyl = C_3H_5 or C_3H_4Ph-3; X = Br, allyl = C_3H_5 or C_3H_4Me-3) with 1 mol of $P(C_6H_{11})_3$ affords the compounds $[PtX(\eta^3\text{-allyl})\{P(C_6H_{11})_3\}]$. Addition of 2 mol of PPh_3 or $P(C_6H_{11})_3$, or 1 equivalent of $Ph_2PCH_2CH_2PPh_2$ (dppe), affords complexes of the type $[PtX(allyl)L_2]$. Treatment of the salts $[Pt(\eta^3\text{-allyl})(cod)][BF_4]$ (allyl = C_3H_5 or C_3H_4Me-3) with py, PPh_3, or dppe gives $[Pt(\eta^3\text{-allyl})(L_2)][BF_4]$ (L_2 = 2py, $2PPh_3$, or dppe). In contrast, 1 mol of PPh_3 followed by 1 equivalent of CO, Bu^tNC, or py yields the complexes $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)L][BF_4]$ (L = CO, $CNBu^t$, or py) possibly *via* the intermediacy of $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)][BF_4]$. Excess of Bu^tNC or py affords the σ-allylic species $[Pt(\sigma\text{-}C_3H_5)(PPh_3)L_2][BF_4]$. In a similar manner, the tris(trimethyl phosphite) complexes $[Pt(\sigma\text{-allyl})\{P(OMe)_3\}_3][BF_4]$ (allyl = C_3H_5, C_3H_4Me-3, or C_3H_4Ph-3) have been synthesised. Detailed n.m.r. studies (^1H, ^{13}C, ^{31}P, variable-temperature) of these complexes has led to an understanding of their behaviour in solution.

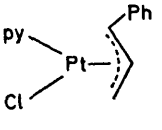
We have previously reported [1] that addition of bis-(cyclo-octa-1,5-diene)platinum to an excess of an allylic halide affords complexes of the type $[PtX(\sigma\text{-allyl})(cod)]$. These species undergo a halide-abstraction reaction with silver tetrafluoroborate to afford the cationic complexes $[Pt(\eta^3\text{-allyl})(cod)][BF_4]$. In both the neutral and cationic species the cyclo-octa-1,5-diene (cod) ligand is labile, providing a synthetic route to a wide range of σ- and η^3-allylic complexes. In this paper we describe such a study, and the elucidation by n.m.r. spectroscopy of the dynamic behaviour of these molecules in solution.

RESULTS AND DISCUSSION

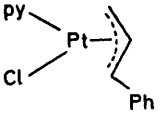
Pyridine (py) rapidly displaces cyclo-octa-1,5-diene from $[PtX(\sigma\text{-}C_3H_5)(cod)]$ (X = Cl or Br) to form the monomeric η^3-allyl species (1) and (2), analogous to the previously described [2] 2-methylallyl complex. The



X
(1) Cl
(2) Br



(3a)

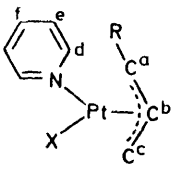


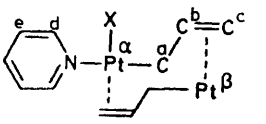
(3b)

structures of these compounds followed from an examination of their n.m.r. spectra. Comparison of the ^{13}C n.m.r. spectra (Table 1) of (1) and (2) allowed assignments to be made for the allylic carbon atoms. Whereas the carbon *trans* to pyridine (C^c) hardly shifts, the allyl carbon *trans* to the halide (C^a) moves *ca.* 3 p.p.m. to lower field when Cl is exchanged for Br. The assignment is supported by the larger coupling constants of carbon C^a, in accord with the smaller *trans* influence of halide relative to pyridine. The central allyl carbon C^b is observed at lower field. The greater coupling constants of the allyl carbons C^a, C^b, and C^c in these complexes, compared with those in the spectra of $[Pt(\eta^3\text{-allyl})(cod)][BF_4]$,[1] are probably due to the electronic properties of the pyridine and halide ligands. Since the complexes (1) and (2) are not cationic, the increased electron density on the metal may also be of importance.

TABLE 1

Carbon-13 n.m.r. data [a] for complexes (1)—(5)





Complex	X	R	δ/p.p.m. a	b	c	d	e	f
(1)	Cl	H	47.5	99.3	40.2	152.6	125.7	138.1
			(267)	(88)	(223)	(15)	(37)	(10)
(2)	Br	H	50.5	99.1	39.9	152.9	125.7	137.9
			(258)	(85)	(212)	(16)	(38)	(11)
(3) [b]	Cl	Ph	65.6	96.1	37.6	151.2	125.7	137.6
			(242)	(90)	(245)			(7)
(4) [c]	Cl	H	12.6	96.9	55.6	151.8	125.9	137.8
			{592}	{68}]	{21}		(20)	
				[170]	[248]			
(5) [c]	Br	H	11.3	98.7	57.9	152.0	125.7	137.6
			{583}	{70}	{35}		(17)	
				[164]	[255]			

[a] Measured in $[^2H_1]$chloroform. Chemical shifts (δ) in p.p.m. relative to $SiMe_4$, positive values to high frequency; $J(PtC)$ in Hz given in parentheses. [b] Not isolated, see text. Ph shifts: 120.0, 127.0, 128.8, and 129.1 p.p.m. [c] Coupling to Pt^α given in braces, to Pt^β in square brackets.

Evidence for a possible equilibrium in solution between the complexes (1) and (2) and the species $[PtX(\sigma\text{-}C_3H_5)(cod)]$ was revealed during an attempt to prepare a pure sample of the cinnamyl compound $[PtCl(\eta^3\text{-}C_3H_4Ph\text{-}3)(py)]$ (3). The ^{13}C n.m.r. spectrum of the product showed signals corresponding to the presence of approximately equimolar amounts of the pyridine- and the cod-substituted species, due perhaps to the bulkiness of the terminal phenyl group favouring an σ-allyl bonding

mode. While the proposed equilibrium must also occur with the unsubstituted allyl ligand, the lack of steric hindrance displaces it in favour of (1) or (2).

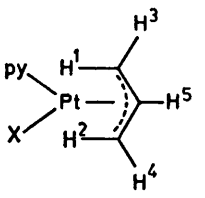
The ^{13}C n.m.r. spectrum of complex (3) (Table 1) was obtained from the mixture and assigned as follows. Terminal substitution on an allyl ligand decreases the platinum–carbon coupling constant of the substituted carbon and also shifts its resonance to lower field.[1] Hence the signal at 65.6 p.p.m. can be assigned to C^a. Correspondingly, the resonance of the unsubstituted carbon atom moves to higher field and J(PtC) increases, as occurs for C^c. Assuming the allyl ligand is the *syn* isomer, since it was derived from the *trans*-CH_2CH=CHPh group, two possible isomers (3a) and (3b) could exist. However, since the signal (37.6 p.p.m.) ascribed to the unsubstituted carbon C^c is at higher field than those of the allyl carbons (C^a) *trans* to halide in complexes (1) and (2), and J(PtC) is smaller, it suggests that this carbon is *trans* to the pyridine ligand, *i.e.* the isomer present is probably (3a).

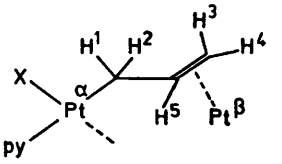
The ^1H n.m.r. spectra of complexes (1) and (2) were easily analysed (Table 2), and show that the species are non-fluxional at ambient temperatures. The geminal pairs of protons were readily identified since a small geminal coupling between H^1 and H^3 was evident in the chloride complex (1.5 Hz). This was not resolved in the corresponding bromide, but the relevant resonances broadened. Since alterations in shifts on changing the halide were more pronounced for the protons H^1 and H^3, these are assigned as being *trans* to the halide.

Another equilibrium in solution was observed for complexes (1) and (2) as a result of the extended data-collection times required for the ^{13}C spectra. Initially clear solutions changed over 2 h to produce fine pale yellow precipitates accompanied by the appearance of several small additional peaks in the ^{13}C spectrum of the monomer. Molecular-weight measurements on these new complexes revealed that they were dimeric, while the appearance of a single Pt–Cl band at 323 cm^{-1} in the i.r. spectrum of the chloro-compound ruled out the presence of halide bridges.[3] The presence of a bridging allyl group was thus suspected in the dimers, as observed previously in the complexes $[\{Pt(acac)(\mu\text{-}C_3H_5)\}_2]$ [4] and $[\{PtCl(\mu\text{-}C_3H_5)\}_4]$.[5] The relatively high value of the Pt–Cl i.r. stretching frequency suggests that the Cl ligand is *trans* to an η^2-olefinic bond, as illustrated, rather than to a platinum–carbon σ bond.[6]

TABLE 2

Hydrogen-1 n.m.r. data for the complexes (1), (2), (4), and (5)





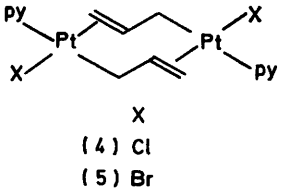
Complex	X	τ[a] H[1]	H[2]	H[3]	H[4]	H[5]	py resonances		
(1)	Cl	7.65 (d of d), J(H[3]) 1.5, J(H[5]) 11, J(Pt) 68	7.67 (d), J(H[5]) 11, J(Pt) 82	6.22 (d of d), J(H[1]) 1.5, J(H[4]) 6, J(Pt) 34	6.15 (d), J(H[3]) 6, J(Pt) 24	5.34 (d of d of d of d), J(H[1]) 11, J(H[2]) 11, J(H[3]) 6, J(H[4]) 6, J(Pt) 84	1.08 (m, 2 H), J(Pt) 35	2.12 (m, 1 H)	2.57 (m, 2 H)
(2)	Br	7.71 (d), J(H[5]) 11.5, J(Pt) 67	7.66 (d), J(H[5]) 11, J(Pt) 81	6.11 (d), J(H[5]) 6, J(Pt) 33	6.17 (d), J(H[5]) 6, J(Pt) 22	5.37 (d of d of d of d), J(H[1]) 11.5, J(H[2]) 11, J(H[3]) 6, J(H[4]) 6, J(Pt) 83	1.08 (m, 2 H), J(Pt) 35	2.13 (m, 1 H)	2.58 (m, 2 H)
(4)[b]	Cl	7.89 (d of d), J(H[2]) 8, J(H[5]) 12 {57}	7.21 (d of d), J(H[1]) 8, J(H[5]) 5 {82}	6.33 (d), J(H[5]) 13 [78]	6.74 (d), J(H[5]) 8, {18} [88]	5.33 (m), [66]	0.96 (m, 2 H)	2.22 (m, 1 H)	2.57 (m, 2 H)
(5)[b]	Br	7.84 (d of d), J(H[2]) 8, J(H[5]) 12 {59}	7.23 (d of d), J(H[1]) 8, J(H[5]) 5 {89}	6.25 (d), J(H[5]) 13 [79]	6.68 (d), J(H[5]) 8 {18} [88]	5.18 (m), [66]	0.97 (m, 2 H)	2.22 (m, 1 H)	2.57 (m, 2 H)

[a] Measured in $[^2H_1]$chloroform at 26 °C, coupling constants in Hz. [b] J(Pt$^\alpha$) in braces, J(Pt$^\beta$) in square brackets; assignment of H^1 and H^2 may be reversed, see text.

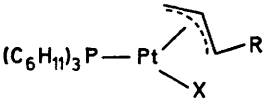
By allowing solutions of the monomers (1) and (2) to stand at room temperature overnight, it proved possible to obtain solutions of the equilibrium mixture, which contained a high enough concentration of the dimers to allow measurement of their ^{13}C spectra (Table 1). Thus the C^a absorption was detected at 12.6 p.p.m. in the spectrum of complex (4) with J(Pt$^\alpha$–C^a) being 592 Hz, both values being characteristic of an sp^3 carbon σ-bonded to platinum.[7] The peak at 96.9 p.p.m. is assigned to C^b, the upfield shift of the signal compared to that found in the spectra of the σ-allyl complexes [PtX(σ-allyl)(cod)] being indicative of olefinic co-ordination.[7] The resonance for C^c is therefore that observed at 55.6 p.p.m. The coupling of C^c to Pt$^\alpha$ (21 Hz) is smaller than that of C^b to the same platinum

(68 Hz). While the coupling of Pt^{β} to C^{b} (170 Hz) is within the observed range of platinum(II)–olefin coupling constants (160–200 Hz),[8] that of 248 Hz for C^{c} is rather larger. This might suggest that some delocalisation of the olefinic bond has taken place, with a resultant increase in the σ component of the Pt^{α}–C^{c} bond.

The ^{1}H n.m.r. spectra of complexes (4) and (5) are complex and were difficult to analyse (Table 2). As a result of the molecular structures, the methylene protons H^{1} and H^{2} are inequivalent. This allows assignment of these protons, since a geminal coupling of *ca.* 8 Hz was present. Definitive assignment of H^{1} and H^{2} was not possible, and the tabulated values could well be reversed. The olefinic protons H^{3} and H^{4} were distinguished by their different coupling constants to H^{5}, the central allylic proton. As in the ^{13}C n.m.r. spectra, platinum coupling constants to the olefinic protons were rather large. Only the resonance due to H^{4} shows identifiable coupling to both platinums, although the complicated splitting pattern of H^{5} would probably hide a small through-chain coupling.



X
(4) Cl
(5) Br



	X	R
(7)	Cl	H
(8)	Br	H
(9)	Br	Me
(10)	Cl	Ph

Treatment of $[PtCl(\eta^{3}\text{-}C_{3}H_{5})(cod)]$ with an equimolar amount of 2,2′-bipyridyl afforded a water-soluble ionic complex (6), which on the basis of analysis and i.r. and n.m.r. spectroscopy (see Experimental section) was assigned the molecular formula $[Pt(\eta^{3}\text{-}C_{3}H_{5})(bipy)]Cl$, with a symmetrically bonded η^{3}-allyl ligand.

Reaction of bis(ethylene)(tricyclohexylphosphine)-platinum with allylic halides gave the η^{3}-allylic species (7)—(10) (Table 3). These complexes can be prepared more readily by treating the compounds $[PtX(\sigma\text{-allyl})(cod)]$ with 1 mol equivalent of tricyclohexylphosphine. In contrast to the reaction of $[PtCl(\sigma\text{-}C_{3}H_{4}Ph\text{-}3)(cod)]$ with pyridine, which only resulted in partial displacement of the cod ligand (see earlier), treatment of this compound

TABLE 3

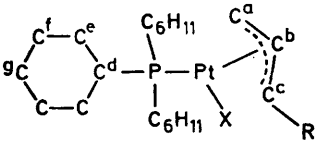
Analytical [a] and physical data for the complexes $[PtX(\eta^{3}\text{-}C_{3}H_{4}R\text{-}3)L]$

	Complex [b]	M.p. (θ_{c}/°C)	Yield (%)	Analysis (%) C	Analysis (%) H
(7)	$[PtCl(\eta^{3}\text{-}C_{3}H_{5})\{P(C_{6}H_{11})_{3}\}]$	177—178 (decomp.)	55	45.7 (45.7)	7.1 (6.9)
(8)	$[PtBr(\eta^{3}\text{-}C_{3}H_{5})\{P(C_{6}H_{11})_{3}\}]$	180—181	69	42.5 (42.3)	6.6 (6.4)
(9)	$[PtBr(\eta^{3}\text{-}C_{3}H_{4}Me)\{P(C_{6}H_{11})_{3}\}]$	174—176 (decomp.)	50	43.0 (43.3)	6.5 (6.6)
(10)	$[PtCl(\eta^{3}\text{-}C_{3}H_{4}Ph)\{P(C_{6}H_{11})_{3}\}]$	178—179	74	51.4 (51.6)	6.9 (6.7)
(11)	$[PtCl(\eta^{3}\text{-}C_{3}H_{5})(PPh_{3})]$		68	47.1 (47.2)	3.9 (3.8)
(12)	$[PtCl(\eta^{3}\text{-}C_{3}H_{4}Me)(PPh_{3})]$		62	48.4 (48.2)	4.2 (4.1)

[a] Calculated values are given in parentheses. [b] All compounds are white.

TABLE 4

Carbon-13 and ^{31}P n.m.r. data for the complexes $[PtX(\eta^{3}\text{-}C_{3}H_{4}R\text{-}3)L]$



Complex	L	R	X	^{13}C (δ) [a] a	b	c	d	e	f	g	Me	$^{31}P(\delta)$ [b]
(7)	$P(C_{6}H_{11})_{3}$	H	Cl	39.0	106.3	69.5	34.2	27.5	29.7	26.4		35.2 [c]
				(225)	(43)	(39) [28]	(39) [28]	[11]	(23)			(4 252)
(8)	$P(C_{6}H_{11})_{3}$	H	Br	42.5	106.0	69.3	34.7	27.5	29.8	26.5		33.8
				(267)	(38)	(38) [29]	(40) [28]	[11]	(24)			(4 281)
(9)	$P(C_{6}H_{11})_{3}$	Me	Br	36.5	106.3	88.2	35.4	27.5	30.0	26.5	16.9	36.7
				(303)	(38)	(8) [24]	(44) [28]	[11]	(26)			(4 517)
(10) [d]	$P(C_{6}H_{11})_{3}$	Ph	Cl	35.3	101.4	90.0	34.7	27.6	29.8	26.5		37.0
				(288)	(43)	(13) [27]	(28) [28]	[11]	(26)			(4 458)
(11)	PPh_{3}	H	Cl	48.3	103.7	68.5						
				(250)	(46)	(55) [32]						
(12)	PPh_{3}	Me	Cl	42.9	109.4	88.7					16.4	23.5 [e]
				(286)	(44)	(25) [28]						(4 752)

[a] Measured in $[^{2}H_{1}]$chloroform at 26 °C. Chemical shifts (δ) in p.p.m. relative to $SiMe_{4}$, positive values to high frequency. Coupling constants in Hz, J(PtC) given in parentheses and J(PC) in square brackets. [b] Measured in $[^{2}H_{6}]$benzene at 26 °C unless otherwise stated. Chemical shifts (δ) in p.p.m. relative to 85% $H_{3}PO_{4}$ external (0.0 p.p.m.). Coupling constants J(PPt) in Hz given in parentheses. [c] In $[^{2}H_{1}]$chloroform, signal at 35.2 p.p.m. (4 276Hz). [d] Ph signals at 137.7 [6], 128.2, 127.6, and 127.0 p.p.m. [e] Measured in $[^{2}H_{1}]$chloroform.

with tertiary phosphines completely displaced the cyclo-octa-1,5-diene.

This substitution reaction also proved successful for the synthesis of the known complexes [PtCl(η^3-C_3H_4R-3)(PPh_3)] [R = H (11) or Me (12)] (Table 3).

Two crystalline forms of [PtCl(η^3-C_3H_5){$P(C_6H_{11})_3$}] (7) were observed. These proved to be interconvertible upon recrystallisation. One of the species was isostructural with the bromide (8), having an identical fingerprint region in the i.r. spectrum, but since $\nu_{max.}$(PtCl) occurs at the same wavenumber (298 cm^{-1}) in both forms of (7), and the ^{31}P n.m.r. spectra proved identical, it is likely the structural difference lies in the crystal.

The ^1H n.m.r. spectra of complexes (7)—(10) were dominated by the large absorption of the cyclohexyl group which obscured several of the ill defined resonances. The ^{13}C spectral investigation proved more revealing and provided details of the stereochemistry and bonding of the allyl groups (Table 4). The central carbon (C^b) resonance at 101—106 [PR_3 = $P(C_6H_{11})_3$] and 104—109 p.p.m. (PR_3 = PPh_3) occurs further downfield than the other allyl signals and is comparable to the values found (96—99 p.p.m.) for the pyridine species (Table 1). As in the case of the pyridine complexes, the introduction of a terminal phenyl group causes a small upfield shift of the central carbon (C^b, 106 to 101 p.p.m.), but, since a downfield shift is observed on addition of a terminal methyl group in the triphenylphosphine complexes (104 to 109 p.p.m.), and no shift occurs for the corresponding tricyclohexylphosphine system, it must be concluded that this effect is rather subtle. The nucleus C^c is readily identified due to a substantial phosphorus coupling, the C^a signal showing no such coupling. A small phosphorus splitting (6 Hz) at the point of attachment of the carbon of the phenyl ring in complex (10) also implies that the Ph substituent is *trans* to the phosphine ligand. A similar stereochemistry probably occurs with (12) since in its ^1H n.m.r. there is coupling between phosphorus and the Me group. This complex was isolated as the *syn* isomer, the proton n.m.r. being identical to that for the complex isolated by Kurosawa and Yoshida.[9]

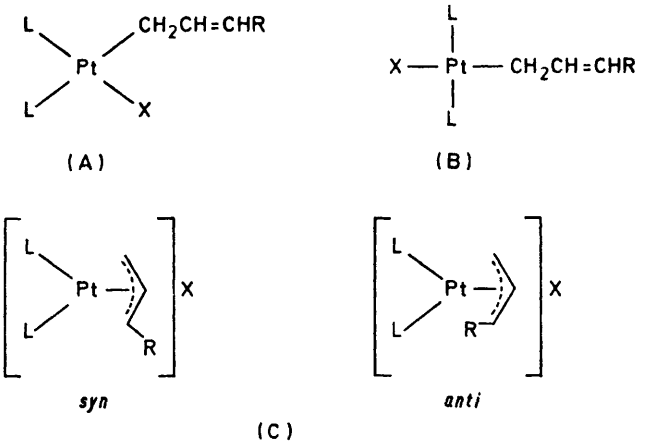
TABLE 5

Analytical [a] data for the complexes [$PtX(C_3H_4R)L_2$] [b]

	Complex [c]	Yield (%)	Analysis (%) C	H
(13)	[$PtCl(C_3H_5)(PPh_3)_2$]	84	58.6 (58.8)	4.3 (4.4)
(14)	[$PtCl(C_3H_4Me)(PPh_3)_2$]	76	59.0 (59.3)	4.5 (4.6)
(15)	[$PtBr(C_3H_4Me)(PPh_3)_2$]	84	56.4 (56.2)	4.5 (4.4)
(16)	[$PtCl(C_3H_4Ph)(PPh_3)_2$]	90	61.7 (62.0)	4.5 (4.5)
(17)	[$PtCl(C_3H_4Me)\{P(C_6H_{11})_3\}_2$]	28	56.3 (56.8)	9.1 (8.7)
(18)	[$PtCl(C_3H_5)$(dppe)]	81	52.0 (54.2)	4.4 (4.7)
(19)	[$PtCl(C_3H_4Me)$(dppe)]	74	52.2 (52.7)	4.7 (4.6)

[a] Calculated values are given in parentheses. [b] For bonding mode of allyl ligands see text. [c] All complexes are colourless except (16) which is yellow.

Addition of 2 mol equivalents of a tertiary phosphine [PPh_3 or $P(C_6H_{11})_3$], or addition of 1 equivalent of the chelating ligand 1,2-bis(diphenylphosphino)ethane (dppe), to the compounds [PtX(σ-allyl)(cod)] afforded the crystalline complexes (13)—(19), which analysed (Table 5) for species of the general formula [$PtX(allyl)L_2$]. Complexes of this stoicheiometry are generally fluxional and cationic with η^3-allyl ligands undergoing *syn–anti* exchange, and much interest has been shown in their dynamic behaviour, in particular, the nature of the dynamic intermediate. Kurosawa and Yoshida[9] have demonstrated that a non-ionic σ-allyl intermediate (A) of *cis* stereochemistry is of importance.



Stereochemistry of the allyl complexes (13)—(19)

Examination of the ^{31}P n.m.r. spectra of complexes (13)—(15) in dichloromethane at −80 °C (Table 6) revealed that these species exist in the ionic form (C), their spectra being almost identical with the corresponding tetrafluoroborate salts (see later, and Table 7). However, the ^{31}P n.m.r. spectrum of the cinnamyl derivative (16) is not analogous to those of the other compounds. Although broad and ill defined signals were observed at ambient temperatures, cooling revealed the presence of two species. The minor product, with resonances consisting of a pair of doublets at 18.9 and 22.3 p.p.m., was readily identified as the isomer with an σ-allyl ligand and *cis* stereochemistry (A). This assignment follows from the observation of the small J(PP) of 13 Hz on both signals, and the magnitude of J(PPt) on the resonance at 22.3 p.p.m. The coupling of 2 538 Hz is as expected for a phosphine ligand *trans* to a σ-bonded cinnamyl group on account of the latter's large *trans* influence.[10]

Since only a singlet is observed (28.0 p.p.m.) for the major species, an ionic structure (C) can be excluded for this component which must therefore be the isomer with the *trans* configuration (B). An ionic isomer of configuration (C) could not be detected by ^{31}P n.m.r. spectroscopy for this complex. However, it is likely that the major dynamic process observed is interconversion of the *cis* and *trans* isomers (A) and (B) of (16) *via* an ionic intermediate (C) the latter species apparently being only present in very small amounts.

This argument involving *cis–trans* isomer conversion

can be extended to complexes (13)—(15) with less bulky allyl groups. In these compounds the neutral species [(A) and (B)] evidently exist in very small and undetectable concentrations in CH_2Cl_2 solution because the cationic η^3-allyl form is now favoured. Rapid interconversion of *cis* and *trans* σ-allyl isomers (A) and (B), with concomitant *syn–anti* exchange, provides a valid explanation of the observed ^{31}P and ^{1}H (ref. 9) spectra. If the argument based on observation of the cinnamyl complex (16) is extended, then, of the two neutral σ isomers, the *trans* species (B) may be expected to be present in larger proportions than isomer (A). This would explain why, when neutral allyl complexes have been isolated and studied by *X*-ray crystallography,[10,11] only *trans* structures, *i.e.* (B), have been found. The failure to isolate even one example of a *cis*-σ-allyl isomer (A), even though Kurosawa and Yoshida [9] have presented evidence for their existence, is thus understandable as being due to the low concentration of this species in solution.

Support for this hypothesis comes from the ^{31}P n.m.r. spectrum of the unsubstituted-allyl complex (13) measured in toluene–[$^2H_6$]benzene at −80 °C (Table 6) which shows only a single resonance at 27.9 p.p.m. [*J*(PtP) 3 218 Hz]. By comparison with the cinnamyl complex (16) this signal is due to the species *trans*-[$PtCl(\sigma\text{-}C_3H_5)(PPh_3)_2$].

Since the substitution of a methyl by a phenyl group at the 3-position of the allyl moiety has such a large effect on isomer distribution, a bis(tricyclohexylphosphine) crotyl species (17) was prepared in order to ascertain if the use of sterically demanding phosphorus ligands would enable the observation of a σ species in a crotyl (but-2-enyl) complex. A ^{31}P n.m.r. study (Table 6) revealed that the complex was formed solely in its *trans*-σ-$CH_2CH{=}CHMe$ form (B). Rather unexpectedly, complex (17) exhibits no dynamic behaviour even at 26 °C. This is possibly due to the steric interactions which would arise if the complex adopted the *cis*-phosphine configuration required for the dynamic η^3-$CH_2CHCHMe$ intermediate (C).

TABLE 6

Phosphorus-31 n.m.r. data [a] for the complexes $[PtX(C_3H_4R)L_2]$

					δ				
					trans to	*trans* to	*trans* to	*trans* to η^3-allyl	
Complex	L_2	R	X	Isomer [b]	halide	σ-allyl	phosphine		
(13)	2 PPh_3	H	Cl	(C)				15.9	
				(B) [c]			27.9	(3 933)	
							(3 218)		
(14)	2 PPh_3	Me	Cl	(C) (*syn*)				20.2	17.4
								(3 884)	(4 133) [9]
				(C) (*anti*)				17.7	16.0
								(3 980)	(3 840) [11]
(15)	2 PPh_3	Me	Br	(C) (*syn*)				20.3	17.2
								(3 895)	(4 136) [9]
				(C) (*anti*)				17.8	16.0
								(3 980)	(3 840) [10]
(16)	2 PPh_3	Ph	Cl	(B)			28.0		
							(3 284)		
				(A)	18.9	22.3			
					(4 490) [13]	(2 538) [13]			
(17) [d]	2 $P(C_6H_{11})_3$	Me	Cl	(B)			18.3		
							(2 914)		
(18)	dppe	H	Cl	(C)				47.5	
								(3 696)	
				(A)	43.5	45.2			
					(4 341)	(1 823)			
				(A) [e]	44.8	39.2			
					(3 629)	(1 796)			
(19)	dppe	Me	Cl	(C) (*syn*)				48.5	46.7
								(3 679)	(3 784)
				(A)	44.3	41.9			
					(4 398)	(1 758)			
				(A) [e]	45.1	38.0			

[a] Measured in [$^2H_2$]dichloromethane–CH_2Cl_2 at −80 °C unless otherwise stated. Chemical shifts (δ) in p.p.m. relative to 85% H_3PO_4 (0.0 p.p.m.). Coupling constants in Hz with *J*(PtP) in parentheses and *J*(PP) in square brackets. [b] See discussion in text. [c] Measured in [$^2H_6$]benzene–C_6H_5Me at −80 °C. [d] Measured in [$^2H_2$]dichloromethane–CH_2Cl_2 at 26 °C. [e] Measured in [$^2H_8$]toluene at −80 °C.

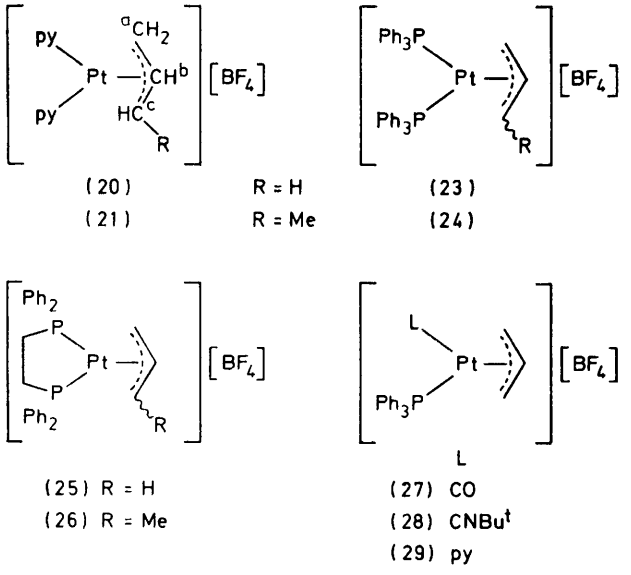
The dppe complexes (18) and (19) are incapable of forming *trans* isomers of type (B). However, the low-temperature ^{31}P n.m.r. spectra reveal the presence of both cationic η^3-allyl species (C) and neutral *cis*-σ-allyl isomers (A). While the presence of the neutral complex $[PtCl(\sigma\text{-}C_3H_5)(dppe)]$ was just detectable the crotyl derivative consisted of *ca.* 75% of the isomer [PtCl-(σ-$CH_2CH{=}CHMe$)(dppe)]. The cationic species were again identified by comparison of the ^{31}P n.m.r. spectra with those of the tetrafluoroborate salts (25) and (26) discussed below. The ready detection of the neutral σ-allyls is perhaps not surprising when the isolation of the isostructural cationic species [Pt{σ-$CH_2C(Me){=}$

CH_2}($PMePh_2$)(pdma)][PF_6] [pdma = *o*-phenylenebis(dimethylarsine)] is considered.[12]

The cyclo-octa-1,5-diene-displacement reactions of the cationic species [Pt(η^3-allyl)(cod)][BF_4] were next examined. Addition of pyridine to dichloromethane solutions of [Pt(η^3-C_3H_5)(cod)][BF_4] and [Pt(η^3-C_3H_4-Me-3)(cod)][BF_4] gave, respectively, the white crystalline air- and solution-stable cationic complexes (20) and (21). Unlike the parent compounds, these species were found to be non-fluxional in solution. The ^{1}H n.m.r. spectrum (Experimental section) of the crotyl derivative (21) shows it to be the *syn* isomer like its precursor, by virtue of the coupling (11 Hz) between the resulting *anti* proton and the central hydrogen. An unusual feature of the ^{1}H n.m.r. spectra of the compounds is the infrequently observed geminal coupling between the *syn*- and *anti*-protons (2 Hz). The ^{13}C n.m.r. spectra show the usual changes in shift from allyl to crotyl, the C^a signal shifting slightly upfield (45 to 41 p.p.m.) and the resonance for C^c moving downfield (45 to 61 p.p.m.).

2,2′-Bipyridyl also reacts with [Pt(η^3-C_3H_5)(cod)][BF_4] yielding [Pt(η^3-C_3H_5)(bipy)][BF_4] (22). This complex is insoluble in all solvents, and identification rests solely on microanalytical and i.r. data.

Two equivalents of triphenylphosphine or 1 equivalent of dppe readily reacted with the salts [Pt(η^3-C_3H_4R-3)(cod)][BF_4] (R = H or Me) to afford the complexes



(20) R = H (23)
(21) R = Me (24)

(25) R = H
(26) R = Me

(27) CO
(28) $CNBu^t$
(29) py

(23)—(26), characterised by elemental analysis and by ^{31}P n.m.r. spectroscopy (Table 7). The compounds (23) and (24) have been previously reported [9] and the 2-methylallyl analogue of the dppe species (25) and (26) has been isolated as its hexafluorophosphate salt.[12] Complexes (24) and (26) exist as a mixture of *syn* and *anti* isomers, this being demonstrated quite clearly by their ^{31}P n.m.r. spectra. The isomerisation probably occurs during the synthesis, since the isolated *syn* or *anti* complexes undergo *syn–anti* exchange very slowly if at all.[9] The isomer ratio for (24) (20% *anti*, 80% *syn*) is identical with that found for the corresponding chloride which does undergo *syn–anti* hydrogen exchange [9] on the n.m.r. time scale. The isomeric mixture for the dppe species (26) contains rather less of the *anti* isomer, the ^{1}H n.m.r. spectrum showing only *ca.* 5% present.

Reactions of equimolar amounts of [Pt(η^3-C_3H_5)(cod)][BF_4] and triphenylphosphine afforded a product containing equal amounts of starting material and (23).

TABLE 7

Phosphorus-31 n.m.r. data [a] for the complexes [Pt(η^3-C_3H_4R-3)L_2][BF_4]

Complex	L_2	R	δ [b]	
(23) [c]	2 PPh_3	H	15.9 (3 933)	
(24)	2 PPh_3	Me (*syn*)	20.2 (3 885)	17.4 (4 128) [10]
		(*anti*)	17.7 (4 015)	16.0 (3 809) [11]
(25)	dppe	H	47.5 (3 702)	
(26)	dppe	Me (*syn*)	48.4 (3 685)	46.5 (3 781) [9]
		(*anti* [d])	47.0 (3 655) [6]	

[a] Measured at −80 °C in [$^2H_2$]dichloromethane–CH_2Cl_2 unless otherwise stated. [b] Hydrogen-1 decoupled chemical shifts in p.p.m. to high frequency of 85% H_3PO_4 (external). Coupling constants in Hz with J(PtP) in parentheses, and J(PP) in square brackets. [c] Measured in [$^2H_1$]chloroform at −60 °C. [d] Other resonance not observed due to overlapping with signals of the *syn* form.

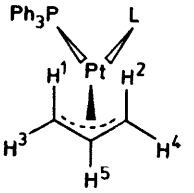
However, when carbon monoxide was bubbled through the solution a new compound [Pt(η^3-C_3H_5)(CO)(PPh_3)][BF_4] (27) was isolated. This reaction was found to be general, and similar complexes (28) and (29) were prepared using equimolar amounts of Bu^tNC or py. Since it has been observed [13] that reactions of [PtCl(η^3-C_3H_5)(PPh_3)] with Ag[ClO_4] in the presence of CO afford the perchlorate analogue of (27), it is possible that in all of these reactions a 14-electron species [Pt(η^3-C_3H_5)(PPh_3)][BF_4] is captured by either CO, Bu^tNC, or py.

Compounds (27) and (28) are stable, both in the solid state and in solution; details of their proton n.m.r. spectra are given in Table 8. However, the pyridine species (29) underwent slow dissociation in solution leading to rather poor quality spectra. Invariably protons H^1 and H^3 occurred at higher field than H^2 and H^4, respectively, this being most obvious in the pyridine complex (29). The protons *trans* to the phosphine were readily identified by their characteristic phosphorus coupling.

The dissociative processes occurring with (29) are of interest since approximately equimolar amounts of (20) and (23) were detected in its n.m.r. spectrum. This suggests that initially dissociation of pyridine occurs, forming [Pt(η^3-C_3H_5)(PPh_3)][BF_4]. This species then reacts with free phosphine to form (23). However, since pyridine is most unlikely to displace phosphine directly, a four-co-ordinate σ-allyl species (30) formed by pyridine addition has to be postulated. Phosphine can then dissociate with concomitant formation of complex

TABLE 8

Hydrogen-1 n.m.r. data [a] for the complexes $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)L][BF_4]$

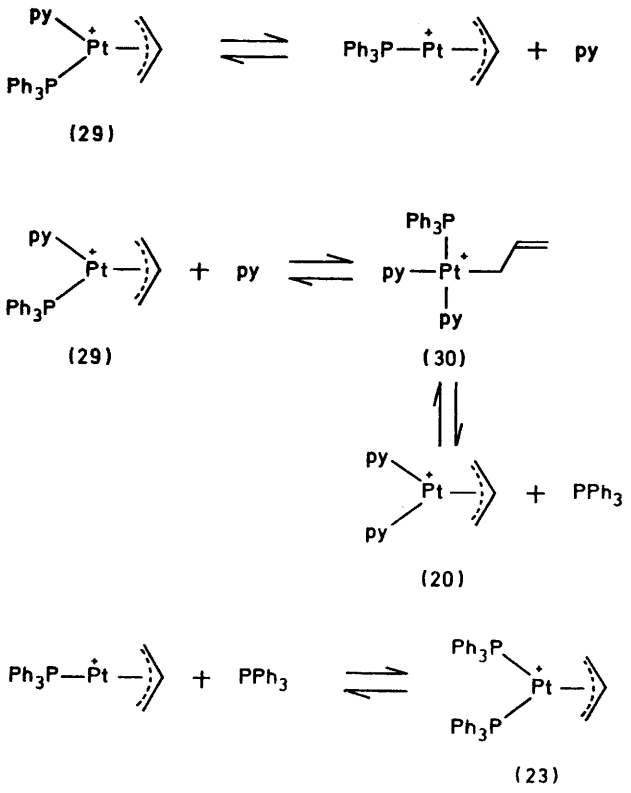


Complex	L	τ H¹	H²	H³	H⁴	H⁵
(27) [b]	CO	6.90 (d of d), J(H³) 3, J(H⁵) 13, J(PtH) 38	6.01 (d of d), J(H⁵) 14, J(PH) 8, J(PtH) 26	5.80 [c] (d of d), J(H¹) 3, J(H⁵) 7	4.51 (d of d), J(H⁵) 3, J(PH) 3	4.14 (m), J(PtH) 65
(28) [d]	CNBu^t	7.22 (d of d), J(H³) 2, J(H⁵) 13, J(PtH) 45	6.70 (d of d), J(H⁵) 13, J(PH) 9, J(PtH) 35	6.17 [e] (d of d), J(H¹) 2, J(H⁵) 7	4.97 (d of d), J(H⁵) 4, J(PH) 4	4.63 (m), J(PtH) 61
(29) [e]	py	7.31 (d of d), J(H³) 3, J(H⁵) 12, J(PtH) 67	6.46 [c] (d of d), J(H⁵) 13, J(PH) 9	6.52 [e] (m), J(H¹) 3	5.35 [e,f] (br,m), J(H⁵) 3	4.54 (m), J(PtH) 68

[a] Measured in $[^2H_1]$chloroform at 26 °C, coupling constants in Hz. [b] τ 2.38—2.62 (m, 15 H, Ph). [c] J(PtH) unobserved. [d] τ 2.36—2.70 (m, 15 H, Ph) and 8.71 (s, 9 H, Bu^t). [e] τ 1.66 [m, 2 H, py, J(Pt) 37 Hz], 2.34 (m, 1 H, py), and 2.50—2.84 (m, 17 H, Ph + py). [f] J(PH) unobserved.

(20). The free phosphine then reacts with the 14-electron species to give (23) as illustrated in Scheme 1.

All the processes appear to be fairly slow on the n.m.r. time scale, since signals due to complexes (20), (23), and



SCHEME 1

(29) could be observed simultaneously. However, it is likely that the first equilibrium is the rate-determining step. Proof of this was found by treatment of equimolar amounts of triphenylphosphine and $[Pt(\eta^3\text{-}C_3H_5)(cod)][BF_4]$ with excess of pyridine. This afforded the σ-allyl intermediate (30). The σ-bonding mode was indicated by a C=C band at 1 614 cm^{-1} in the i.r., and a resonance at 8.1 p.p.m. [J(PtC) 360 Hz] in the ^{13}C n.m.r. spectrum due to the allyl–platinum contact carbon. The *cis* stereochemistry at the metal centre is proven by the lack of phosphorus coupling to the signal at 8.1 p.p.m. and a value of 4 269 Hz for J(PtP). A phosphine *trans* to a ligand with a large *trans* influence such as a σ-allyl [10] would have a coupling constant of less than 3 000 Hz. Complex (30) also readily dissociates in solution affording compounds (23) and (29) in appreciable amounts a few minutes after dissolution. Ultimately (29) and trace amounts of (23) are the final products detected by ^{31}P n.m.r. spectroscopy.

It was observed that the cinnamyl analogue (31) of (30), which was prepared in a similar manner, was more stable, dissociation in solution only being evident after several hours. This difference in stability may be due to the reluctance of the cinnamyl group to form η^3 complexes as has been demonstrated for $[PtCl(\eta^3\text{-}C_3H_4Ph\text{-}3)(py)]$ (3) (see earlier).

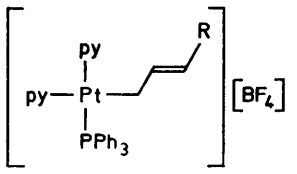
The salt (28) reacts further with Bu^{t}NC to give the σ-allyl complex (32). The *trans* disposition of the isocyanide ligands is demonstrated by a single band in the i.r. at 2 208 cm^{-1}, a single ^{1}H n.m.r. resonance (τ 8.73) for the tertiary butyl group, and a relatively small platinum–phosphorus coupling constant (1 476 Hz). The presence of the σ-allyl group is indicated by an i.r. band at 1 616 cm^{-1} and the ^{13}C n.m.r. spectrum which shows the allyl sp^3 carbon (17.0 p.p.m.) as a doublet [J(PC) 68, J(PtC) 382 Hz].

The ^{1}H and ^{13}C n.m.r. spectra show that complex (32) is fluxional at ambient temperatures. The broadening of the ^{31}P n.m.r. spectrum at 27 °C indicates that phosphorus dissociation is occurring. This is borne out by the loss of phosphorus coupling to the methylene hydrogens at this temperature. Since, on cooling the n.m.r. samples, signals of the original static complex are

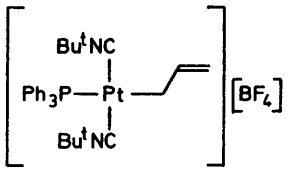
observed, it would appear that the only equilibrium present involves fairly slow phosphine dissociation, *viz.* equation (1). However, a fluxional process involving a

$$cis\text{-}[Pt(\sigma\text{-}C_3H_5)(CNBu^t)_2(PPh_3)]^+ \rightleftharpoons [Pt(\eta^3\text{-}C_3H_5)(CNBu^t)_2]^+ + PPh_3 \quad (1)$$

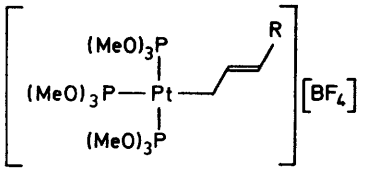
five-co-ordinate intermediate cannot be excluded (see later). The limiting high-temperature spectrum could not be obtained, since (32) is converted into other species above 60 °C which were not investigated further.



(30) R = H
(31) R = Ph



(32)



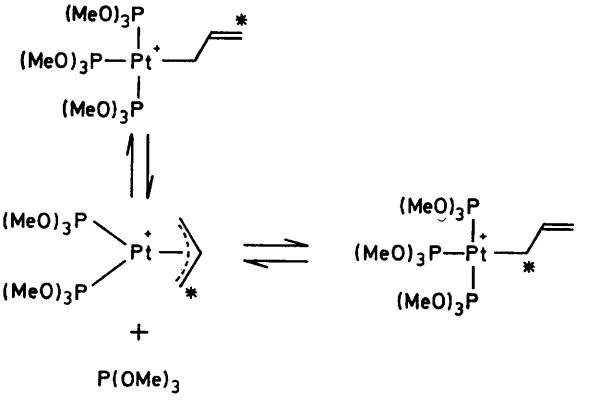
(33) R = H
(34) R = Me
(35) R = Ph

Unlike tertiary phosphines, addition of an excess of trimethyl phosphite to the cations $[Pt(\eta^3\text{-allyl})(cod)][BF_4]$ affords the tris(trimethyl phosphite)(σ-allyl)platinum salts (33)—(35). Complex (33) was the first member of the series to be synthesised and, at first, proved a structural enigma. An absorption at 1 618 cm^{-1} [$\nu_{max.}$(C=C)] in the i.r. spectrum of this complex demonstrated that it was an σ-allyl species and microanalysis was consistent with the formula $[Pt(\sigma\text{-}C_3H_5)\{P(OMe)_3\}_3][BF_4]$. Solutions of complex (33) smelt strongly of free phosphite and measurement of the ^{31}P n.m.r. spectrum at 26 °C showed no distinct resonance, both factors being indicative of phosphite dissociation. Such a process should produce equivalence of the ends of the allyl moiety (Scheme 2). The ^{13}C n.m.r. spectrum of complex (33) at 26 °C confirmed this equivalence, with only a single resonance at 65.5 p.p.m. [J(PtC) 203 Hz] being observed for the terminal allyl carbons. The absence of a phosphorus coupling to this signal is also indicative of phosphite exchange on the platinum.

At −90 °C the ^{31}P n.m.r. spectrum sharpened to a singlet at 115.8 p.p.m., the platinum satellites [J(PtP) 4 097 Hz] showing that phosphite dissociation had ceased. The singlet in the ^{13}C n.m.r. spectrum due to the terminal allyl carbons had broadened at this temperature. However, changing the solvent from $[^2H_6]$-acetone to $[^2H_2]$dichloromethane resolved this resonance into a quartet. This splitting [J(PC) 16 Hz] arises from coupling to three equivalent trimethyl phosphite ligands. The dominant factor which produced this resolution was later proved to be the temperature rather than the solvent.

These low-temperature spectra are inconsistent with a static square-planar structure, as in for example $[PtH\{P(OPh)_3\}_3][BF_4]$,[14] and a fluxional process with a low activation energy must be invoked. The concomitant exchange of the ends of the allyl moiety with phosphite scrambling affords some insight into the mechanism. It is envisaged that a five-co-ordinate trigonal-bipyramidal intermediate is first formed, the fifth site being occupied by the double bond of the allyl group. The allylic double bond is then delocalised to form a trigonal-bipyramidal η^3-allyl complex which can undergo Berry pseudo-rotations. This equilibrates both the trimethyl phosphites and the ends of the allyl moiety (Scheme 3). A similar process can be invoked to explain the dynamic behaviour of $[Pt\{\sigma\text{-}CH_2C(Me)=CH_2\}(PMePh_2)(pdma)][PF_6]$ [12] between −10 and −70 °C.

The complexes (34) and (35) show no evidence of phosphite scrambling through a five-co-ordinate intermediate. This is probably due to the steric hindrance of the substituent groups. At low temperatures the ^{31}P n.m.r. spectra of these complexes consist of an AB_2 pattern, as expected for a static square-planar structure. However, like complex (33), the cations (34) and (35) undergo phosphite dissociation upon warming their solutions and the ^{31}P n.m.r. signals broaden. Examination of the ^{13}C n.m.r. spectra confirms this. Whereas, at −90 °C, four-bond phosphorus–carbon coupling



SCHEME 2

(9 Hz) to the *trans*-trimethyl phosphite ligand can be observed along the allyl chain in (34), no phosphorus coupling is observed at 26 °C. The ^{13}C n.m.r. spectra are also consistent with an σ-allyl formulation, the sp^3-carbon resonance having, at 26 °C, a shift of 17.2 p.p.m. in complex (34) with a relatively large J(PtC) of 374 Hz. At −90 °C a phosphorus–carbon coupling of 96 Hz is observed. Analogous results are found for the cinnamyl derivative (35), although, as a result of the bulky phenyl substituent inhibiting η^3-allyl formation, phos-

phite exchange is slower and fully dynamic ^{13}C and ^{1}H n.m.r. spectra are not obtained until 90 °C.

The ^{1}H n.m.r. spectrum of the crotyl complex (34) reveals an *E* configuration for the allyl group, the olefinic hydrogens affording an approximate ABX_2 resonance with J(AB) 14 Hz. The ^{31}P n.m.r. spectrum at −90 °C also reveals the presence of a small amount of *cis* isomer (<1%). It is assumed that an *E* stereochemistry is adopted by the PhCH=CHCH$_2$Pt group of (35); however, the required proton–proton coupling constant could not be measured.

EXPERIMENTAL

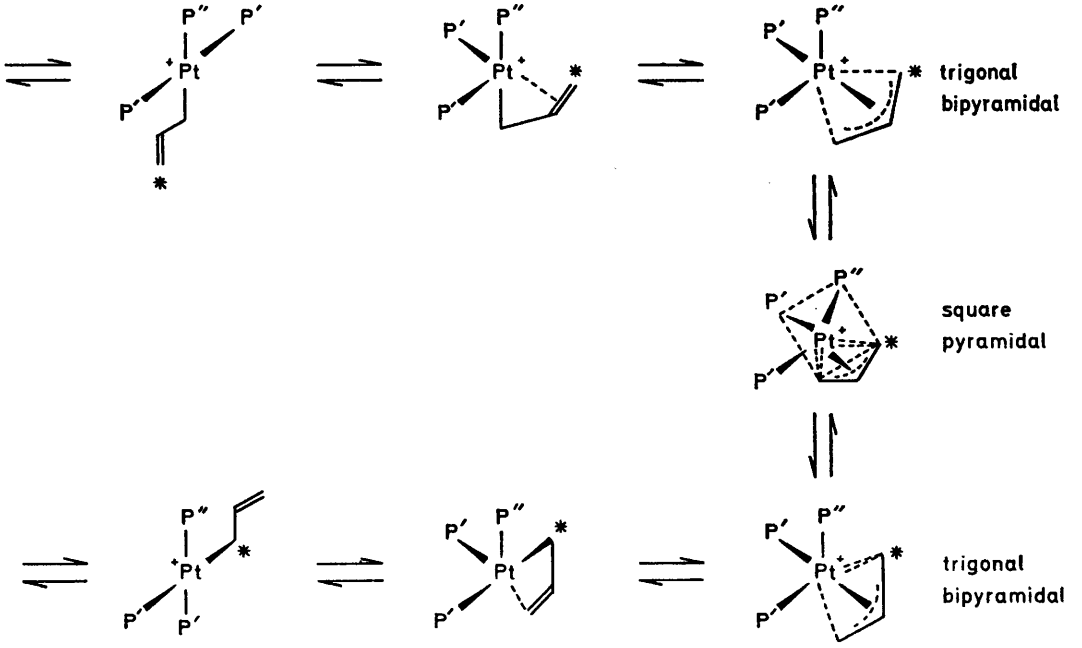
The instrumentation used and techniques employed were as previously described.[1] Carbon-13 chemical shifts in p.p.m. are relative to $SiMe_4$, positive values to high frequency. Phosphorus-31 chemical shifts in p.p.m. are to high frequency of 85% H_3PO_4 (external). All n.m.r. spectra were measured at room temperature unless otherwise stated. Infrared spectra were recorded as Nujol mulls unless otherwise stated.

Light petroleum refers to that fraction of b.p. 30—40 °C. The complexes [PtX(σ-allyl)(cod)] (X = Cl or Br; allyl = C_3H_5, C_3H_4Me-3, or C_3H_4Ph-3) and [Pt(η^3-allyl)(cod)][BF_4] used as starting materials were prepared as described earlier.[1] Analytical data for the new compounds (7)—(19) are given in Tables 3 and 5, and for the other compounds are given below.

Preparations of the Complexes.—[PtX(η^3-C_3H_5)(py)]. To a suspension of [PtCl(σ-C_3H_5)(cod)] (0.19 g, 0.5 mmol) in toluene (5 cm^3) was added excess of py (0.2 cm^3). The solution immediately cleared and, after 30 s, light petroleum was added to afford white *plates* of [PtCl(η^3-C_3H_5)(py)] (1) (0.17 g, 94%), m.p. 143—144 °C (decomp.) [Found: C, 27.5; H, 3.0; N, 4.0%; *M* ($CHCl_3$) 335. $C_8H_{10}ClNPt$ requires C, 27.4; H, 2.9; N, 4.0%; *M* 350]; $\nu_{max.}$ at 3 040w, 3 022w, 1 605s, 1 487m, 1 448vs, 1 360w, 1 356w, 1 243m, 1 226m, 1 220m, 1 216m, 1 198w, 1 160w, 1 151w, 1 077m, 1 068s, 1 051m, 1 023m, 1 009w, 988m, 981(sh), 957m, 904w, 828m, 777m, 766vs, 732w, 708s, 701vs, 657m, 588m, 457w, 436m, 399w, 326w, and 298s, br (PtCl) cm^{-1}.

The complex [PtBr(η^3-C_3H_5)(py)] (2) was prepared (74% yield) in a similar manner, m.p. 129—130 °C (decomp.) [Found: C, 24.0; H, 2.5; N, 3.6%; *M* ($CHCl_3$) 425. $C_8H_{10}BrNPt$ requires C, 24.3; H, 2.5; N, 3.5%; *M* 395].

[{PtX(μ-σ-C_3H_5)(py)}$_2$]. Compound (4) was prepared in an analogous manner to that for (1), except that the solution was stirred for 24 h resulting in precipitation of the product. Addition of light petroleum, removal of the supernatant, followed by washing with light petroleum (2 × 5 cm^3), and drying *in vacuo* afforded pale yellow *microcrystals* of [{PtCl(μ-σ-C_3H_5)(py)}$_2$] (4) (74%), m.p. 144—145 °C (decomp.) [Found: C, 27.3; H, 2.8; N, 4.0%; *M* ($CHCl_3$)



SCHEME 3 Dynamic behaviour in the complex cation [Pt(σ-C_3H_5){P(OMe)$_3$}$_3$]$^+$

Light petroleum refers to that fraction of b.p. 30—40 °C. The complexes [PtX(σ-allyl)(cod)] (X = Cl or Br; allyl = C_3H_5, C_3H_4Me-3, or C_3H_4Ph-3) and [Pt(η^3-allyl)(cod)][BF_4] used as starting materials were prepared as described earlier.[1] Analytical data for the new compounds (7)—(19) are given in Tables 3 and 5, and for the other compounds are given below.

Preparations of the Complexes.—[PtX(η^3-C_3H_5)(py)]. To a suspension of [PtCl(σ-C_3H_5)(cod)] (0.19 g, 0.5 mmol) in toluene (5 cm^3) was added excess of py (0.2 cm^3). The solution immediately cleared and, after 30 s, light petroleum was added to afford white *plates* of [PtCl(η^3-C_3H_5)(py)] (1) (0.17 g, 94%), m.p. 143—144 °C (decomp.) [Found: C, 27.5; H, 3.0; N, 4.0%; *M* ($CHCl_3$) 335. $C_8H_{10}ClNPt$ requires C, 27.4; H, 2.9; N, 4.0%; *M* 350]; $\nu_{max.}$ at 3 040w, 3 022w, 1 605s, 1 487m, 1 448vs, 1 360w, 1 356w, 1 243m, 1 226m, 1 220m, 1 216m, 1 198w, 1 160w, 1 151w, 1 077m, 1 068s, 1 051m, 1 023m, 1 009w, 988m, 981(sh), 957m, 904w, 828m, 777m, 766vs, 732w, 708s, 701vs, 657m, 588m, 457w, 436m, 399w, 326w, and 298s, br (PtCl) cm^{-1}.

The complex [PtBr(η^3-C_3H_5)(py)] (2) was prepared (74% yield) in a similar manner, m.p. 129—130 °C (decomp.) [Found: C, 24.0; H, 2.5; N, 3.6%; *M* ($CHCl_3$) 425. $C_8H_{10}BrNPt$ requires C, 24.3; H, 2.5; N, 3.5%; *M* 395].

[{PtX(μ-σ-C_3H_5)(py)}$_2$]. Compound (4) was prepared in an analogous manner to that for (1), except that the solution was stirred for 24 h resulting in precipitation of the product. Addition of light petroleum, removal of the supernatant, followed by washing with light petroleum (2 × 5 cm^3), and drying *in vacuo* afforded pale yellow *microcrystals* of [{PtCl(μ-σ-C_3H_5)(py)}$_2$] (4) (74%), m.p. 144—145 °C (decomp.) [Found: C, 27.3; H, 2.8; N, 4.0%; *M* ($CHCl_3$) 893. $C_{16}H_{20}Cl_2N_2Pt_2$ requires C, 27.4; H, 2.9; N, 4.0%; *M* 701]; $\nu_{max.}$ at 3 045w, 1 601s, 1 491m, br, 1 486m, 1 448vs, 1 422w, 1 355w, 1 216m, 1 208s, 1 162w, 1 158w, 1 134w, 1 097w, 1 077(sh), 1 072s, 1 067w, 1 051m, 1 022m, 1 016m, 998m, 990s, 982w, 912m, 907w, 848w, 838w, 825m, 820w, 753vs, 730w, 702vs, 659w, 648m, 625w, 500w, 460w, 444w, 433w, 399w, and 323s (PtCl) cm^{-1}.

The complex [{PtBr(μ-σ-C_3H_5)(py)}$_2$] (5), m.p. 127 °C (decomp.), was similarly prepared (87% yield) [Found: C, 24.4; H, 2.7; N, 3.5%; *M* ($CHCl_3$) 835. $C_{16}H_{20}Br_2N_2Pt_2$ requires C, 24.3; H, 2.5; N, 3.5%; *M* 790].

[Pt(η^3-C_3H_5)(bipy)]Cl. To a solution of [PtCl(σ-C_3H_5)-(cod)] (0.10 g, 0.26 mmol) in toluene (7 cm^3) was added 2,2′-bipyridyl (0.10 g, 0.65 mmol). An immediate reaction took place and a yellow precipitate formed. This was washed with light petroleum (3 × 10 cm^3) and dried *in vacuo* affording yellow *microcrystals* of [Pt(η^3-C_3H_5)(bipy)]Cl (0.105 g, 94%) (Found: C, 35.7; H, 3.2; N, 6.0. $C_{13}H_{13}ClN_2Pt$ requires C, 36.5; H, 3.1; N, 6.5%); $\nu_{max.}$ at 3 105w, 2 990w, 1 601s, 1 494m, 1 471s, 1 448s, 1 370m, 1 320m,

1 254w, 1 223w, 1 167w, br, 1 115m, 1 078w, 1 031m, 993m, 815w, 781s, 733s, 573w, 491w, 435w, 425m, and 382w cm^{-1}. N.m.r. ([$^2H_2$]water): ^1H, τ 1.39 [m, 2 H, bipy, J(PtH) 34.5], 1.96 (m, 4 H, bipy), 2.48 (m, 2 H, bipy), 6.14 [d of d, *syn*-H, J(*gem*) 1, J(HH) 6, J(PtH) 36], and 7.31 [d of d, 2 H, *anti*-H, J(*gem*) 1, J(HH) 12, J(PtH) 75 Hz], central allylic proton obscured by solvent; ^{13}C, δ 155.2 [s, bipy, J(PtC) 61], 154.5 (s, bipy), 142.0 (s, bipy), 129.7 [s, bipy, J(PtC) 42], 124.2 [s, bipy, J(PtC) 22], 109.3 [s, CH, ^1J(PtC) 76], and 46.3 p.p.m. [s, CH_2, J(PtC) 232 Hz].

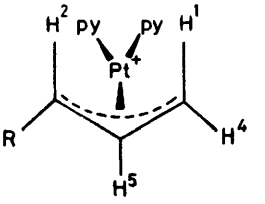
[PtX(η^3-C_3H_4R-3)(PR_3)]. To a suspension of [PtCl(σ-C_3H_5)(cod)] (0.19 g, 0.5 mmol) in light petroleum (5 cm^3) was added a solution of $P(C_6H_{11})_3$ (0.14 g, 0.5 mmol) in light petroleum (10 cm^3). The resultant suspension was stirred for 30 min, then reduced in volume *in vacuo*. Removal of the supernatant, followed by washing with light petroleum (2 × 3 cm^3) and drying *in vacuo*, afforded a white powder (0.11 g, 54%) which was recrystallised from toluene–light petroleum to give white *crystals* of [PtCl(η^3-C_3H_5){$P(C_6H_{11})_3$}] (7), m.p. 177—178 °C (decomp.), $\nu_{max.}$(PtCl) at 307 cm^{-1}.

Prepared in a similar manner were [PtBr(η^3-C_3H_5){$P(C_6H_{11})_3$}] (8), [PtBr(η^3-C_3H_4Me-3){$P(C_6H_{11})_3$}] (9), and [PtCl(η^3-C_3H_4Ph-3){$P(C_6H_{11})_3$}] (10) [$\nu_{max.}$ (PtCl) at 309 cm^{-1}]. Using 1 mol equivalent of PPh_3 the following were prepared: [PtCl(η^3-C_3H_5)(PPh_3)] (11) and [PtCl(η^3-C_3H_4Me-3)(PPh_3)] (12) (Table 3).

[PtX(η^3-C_3H_4R-3)L_2]. To a solution of [PtCl(σ-C_3H_5)(cod)] (0.19 g, 0.5 mmol) in dichloromethane (5 cm^3) was added PPh_3 (0.26 g, 1.0 mmol). The solution was stirred for 5 min, and diethyl ether added to afford white *crystals* of [PtCl(η^3-C_3H_5)(PPh_3)$_2$] (13) (0.335 g, 84%). Prepared in a similar manner were [PtCl(η^3-C_3H_4Me-3)(PPh_3)$_2$] (14), [PtBr(η^3-C_3H_4Me-3)(PPh_3)$_2$] (15), and [PtCl(η^3-C_3H_4Ph-3)(PPh_3)$_2$] (16). The complex [PtCl(σ-C_3H_4Me-3){$P(C_6H_{11})_3$}$_2$] (17) was prepared in an analogous manner using tricyclohexylphosphine. Prepared similarly using 1 mol equivalent of dppe were [Pt(η^3-C_3H_4R-3)(dppe)]Cl [R = H (18) or Me (19)] (Table 5).

[Pt(η^3-C_3H_4R-3)L_2][BF_4]. (*a*) To a solution of [Pt(η^3-C_3H_5)(cod)][BF_4] (0.22 g, 0.5 mmol) in dichloromethane (5 cm^3) was added pyridine (0.4 cm^3, excess). The solution immediately lightened in colour. After stirring for 30 min, diethyl ether was added affording white *crystals* of [Pt(η^3-C_3H_5)(py)$_2$][BF_4] (20) (0.21 g, 86%) (Found: C, 32.7; H, 3.1; N, 5.8. $C_{14}H_{15}BF_4N_2Pt$ requires C, 32.5; H, 3.1; N, 5.8%), m.p. 143—144 °C (decomp.); $\nu_{max.}$ at 3 115w, 3 078w, 1 605s, 1 487m, 1 452s, 1 360w, 1 290m, 1 246m, 1 223m, 1 162m, 1 109s, 1 050vbr, vs, 1 019s, 998m, 991m, 973m, 956w, 952m, 941m, 835w, 815w, 785s, 776s, 734w, 720s, 713s, 707s, 659w, 626w, 569s, 533s, and 437m cm^{-1}. N.m.r.: ^1H ([$^2H_1$]chloroform), τ 1.34 [m, 4 H, py, J(PtH) 36], 2.04 (m, 2 H, py), 2.43 (m, 4 H, py), 4.94 [t of t, 1 H, H^5, $J(H^1H^2)$ 11, $J(H^3H^4)$ 7, J(PtH) 85], 6.05 [d of d, 2 H, H^3, H^4, $J(H^5)$ 7, $J(H^1H^2)$ 2, J(PtH) 24], and 7.23 [d of d, 2 H, H^1H^2, $J(H^5)$ 11, $J(H^3H^4)$ 2, J(PtH) 71 Hz]; ^{13}C ([$^2H_2$]dichloromethane–CH_2Cl_2), δ 152.0 [s, py, α-C, J(PtC) 11], 140.0 [s, py, γ-C, J(PtC) 10], 127.4 [s, py, β-C, J(PtC) 39], 108.3 [s, CH, J(PtC) 81], and 45.3 p.p.m. [s, CH_2, J(PtC) 221 Hz].

(*b*) The complex [Pt(η^3-C_3H_4Me-3)(py)$_2$][BF_4] (21) was prepared (0.20 g, 88%) as white hygroscopic *crystals* (Found: C, 33.8; H, 3.5; N, 5.5. $C_{14}H_{17}BF_4N_2Pt$ requires C, 34.0; H, 3.5; N, 5.7%) in a similar manner to (20) from [Pt(η^3-C_3H_4Me-3)(cod)][BF_4]; $\nu_{max.}$ at 3 110w, 3 075w, 1 605s, 1 487m, 1 470m, 1 452s, 1 289w, 1 244w, 1 222m, 1 170m, 1 095(sh), 1 050vbr, vs, 898w, 776s, 767s, 730w, 711s, 701s, 656w, 568m, 541w, and 530m cm^{-1}. N.m.r.: ^1H ([$^2H_1$]chloroform), τ 1.30 (br, m, 4 H, py), 2.10 (br, m, 2 H, py), 2.43 (br, m, 4 H, py), 5.19 [m, 1 H, H^5, J(PtH) 88], 6.22 [d of d, 1 H, H^4, $J(H^5)$ 7, $J(H^1)$ 2, J(PtH) 27], 6.58 [d of q, 1 H, H^2, $J(H^5)$ 11, J(Me) 6, J(PtH) 88], 7.41 [d of d, 1 H, H^1, $J(H^5)$ 11, $J(H^4)$ 2, J(PtH) 71], and 8.83 [d, 3 H, Me, $J(H^2)$ 6, J(PtH) 12]; ^{13}C ([$^2H_2$]dichloromethane–CH_2Cl_2), δ 152.2 [s, py, α-C, J(PtC) 13], 151.4 (s, py, α-C), 139.9 [s, py, γ-C, J(PtC) 11], 127.7 [s, py, β-C, J(PtC) 39], 127.3 [s, py, β-C, J(PtC) 40], 108.7 [s, CH_2CH, J(PtC) 88], 61.2 [s, $CHCH_3$, J(PtC) 197], 41.0 [s, CH_2, J(PtC) 250], and 17.1 p.p.m. [s, CH_3, J(PtC) 10 Hz].



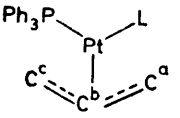
(*c*) To a solution of [Pt(η^3-C_3H_5)(cod)][BF_4] (0.22 g, 0.5 mmol) in dichloromethane (10 cm^3) was added 2,2′-bipyridyl (0.16 g, 1 mmol). Within a few minutes a yellow precipitate started to form. After 30 min, precipitation was completed with diethyl ether (10 cm^3). Washing the product with diethyl ether (2 × 10 cm^3) and drying *in vacuo* afforded yellow *microcrystals* of [Pt(η^3-C_3H_5)(bipy)][BF_4] (22) (0.22 g, 92%) (Found: C, 32.7; H, 3.1; N, 5.8. $C_{13}H_{13}BF_4N_2Pt$ requires C, 32.5; H, 3.1; N, 5.8%), m.p. > 350 °C (decomp.); $\nu_{max.}$ at 3 100w, 1 595w, 1 487w, 1 438s, 1 412m, 1 312m, 1 282w, 1 248w, 1 216w, 1 198w, 1 174w, 1 156w, 1 118(sh), 1 104(sh), 1 050br, vs, 1 028vs, 1 003(sh), 988m, 971m, 905w, 766s, 725s, 559m, 524m, 484s, and 420w cm^{-1}.

(*d*) The compound [Pt(η^3-C_3H_5)(PPh_3)$_2$][BF_4] (23) was prepared as white *crystals* (0.24, 81%) (Found: C, 55.1; H, 4.2. Calc. for $C_{39}H_{35}BF_4P_2Pt$: C, 55.3; H, 4.2%) from [Pt(η^3-C_3H_5)(cod)][BF_4] (0.10 g, 0.23 mmol) and PPh_3 (0.12 g, 0.46 mmol). Prepared in an analogous manner as white *crystals* or *microcrystals* were [Pt(η^3-C_3H_4Me-3)(PPh_3)$_2$][BF_4] (24) (78%) (Found: C, 55.6; H, 4.3. Calc. for $C_{40}H_{37}BF_4P_2Pt$: C, 55.8; H, 4.3%), [Pt(η^3-C_3H_5)(dppe)][BF_4] (25) (72%) (Found: C, 48.7; H, 4.2. $C_{29}H_{29}BF_4P_2Pt$ requires C, 48.3; H, 4.1%), and [Pt(η^3-C_3H_4Me-3)(dppe)][BF_4] (26) (Found: C, 48.6; H, 4.4. $C_{30}H_{31}BF_4P_2Pt$ requires C, 49.0; H, 4.3%).

[Pt(η^3-C_3H_4R-3)L(PPh_3)][BF_4]. (*a*) To a solution of [Pt(η^3-C_3H_5)(cod)][BF_4] (0.20 g, 0.46 mmol) in dichloromethane (3 cm^3) was added PPh_3 (0.12 g, 0.46 mmol). Carbon monoxide was then bubbled through the solution for 5 min. Addition of diethyl ether afforded white platelets of [Pt(η^3-C_3H_5)(CO)(PPh_3)][BF_4] (27) (0.24 g, 84%) (Found: C, 43.1; H, 3.4. $C_{22}H_{20}BF_4OPPt$ requires C, 43.1; H, 3.3%), m.p. 170—171 °C (decomp.); $\nu_{max.}$ at 3 051w, 2 127s, 2 105s (CO), 1 478w, 1 435m, 1 309w, 1 282w, 1 183w, 1 163w, 1 101s, 1 063s, br, 997m, 964w, 762m, 755m, 751(sh), 713m, 702(sh), 699m, 691(sh), 538m, 522m, 496m, 482m, 441w, and 428w cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{31}P, δ 15.2 p.p.m. [s, J(PtP) 3 938]; ^{13}C, δ 175.3 [d, CO, J(PC) 6, J(PtC) 1 804], 133.4 [d, Ph, β-C, J(PC) 12, J(PtC) 21], 132.4 (s, Ph, δ-C), 129.6 [d, Ph, γ-C, J(PC) 12], 128.6 [d, Ph, α-C, J(PC) 60, J(PtC) 37], 124.0 [s, C^b, J(PtC) 34],

73.5 [d, C^c, J(PC) 21, J(PtC) 35], and 66.1 p.p.m. [s, C^a, J(PtC) 131 Hz].

(*b*) To a solution of [Pt(η^3-C_3H_5)(cod)][BF_4] (0.20 g, 0.46 mmol) and PPh_3 (0.46 mmol) in dichloromethane (3 cm^3) was added a solution of Bu^tNC (0.039 g, 0.46 mmol) in dichloromethane (2.4 cm^3). An immediate exothermic reaction took place. Addition of diethyl ether afforded white *needles* of [Pt(η^3-C_3H_5)($CNBu^t$)(PPh_3)][BF_4] (28) (0.27 g, 85%) (Found: C, 46.9; H, 4.7; N, 2.1. $C_{26}H_{29}BF_4NPPt$



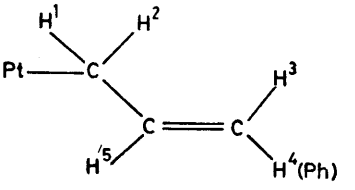
requires C, 46.7; H, 4.4; N, 2.1%); $\nu_{max.}$ at 3 056w, 2 230s, (NC), 1 483m, 1 440m, 1 305w, 1 280w, 1 236w, 1 195m, br, 1 100s, 1 092(sh), 1 054s, br, 1 039s, 998m, 764m, 753w, 715m, 705m, 694w, 639m, 526m, 515m, 506m, 454w, 446w, and 437w cm^{-1}. N.m.r.: ([$^2H_1$]chloroform): ^{31}P, δ 16.8 p.p.m. [s, J(PtP) 3 943 Hz]; ^{13}C, δ 133.4 [d, Ph, β-C, J(PC) 12, J(PtC) 22], 131.8 (s, Ph, δ-C), 129.9 [d, Ph, α-C, J(PC) 61, J(PtC) 33], 129.2 [d, Ph, γ-C, J(PC) 11], 119.0 [s, C^a, J(PtC) 38], 66.1 [s, C^b, J(PC) 26, J(PtC) 53], 60.9 [s, C^c, J(PtC) 131], 59.5 [s, $C(CH_3)_3$, J(PtC) 12 Hz], and 29.3 p.p.m. (s, CH_3).

(*c*) The compound [Pt(η^3-C_3H_5)(PPh_3)(py)][BF_4] (29) was prepared as for (28) but using an equimolar amount of pyridine. The product (29) was isolated as white *crystals* (94%) (Found: C, 47.0; H, 4.0; N, 2.2. $C_{26}H_{25}BF_4NPPt$ requires C, 47.0; H, 3.8; N, 2.1%); $\nu_{max.}$ at 3 007w, 1 622w, 1 604m, 1 594w, 1 568w, 1 481m, 1 452s, 1 438(sh), 1 334s, 1 307w, 1 278w, 1 238w, 1 215w, 1 213w, 1 183w, 1 158w, 1 098s, br, 1 055s, br, 998w, 963w, 758m, br, 711(sh), 698s, 645(sh), 642w, 616w, 548s, 518m, and 504w cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{31}P, δ 26.9 p.p.m. [s, J(PtP) 4 373 Hz]; ^{13}C, δ 152.1 (s, py, α-C), 138.3 [s, py, γ-C, J(PtC) 12], 133.4 [d, Ph, β-C, J(PC) 12, J(PtC) 18], 131.3 (s, Ph, δ-C), 128.9 [d, Ph, γ-C, J(PC) 11], 128.8 [d, Ph, α-C, J(PC) 56, J(PtC) 36], 126.5 [s, py, β-C, J(PtC) 42], 115.4 [s, C^b, J(PtC) 44], 71.5 [d, C^a, J(PC) 27, J(PtC) 60], and 43.3 p.p.m. [s, C^c, J(PtC) 205 Hz].

[Pt(σ-C_3H_4R-3)L_2(PPh_3)][BF_4]. (*a*) The compound *cis*-[Pt(σ-C_3H_5)(PPh_3)$(py)_2$][BF_4] (30) was prepared as white *microcrystals* (64%) (Found: C, 49.9; H, 4.0; N, 3.9. $C_{31}H_{30}BF_4N_2PPt$ requires C, 50.1; H, 4.1; N, 3.8%) by the method used to obtain (28), except that excess of pyridine was added; $\nu_{max.}$ at 3 114w, 3 094w, 3 064m, 3 023m, 1 614m (C=C), 1 608s, 1 588m, 1 572m, 1 483m, 1 450s, 1 438s, 1 433s, 1 362m, 1 333w, 1 308w, 1 281w, 1 240w, 1 221m, 1 215m, 1 190m, 1 182m, 1 158m, 1 150m, 1 097s, br, 1 045vs, vbr, 994m, 874m, 818w, 764s, 761s, 753s, 742s, 706s, 693s, 649w, and 643w cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{1}H, τ 1.20—3.00 (m br, 25 H, py + Ph), 4.95 (m br, 1 H, H^5), 5.78 [d, br, 1 H, H^4, J(H^5) 10], 6.15 [d, br, 1 H, H^3, J(H^5) 16], and 7.76 [s, br, 2 H, H^1 + H^2, J(PtH) 82 Hz]; τ (−60 °C) no change; ^{31}P (−60 °C), δ 16.9 p.p.m. [s, J(PtP) 4 269 Hz]; ^{13}C (−60 °C), δ 150.1 (s, py, α-C), 140.9 [s, CH, J(PtC) 65], 139.2, 137.9 (s + s, py, γ-C), 133.8 [d, Ph, β-C, J(PC) 11, J(PtC) 23], 131.1 (s, Ph, δ-C), 128.5 [d, Ph, γ-C, J(PC) 11], 126.6, 126.2 (s + s, py, β-C), 109.5 [s, CH_2, J(PtC) 42], and 8.11 p.p.m. [s, CH_2, J(PtC) 360 Hz].

(*b*) To a mixture of [Pt(C_3H_4Ph-3)(cod)][BF_4] (0.15 g, 0.30 mmol) and PPh_3 (0.08 g, 0.30 mmol) in dichloromethane was added excess of pyridine (0.2 cm^3). An immediate exothermic reaction ensued. All volatiles were then removed *in vacuo* and the residue recrystallised from CH_2Cl_2–Et_2O to afford white *crystals* of *cis*-[Pt(σ-C_3H_4Ph-3)(PPh_3)$(py)_2$][BF_4] (31) (0.17 g, 70%) (Found: C, 54.0; H, 4.3; N, 3.3. $C_{37}H_{34}BF_4N_2PPt$ requires C, 54.2; H, 4.2; N, 3.4%); $\nu_{max.}$ at 3 007w, 1 622w (C=C), 1 604m, 1 594w, 1 568w, 1 481m, 1 452s, 1 438(sh), 1 334s, 1 307w, 1 278w, 1 238w, 1 215w, 1 213w, 1 183w, 1 158w, 1 098s, br, 1 055s, br, 998w, 963w, 758m, br, 711(sh), 698s, 645(sh), 642w, 616w, 548s, 518m, and 504w cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{1}H, τ 0.90—3.1 (m, 30 H, Ph + py), 4.44 and 4.79 [br, AB pattern, 2 H, H^5 and H^3, J(H^3H^5) 15, J(PtH) 15 and 18], and 7.66 [s, br, 2 H, H^1 + H^2, J(PtH) 90 Hz]; ^{31}P, δ 16.4 p.p.m. [s, J(PtP) 4 313 Hz], δ (−60 °C) 17.0 p.p.m. [s, J(PtP) 4 276 Hz].

(*c*) White *needles* of the compound *trans*-[Pt(σ-C_3H_5)-$(CNBu^t)_2$(PPh_3)][BF_4] (32) (83% yield) were prepared in a similar manner to complex (31) but using an excess of Bu^tNC (Found: C, 49.9; H, 5.2; N, 3.7. $C_{31}H_{38}BF_4N_2PPt$ requires C, 49.5; H, 5.1; N, 3.7%), m.p. >300 °C (decomp.); $\nu_{max.}$ (CH_2Cl_2) at 2 208s cm^{-1} (NC), $\nu_{max.}$ at 3 067w, 2 257m (NC), 2 020vs (NC), 1 616m (C=C), 1 486m, 1 444s, 1 405w, 1 316w, 1 244m, 1 197w, br, 1 105s, 1 063vs, br, 1 045(sh), 1 007m, 888m, 775m, 755m, 725m, 711s, 706m, 557m, 541s, 522m, 510m, and 464m cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{1}H (−60 °C), τ 2.30—2.74 (m, 15 H, Ph), 7.97 [d of d of t, 1 H,



(30) → (32)

H^5, J(H^1H^2) 9, J(H^3) 18, J(H^4) 10], 5.13 [d, 1 H, H^4, J(H^5) 10, J(PtH) 19], 5.30 [d, 1 H, H^3, J(H^5) 18, J(PtH) 23], 7.35 [d of d, 2 H, H^1 + H^2, J(H^5) 9, J(PH) 9, J(PtH) 80 Hz], and 8.70 (s, 18 H, Me); ^{31}P, δ 14.9 p.p.m. [s, J(PPt) *ca.* 1 490 Hz], δ (−60 °C) 14.1 p.p.m. [s, J(PPt) 1 476 Hz]; ^{13}C (−60 °C), δ 141.5 [d, CH, J(PC) 7, J(PtC) 46], 133.4 [d, Ph, β-C, J(PC) 11, J(PtC) 11], 131.8 (s, Ph, δ-C), 129.3 [d, Ph, α-C, J(PC) 51, J(PtC) 16], 128.8 [d, Ph, γ-C, J(PC) 11], 125.4 [d, CN, J(PC) 13, J(PtC) 758], 109.9 [d, CH_2, J(PC) 7, J(PtC) 46], 59.6 [s, CMe_3, J(PtC) 15], 28.9 (s, CH_3), and 17.0 p.p.m. [d, CH_2, J(PC) 68, J(PtC) 382 Hz].

[Pt(σ-C_3H_4R-3){$P(OMe)_3$}$_3$][BF_4]. (*a*) To a solution of [Pt(η^3-C_3H_5)(cod)][BF_4] (0.22 g, 0.5 mmol) in dichloromethane (3 cm^3) was added excess of trimethyl phosphite (0.6 cm^3). The solution was stirred for 5 min, and on addition of diethyl ether (10 cm^3) afforded white *crystals* of [Pt(σ-C_3H_5){$P(OMe)_3$}$_3$][BF_4] (33) (0.55 g, 73%) (Found: C, 20.7; H, 4.7. $C_{12}H_{32}BF_4O_9Pt$ requires C, 20.7; H, 4.7%), $\nu_{max.}$ at 3 077w, 1 618m (C=C), 1 287w, 1 190m, 1 100(sh), 1 060vs, br, 1 019vs, br, 902m, 848s, br, 803m, 788m, 762s, 752s, 631(sh), 608w, 581w, 547s, 531w, and 462w cm^{-1}. N.m.r.: ^{1}H ([$^2H_6$]acetone), τ 4.11 [qt, 1 H, CH, J(HH) 11, J(PtH) 14], 6.10 (s, 27 H, OMe), 6.31 [d, 4 H, CH_2, J(HH) 11, J(PtH) 42 Hz], τ (−90 °C) 4.14 [qt, br, 1 H, CH, J(HH) 10, J(PtH) unobserved], 6.14 [s, br, 27 H, OMe, J(PtH) 7], and 6.36 [d, br, 4 H, CH_2, J(HH) 10, J(PtH) 44 Hz]; ^{31}P ([$^2H_2$]dichloromethane, −90 °C), δ 115.8 p.p.m. [s, J(PtP) 4 097 Hz]; ^{13}C ([$^2H_6$]acetone), δ 139.3 [s, CH, J(PtC) 57], 65.5 [s, CH_2, J(PtC) 203 Hz], and

54.0 (s, OMe); δ (−90 °C) 140.1 [s, CH, J(PtC) 57], 66.3 [s, br, CH_2, J(PtC) 192 Hz], and 54.0 (s, OMe); δ (−90 °C, [$^2H_2$]dichloromethane–CH_2Cl_2) 139.0 [s, CH, J(PtC) 46], 65.4 [q, CH_2, J(PC) 15, J(PtC) 195 Hz], and 54.2 p.p.m. (s, OMe).

(*b*) White *crystals* (0.15 g, 44%) of the compound [Pt(σ-C_3H_4Me-3){P(OMe)$_3$}$_3$][BF_4] (34) (Found: C, 22.1; H, 4.8. $C_{13}H_{34}BF_4O_9P_3Pt$ requires C, 22.0; H, 4.8%) were prepared from [Pt(η^3-C_3H_5)(cod)][BF_4] (0.19 g, 0.42 mmol) in an analogous manner to (33). For (34), $\nu_{max.}$ at 1 365m, 1 282w, 1 178s, 1 102(sh), 1 060vs, br, 1 020vs, br, 978s, 969s, 909w, 838s, 812s, 787s, 749s, and 740s cm^{-1}. N.m.r.: ^{1}H ([$^2H_6$]acetone), τ 4.54 [d of t, 1 H, CH_2CH, J(HH) 14, 8], 4.74 [d of q, 1 H, $CHMe$, J(HH) 14, 6], 6.10 (s, 27 H, OMe), 7.50 [d, 2 H, CH_2, J(HH) 8, J(PtH) 65], and 8.35 [d, 3 H, Me, J(HH) 6, J(PtH) 12 Hz]; τ (−90 °C) 4.65 (s, br, 2 H, CHCH), 6.13 (s, 18 H, OMe), 6.20 (s, 9 H, OMe), 7.66 (s, br, 2 H, CH_2), and 8.41 (s, br, 3 H, Me); ^{31}P ([$^2H_2$]-dichloromethane–CH_2Cl_2, −10 °C), δ 114.7 p.p.m. (br, s); δ (−90 °C), AB_2 spectrum (*E*-crotyl), A, 123.5 [m, 1 P, J(PP) 57, J(PtP) 2 931], B, 113.8 p.p.m. [m, 2 P, J(PP) 57, J(PtP) 4 770 Hz], AB_2 spectrum (*Z*-crotyl) A, 122.8 [m, 1 P, J(PP) 55, J(PtP) 2 921], B, 113.4 p.p.m. [m, 2 P, J(PP) 55, J(PtP) 4 691 Hz]; ^{13}C ([$^2H_6$]acetone), δ 132.1 [s, CH_2CH, J(PtC) 50], 123.0 [s, CHMe, J(PtC) 31], 53.9 (s, OMe), 17.5 (s, Me), and 17.2 [s, CH_2, J(PtC) 374 Hz]; δ (−90 °C) 131.8 [d, CH_2CH, J(PC) 19, J(PtC) 50], 123.5 [d, CHMe, J(PC) 9, J(PtC) unobserved], 53.7 (s, OMe), 19.1 (s, Me), and 18.6 p.p.m. [d, CH_2, J(PC) 96 Hz, J(PtC) unobserved].

(*c*) White *crystals* (0.55 g, 62%) of the salt [Pt(σ-C_3H_4-Ph-3){P(OMe)$_3$}$_3$][BF_4] (35) (Found: C, 28.0; H, 4.7. $C_{18}H_{36}BF_4O_9P_3Pt$ requires C, 28.0; H, 4.7%) were prepared similarly to (33) from [Pt(η^3-C_3H_4Ph-3)(cod)][BF_4] (0.2 g, 0.39 mmol). For (35), $\nu_{max.}$ at 1 617w (C=C), 1 594m, 1 573w, 1 497w, 1 470s, 1 383w, 1 366w, 1 303w, 1 185s, 1 100s, *ca.* 1 030vs, vbr, 867w, 842s, 835s, 821s, 801m, 783m, 762s, 746s, 704s, 697w, 614w, 567m, 538s, 492w, and 452w cm^{-1}. N.m.r.: ^{1}H ([$^2H_3$]nitromethane, 90 °C), τ 2.66—2.94 (m, 5 H, Ph), 3.65 (m, 2 H, CHCH), 6.12 (s, br, 27 H, OMe), and 7.20 [d, 2 H, CH_2, J(HH) 8, J(PtH) 70 Hz]; τ ([$^2H_6$]acetone, −90 °C) 2.52—3.00 (m, 5 H, Ph), 2.71 (s, br, 2 H, CHCH), 6.12 [s, 27 H, OMe, J(PtH) 12 Hz], and 7.35 (s, br, 2 H, CH_2); ^{31}P ([$^2H_2$]dichloromethane–CH_2Cl_2), δ 121.4 (s, br, 1 P) and 110.7 p.p.m. (s, br, 2 P, AB_2 pattern); δ (−85 °C) 120.3 [m, 1 P, J(PP) 57, J(PtP) 3 040] and 112.9 p.p.m. [m, 2 P, J(PP) 57, J(PtP) 4 692 Hz]; ^{13}C, δ ([$^2H_3$]nitromethane, 90 °C) 140.3 [s, Ph, α-C, J(PtC) 12], 131.9 [s, CH_2CH, J(PtC) 40], 130.0, 126.8 (s + s, Ph, β- + γ-C), 127.7 [s, CHPh, J(PtC) 52], 127.7 (s, Ph, δ-C), 54.6 (s, OCH_3), and 21.2 p.p.m. [s, CH_2, J(PtC) 353 Hz]; δ ([$^2H_6$]acetone, −50 °C) 139.5 [s, Ph, α-C, J(PtC) 14], 131.6 [s, CH_2CH, J(PtC) 52], 127.8 [s, CHPh, J(PtC) 40], 126 8 (s, Ph, δ-C), 129.3 and 126.0 (s + s, Ph, β- + γ-C), 54.2 (s, OCH_3), and 19.5 p.p.m. [s, br, CH_2, J(PtC) 354 Hz]; δ (−90 °C) 138.9 [d, Ph, α-C, J(PC) 5, J(PtC) unobserved], 131.2 [d, CH_2CH, J(PC) 14, J(PtC) unobserved], 127.7 [d, CHPh, J(PC) 10, J(PtC) unobserved], 126.9 (s, Ph, δ-C), 129.4, 125.8 (s + s, Ph, β- + γ-C), 54.2 (s, OCH_3), 53.8 (s, OCH_3), and 19.9 p.p.m. [br, d, CH_2, J(PC) 92, J(PtC) 358 Hz].

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