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The synthesis and structural characterization of the η^1; η^3-allyl bridged bimetallic complexes $[\eta^3\text{-}\{2\text{-}(\eta^5\text{-Cp})(OC)(PR_3)\text{-}Fe\text{-allyl}\}Pt(PPh_3)_2]PF_6$ ($PR_3 = PPh_2H$, PPh_2Me)

Michael R. Gregg, John Powell * and Jeffery F. Sawyer

Lash Miller Chemical Laboratories, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 1A1 (Canada)

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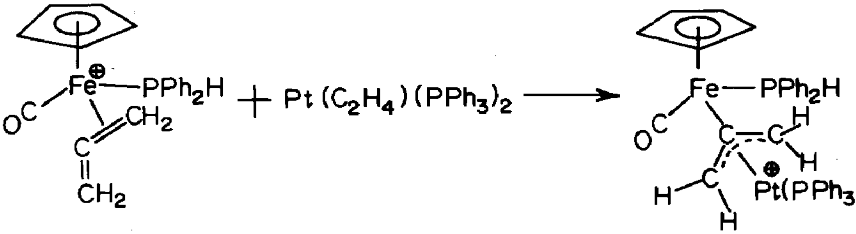
Abstract

The cationic complex $[\eta^5\text{-Cp}(OC)(\eta^2\text{-allene})Fe(PPh_2H)]PF_6$ reacts with $Pt(C_2H_4)(PPh_3)_2$ via C_2H_4 substitution (rather than oxidative addition of the P–H bond) to give $[\eta^3\text{-}(2\text{-}\eta^5\text{-Cp}(OC)(PR_3)Fe\text{-allyl})Pt(PPh_3)_2]PF_6$ $\{PR_3 = PPh_2H\}$ the structure of which has been determined by a single crystal X-ray diffraction study of its dimethylphenylphosphine analog $[PR_3 = PMe_2Ph]$. Crystal data: $[C_{53}H_{50}FeOP_3Pt^+]$ $[PF_6^-] \cdot 2[C_6H_6]$ is triclinic, space group $P\bar{1}$ with a 13.504(2), b 14.044(6), c 17.759(4) Å, α 98.05(2), β 108.59(1), γ 104.44(2)°, U 3002(3) Å^3, $Z = 2$, D_x 1.49 Mg m^{-3}, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, μ 27.6 cm^{-1}, $F(000) = 1356$, T 298 K, $R = 0.0527$ ($R_w = 0.0575$) for 7731 observed ($I > 3\sigma(I)$) reflections. The compound contains an ordered η^1-Fe, η^3-Pt allyl moiety with Pt–C distances of 2.151(9) and 2.165(8) Å to the terminal atoms and 2.272(7) Å to the central atom; the Fe–C distance is 1.967(7) Å. The plane of the allyl group is canted at an angle of 122.5° with respect to the PtP_2 plane. The Pt...Fe separation is 3.794(1) Å.

Introduction

Oxidative addition of the P–H bond of a secondary phosphine complex to platinum(0) complexes provides easy access to singly bridged μ-phosphido heterobimetallic hydrides of the type $L_xM(\mu\text{-PR}_2)PtH(PPh_3)_2$ [1–4]. Because of the available stereochemical sign-posting these systems are particularly suited for the study of cluster assembly and cluster rearrangement processes [5] and for the study of ligand reactivities in multimetallic systems. As part of these investigations it was anticipated that oxidative addition of the P–H bond of the complex $[\eta^5\text{-Cp}(OC)(\eta^2\text{-allene})Fe(PPh_2H)]^+PF_6^-$ (**1a**) to $Pt(C_2H_4)(PPh_3)_2$ would lead initially to $[\eta^5\text{-Cp}(OC)(\eta^2\text{-allene})Fe(\mu\text{-PPh}_2)PtH(PPh_3)_2]^+$, a suitable candidate for the study of hydride transfer from one metal to an unsaturated ligand (i.e. the η^2-allene) coordinated to an adjacent metal centre. (NB. Reaction of [η^5-Cp(OC)(η^2-allene)Fe(PPh$_3$)]$^+$ and [η^5-Cp(OC)$_2$(η^2-allene)Fe]$^+$ with hydride donors and nucleophiles lead to products containing the FeC(CH$_2$Nu)=CH$_2$ unit [6,7]). In this case it was envisaged that subsequent reaction of [η^5-Cp(OC)(η^2-allene)Fe(μ-PPh$_2$)PtH(PPh$_3$)$_2$]$^+$ (if formed) may lead to a product containing a bridging vinyl group between Fe and Pt. (Shaw et al. [8] have recently reported the reaction of (OC)$_3$Fe(μ-dppm)(μ-CO)Pt(PPh$_3$) (dppm = Ph$_2$PCH$_2$PPh$_2$) with allene at 80 °C to give (OC)$_3$Fe(μ-dppm)(μ-CH$_2$CCH$_2$)Pt(PPh$_3$) a complex containing a dimetallocyclobutane with an exocyclic methylene group.) However, it should be noted that the cation **1a** contains an uncoordinated olefinic function and that reaction with Pt(C$_2$H$_4$)(PPh$_3$)$_2$ could proceed via the alternative pathway of C$_2$H$_4$ substitution rather than P–H oxidative addition.

In this paper we report the synthesis of **1a** and its PMe$_2$Ph analog [η^5-Cp(OC)(η^2-allene)Fe(PMe$_2$Ph)]$^+$ PF$_6^-$ (**1b**) and their reaction with Pt(C$_2$H$_4$)(PPh$_3$)$_2$ to give "η^1,η^3-allylic bridged" complexes [2-(η^5-Cp(OC)(PR$_3$)Fe)C$_3$H$_4$Pt(PPh$_3$)$_2$]PF$_6$ (**2**) (i.e. products of the olefinic substitution pathway). The structure of **2b** (PR$_3$ = PMe$_2$Ph) has been determined by X-ray crystallography and contains an interesting disorder amongst the phenyl rings of the Pt(PPh$_3$)$_2$ moiety.



(eq 1)

1a

2a

Results and discussion

The cationic complexes [η^5-Cp(OC)(η^2-allene)Fe(PR$_3$)]PF$_6$ (**1a**, PR$_3$ = PPh$_2$H; **b**, PR$_3$ = PMe$_2$Ph), were prepared in ca. 50% yield from [η^5-Cp(OC)IFe(PR$_3$)] and AgPF$_6$ following the procedure of Reger et al. [6] for the syntheses of **1** (PR$_3$ = PPh$_3$). Complexes **1** are structurally similar to [η^5-Cp(OC)(η^2-cyclohepta-1,2-diene)Fe(PPh$_3$)]PF$_6$, the structure of which has recently been determined by X-ray diffraction [9]. The ^{1}H NMR spectrum of **1b** exhibits separate multiplet resonances at 5.05 and 5.60 ppm assignable to the two non-equivalent protons of the uncoordinated olefin together with a broad resonance at 2.1 ppm due to the two diastereotopic methylene protons of the coordinated double bond. Thus migration of the "η^5-Cp(OC)(PMe$_2$Ph)Fe unit" from one double bond to the other (if occurring) is slow on the NMR time scale [10]. The proton NMR of **1b** was also expected to give two methyl doublet resonances of equal intensity as is observed in the case of [η^5-Cp(OC)IFe(PMe$_2$Ph)] and [η^5-Cp(OC)(MeC≡CMe)Fe(PMe$_2$Ph)]PF$_6$ [11] since the methyl groups of **1b** are diastereotopic. However, only one methyl doublet resonance is observed for **1b** (20 °C) at 1.80 ppm (^2J (^{31}P–^{1}H) = 10 Hz). {The low temperature ^{1}H NMR spectrum of **1b** at −60 °C is consistent with the presence in solution of two conformational isomers in the ratio ca. 2 : 1, probably due to two preferred orientations of the η^2-allene ligand. However, the exact nature of the process leading to coalescence of the diastereotopic allenic protons and PMe_2Ph methyl groups has not as yet been fully established and further studies are in progress.} The room temperature ^{1}H NMR of **1a** is similar (allenic protons) to that of **1b**.

The secondary phosphine complex **1a** reacts rapidly with $Pt(C_2H_4)(PPh_3)_2$ in CH_2Cl_2 at room temperature (reaction complete in < 5 min) to give the bimetallic cation $[2\text{-}(\eta^5\text{-}Cp(OC)(PPh_2H)Fe)C_3H_4Pt(PPh_3)_2]^+$ PF_6^- (**2a**) containing an η^3-allyl-$Pt(PPh_3)_2{}^+$ cation [12] with a "η^5-Cp(OC)(PPh_2H)Fe" moiety attached to the central carbon of the allyl ligand (eq. 1). Complex **1b** reacts similarly to give **2b**. Spectroscopic data for **2** (Experimental section) readily establishes the presence of the "η^5-Cp(OC)(PR_3)Fe" and "Pt(PPh_3)$_2$" moieties in the molecule. The lack of a plane of symmetry in **2** implies diastereotopic *syn* protons and *anti* protons (allylic ligand) and diastereotopic PMe_2Ph methyl protons (for **2b**) (observed – see Experimental). Larger $^2J(^{195}Pt-^1H)$ coupling to the allylic *anti* protons vis à vis *syn* protons is consistent with previous data for η^3-allylplatinum(II) systems [13]. However, whilst the spectroscopic data of **2** are consistent with an η^1,η^3-allylic bridged structure, they do not unambiguously establish the structure. Consequently the molecular structure of the cation **2b** has been determined by single crystal X-ray diffraction methods.

The molecular structure of 2b

A view of the molecular structure (Fig. 1) shows that the allyl group is η^3-bonded to the platinum atom with Pt–C distances of 2.151(9) and 2.165(8) Å to the terminal atoms and 2.272(7) Å to the central atom which also forms a σ (η^1-)bond to the Fe atom of length 1.967(7) Å. The Pt–Fe separation of 3.794(1) Å is clearly non-bonding. The plane of the allyl group is canted by 122.5° with respect to the PtP(1)P(2) plane and the Fe atom is displaced out of this plane by 0.185(1) Å towards the Pt. This allyl plane is further rotated by ca. 2° from a symmetric arrangement with respect to the PtP_2 plane {displacements of the C(1, 2, 3) atoms from this latter plane are respectively $-0.286(9)$, $+0.385(9)$ and $-0.369(10)$ Å}. It is notable that

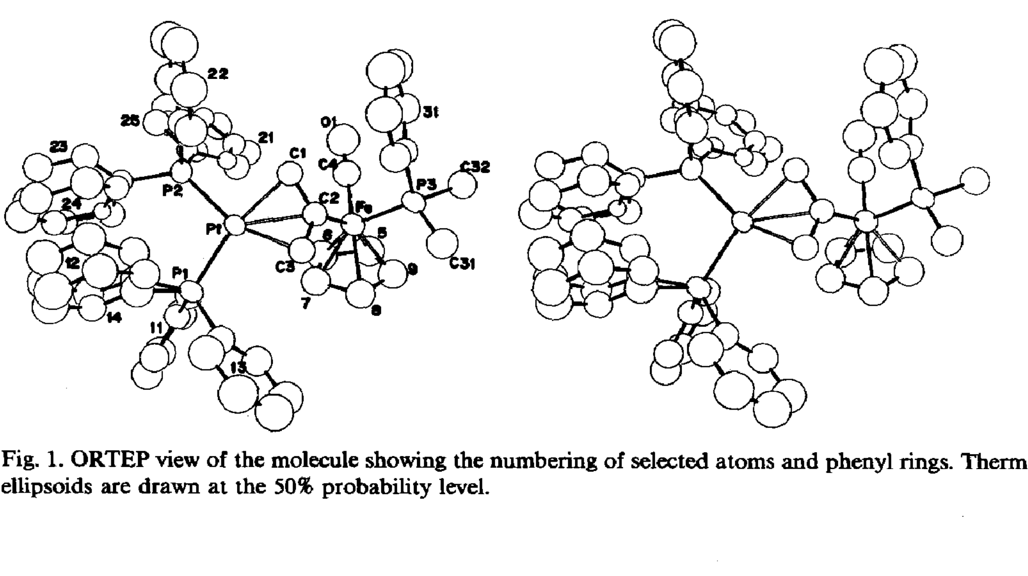


Fig. 1. ORTEP view of the molecule showing the numbering of selected atoms and phenyl rings. Thermal ellipsoids are drawn at the 50% probability level.

Table 1

Final atomic positional ($\times 10^4$) and thermal ($\times 10^3$) parameters with estimated standard deviations in parentheses.

Final [a]	x	y	z	U or U_{eq} (Å^2) [b]
Pt	601.8(3)	2803.5(2)	2549.1(2)	37.9(2)*
Fe	−1983.9(10)	1700.4(9)	636.3(7)	44.7(7)*
P(1)	921(2)	2018(2)	3603(1)	45(1)*
P(2)	1151(2)	4484(2)	3180(1)	48(1)*
P(3)	−1697(2)	1333(2)	−499(1)	44(1)*
P(4)	4475(3)	2230(3)	2136(2)	89(3)*
F(1)	3572(12)	1467(10)	2311(8)	200(14)*
F(2)	5319(10)	2954(10)	1945(9)	184(14)*
F(3)	4499(10)	3017(11)	2790(7)	187(13)*
F(4)	3541(11)	2363(13)	1483(10)	242(17)*
F(5)	4402(11)	1288(10)	1525(8)	205(14)*
F(6)	5427(11)	2084(10)	2772(8)	200(13)*
O(1)	−2154(6)	3618(6)	328(5)	99(2)
C(1)	368(6)	3141(6)	1372(5)	52(2)
C(2)	−374(6)	2149(6)	1189(5)	50(2)
C(3)	244(7)	1511(6)	1571(5)	55(2)
C(4)	−2074(8)	2841(7)	457(6)	68(2)
C(5)	−3653(10)	1167(9)	519(7)	91(3)
C(6)	−2968(9)	1611(9)	1366(7)	87(3)
C(7)	−2201(8)	1073(8)	1601(6)	76(3)
C(8)	−2435(9)	272(8)	892(6)	78(3)
C(9)	−3338(9)	350(8)	237(7)	80(3)
C(31)	−1411(8)	144(8)	−718(6)	77(3)
C(32)	−2853(8)	1207(7)	−1421(6)	71(2)
C(111)	−74(7)	1856(6)	4100(5)	59(2)
C(112)	−910(8)	2283(8)	3876(6)	74(3)
C(113)	−1747(10)	2113(9)	4237(8)	95(3)
C(114)	−1635(10)	1564(10)	4825(8)	98(4)
C(115)	−827(9)	1174(9)	5061(7)	88(3)
C(116)	12(8)	1296(8)	4710(6)	76(3)
C(121) [a]	2227(13)	2741(13)	4398(9)	55(4)
C(122) [a]	2422(15)	3016(15)	5250(11)	74(5)
C(123) [a]	3527(17)	3565(17)	5790(12)	98(6)
C(124) [a]	4349(15)	3835(15)	5516(12)	95(6)
C(125) [a]	4181(14)	3645(14)	4689(10)	84(5)
C(126) [a]	3108(12)	3062(14)	4139(9)	70(4)
C(131)	910(7)	703(7)	3320(5)	63(2)
C(132)	1913(10)	499(9)	3508(8)	96(3)
C(133)	1787(12)	−584(11)	3186(9)	114(4)
C(134)	828(12)	−1249(11)	2778(8)	108(4)
C(135)	−117(10)	−1061(9)	2600(8)	98(4)
C(136)	−86(8)	−27(8)	2900(6)	75(3)
C(141) [b]	2357(32)	2460(32)	4367(24)	86(12)
C(142) [b]	3145(22)	2520(24)	4051(16)	68(7)
C(143) [b]	4267(26)	2889(26)	4618(20)	90(10)
C(144) [b]	4477(30)	3073(30)	5473(22)	105(12)
C(145) [b]	3650(32)	3003(33)	5755(23)	105(12)
C(146) [b]	2555(24)	2666(24)	5219(17)	63(8)
C(211) [c]	−66(17)	5015(9)	2910(9)	46(4)
C(212) [c]	−1115(18)	4361(14)	2347(10)	65(4)
C(213) [c]	−2056(18)	4724(14)	2128(10)	70(4)
C(214) [c]	−1878(20)	5722(14)	2518(11)	75(5)
C(215) [c]	−829(20)	6382(13)	3091(12)	70(5)

Table 1 (continued)

Final [a]	x	y	z	U or U_{eq} (Å^2) [b]
C(216) [c]	64(16)	6025(10)	3303(9)	60(4)
C(221)	2162(7)	5186(7)	2833(5)	62(2)
C(222)	2862(9)	4704(8)	2648(7)	82(3)
C(223)	3748(10)	5252(10)	2417(8)	96(3)
C(224)	3839(10)	6209(10)	2360(8)	100(4)
C(225)	3201(11)	6701(10)	2569(8)	105(4)
C(226)	2296(9)	6181(9)	2793(7)	88(3)
C(231) [d]	1683(14)	5004(11)	4260(9)	47(4)
C(232) [d]	2766(12)	5714(11)	4647(9)	63(4)
C(233) [d]	3190(13)	6073(12)	5503(10)	74(5)
C(234) [d]	2558(14)	5754(13)	5978(10)	69(4)
C(235) [d]	1460(16)	5069(12)	5566(10)	60(5)
C(236) [d]	944(17)	4669(13)	4699(11)	64(5)
C(241) [e]	1974(26)	4862(22)	4333(17)	54(8)
C(242) [e]	3081(27)	5069(26)	4686(20)	88(10)
C(243) [e]	3607(26)	5329(24)	5581(19)	86(10)
C(244) [e]	2985(32)	5373(29)	6056(22)	97(11)
C(245) [e]	1911(28)	5083(21)	5687(17)	57(7)
C(246) [e]	1347(20)	4762(14)	4804(12)	28(5)
C(251) [f]	277(23)	5085(15)	3040(14)	39(9)
C(252) [f]	494(23)	6077(15)	3459(14)	66(11)
C(253) [f]	−335(23)	6531(15)	3300(14)	68(11)
C(254) [f]	−1382(23)	5994(15)	2722(14)	48(9)
C(255) [f]	−1599(23)	5002(15)	2304(14)	49(9)
C(256) [f]	−770(23)	4547(15)	2463(14)	34(8)
C(311)	−549(7)	2252(7)	−595(5)	60(2)
C(312)	467(8)	2075(7)	−400(6)	73(3)
C(313)	1396(10)	2838(10)	−433(8)	96(3)
C(314)	1228(11)	3664(11)	−692(9)	110(4)
C(315)	223(11)	3855(10)	−880(8)	107(4)
C(316)	−694(9)	3105(8)	−847(6)	79(3)
C(15)	5086(26)	−450(31)	4314(21)	263(14)
C(25)	5021(27)	527(30)	4410(21)	252(13)
C(35)	4954(26)	1056(25)	5079(23)	262(14)
C(45)	5772(14)	4748(13)	−211(11)	134(5)
C(55)	5349(14)	4237(13)	280(10)	137(5)
C(65)	4545(14)	4492(13)	495(10)	134(5)
C(75)	5891(13)	−1787(12)	1452(10)	127(5)
C(85)	5810(13)	−911(12)	1795(10)	125(5)
C(95)	6328(15)	−475(14)	2613(12)	146(6)
C(105)	7030(16)	−953(16)	3118(12)	164(7)
C(115)	7076(15)	−1863(15)	2757(12)	150(6)
C(125)	6424(16)	−2327(15)	1886(12)	157(6)

[a] Population parameters: $a = 0.66(2)$, $b = (0.37(2)$, $c = 0.68(4)$, $d = 0.62(2)$, $e = 0.36(2)$ and $f = 0.30(4)$.
[b] Values marked with an asterisk are refined anisotropically and given in terms of the equivalent isotropic thermal parameter $U_{eq} = 1/3$ trace U.

the bulky substituent in the 2 position effectively prevents the disordered allyl orientations observed in several other η^3-allylplatinum(II) compounds [12,14–16]. In the one example with a single allyl orientation disorder is observed in the methyl groups of the phosphine [16] and a similar situation is observed in the PPh_3 ligands

Table 2

Selected bond distances (Å) and bond angles (deg.)

Bond distances (Å)			
Pt–Fe	3.794(1)	P(1)–C(111)	1.817(11)
Pt–P(1)	2.281(2)	P(1)–C(121)	1.803(13)
Pt–P(2)	2.287(2)	P(1)–C(131)	1.839(10)
Pt–C(1)	2.151(9)	P(1)–C(141)	1.86(4)
Pt–C(2)	2.272(7)	P(2)–C(211)	1.92(2)
Pt–C(3)	2.165(8)	P(2)–C(221)	1.805(11)
Fe–P(3)	2.188(3)	P(2)–C(231)	1.79(2)
Fe–C(1)	3.049(7)	P(2)–C(241)	1.91(3)
Fe–C(2)	1.967(7)	P(2)–C(251)	1.59(3)
Fe–C(3)	3.036(9)	P(3)–C(31)	1.823(12)
Fe–C(4)	1.703(11)	P(3)–C(32)	1.816(9)
Fe–C(5)	2.121(13)	P(3)–C(311)	1.825(10)
Fe–C(6)	2.127(14)	P(4)–F(1)	1.55(2)
Fe–C(7)	2.101(12)	P(4)–F(2)	1.49(2)
Fe–C(8)	2.103(11)	P(4)–F(3)	1.47(1)
Fe–C(9)	2.124(10)	P(4)–F(4)	1.49(2)
C(4)–O(1)	1.168(14)	P(4)–F(5)	1.55(2)
C(1)–C(2)	1.421(10)	P(4)–F(6)	1.50(1)
C(2)–C(3)	1.464(13)		
C(5)–C(6)	1.44(2)		
C(5)–C(9)	1.40(2)		
C(6)–C(7)	1.42(2)		
C(7)–C(8)	1.46(2)		
C(8)–C(9)	1.43(2)		
Bond angles (deg.)			
P(1)–Pt–P(2)	104.17(8)	Pt–P(1)–C(111)	116.6(3)
P(1)–Pt–C(1)	162.5(2)	Pt–P(1)–C(121)	109.4(6)
P(1)–Pt–C(2)	130.3(2)	Pt–P(1)–C(131)	115.0(3)
P(1)–Pt–C(3)	97.6(2)	Pt–P(1)–C(141)	116(1)
P(2)–Pt–C(1)	91.6(2)	C(111)–P(1)–C(121)	105.6(7)
P(2)–Pt–C(2)	124.2(2)	C(111)–P(1)–C(131)	100.7(5)
P(2)–Pt–C(3)	156.1(3)	C(111)–P(1)–C(141)	111 (2)
C(1)–Pt–C(2)	37.4(3)	C(121)–P(1)–C(131)	108.8(7)
C(1)–Pt–C(3)	65.6(3)	C(121)–P(1)–C(141)	15 (2)
C(2)–Pt–C(3)	38.4(3)	C(131)–P(1)–C(141)	94 (2)
P(3)–Fe–C(2)	86.2(3)	Pt–P(2)–C(211)	111.0(3)
P(3)–Fe–C(4)	90.2(4)	Pt–P(2)–C(221)	109.4(3)
P(3)–Fe–C(5)	114.6(3)	Pt–P(2)–C(231)	125.8(5)
P(3)–Fe–C(6)	153.9(3)	Pt–P(2)–C(241)	116.9(9)
P(3)–Fe–C(7)	141.4(3)	Pt–P(2)–C(251)	119.7(7)
P(3)–Fe–C(8)	102.3(3)	C(211)–P(2)–C(221)	107.5(6)
P(3)–Fe–C(9)	90.3(3)	C(211)–P(2)–C(231)	97.2(8)
C(2)–Fe–C(4)	96.0(4)	C(211)–P(2)–C(241)	111(1)
C(2)–Fe–C(5)	157.2(4)	C(211)–P(2)–C(251)	8.8(7)
C(2)–Fe–C(6)	118.5(4)	C(221)–P(2)–C(231)	104.4(6)
C(2)–Fe–C(7)	91.6(4)	C(221)–P(2)–C(241)	100(1)
C(2)–Fe–C(8)	101.8(4)	C(221)–P(2)–C(251)	103(1)
C(2)–Fe–C(9)	139.3(4)	C(231)–P(2)–C(241)	14 (1)
C(4)–Fe–C(5)	93.3(5)	C(231)–P(2)–C(251)	91 (1)
C(4)–Fe–C(6)	94.8(5)	C(241)–P(2)–C(251)	106 (1)
C(4)–Fe–C(7)	128.3(5)	Fe–P(3)–C(31)	116.8(4)
C(4)–Fe–C(8)	158.8(5)	Fe–P(3)–C(32)	114.3(4)

Table 2 (continued)

Bond angles (deg.)			
C(4)-Fe-C(9)	124.6(4)	Fe-P(3)-C(311)	115.6(3)
C(5)-Fe-C(6)	39.6(4)	C(31)-P(3)-C(32)	102.0(4)
C(5)-Fe-C(7)	66.5(5)	C(31)-P(3)-C(311)	102.6(5)
C(5)-Fe-C(8)	66.0(5)	C(32)-P(3)-C(311)	103.6(5)
C(5)-Fe-C(9)	38.5(5)	F(1)-P(4)-F(2)	178.4(7)
C(6)-Fe-C(7)	39.3(5)	F(1)-P(4)-F(3)	88.7(8)
C(6)-Fe-C(8)	66.5(5)	F(1)-P(4)-F(4)	85.3(9)
C(6)-Fe-C(9)	65.8(4)	F(1)-P(4)-F(5)	83.9(8)
C(7)-Fe-C(8)	40.6(4)	F(1)-P(4)-F(6)	95.6(8)
C(7)-Fe-C(9)	66.9(4)	F(2)-P(4)-F(3)	92.3(8)
C(8)-Fe-C(9)	39.6(4)	F(2)-P(4)-F(4)	93.3(9)
Pt-C(1)-C(2)	75.9(5)	F(2)-P(4)-F(5)	95.3(8)
Pt-C(2)-Fe	126.9(5)	F(2)-P(4)-F(6)	85.8(8)
Pt-C(2)-C(1)	66.7(4)	F(3)-P(4)-F(4)	95.5(9)
Pt-C(2)-C(3)	66.8(4)	F(3)-P(4)-F(5)	171.3(9)
Fe-C(2)-C(1)	127.6(7)	F(3)-P(4)-F(6)	86.2(8)
Fe-C(2)-C(3)	123.8(5)	F(4)-P(4)-F(5)	88.3(9)
C(1)-C(2)-C(3)	108.3(6)	F(4)-P(4)-F(6)	178.1(10)
Pt-C(3)-C(2)	74.7(5)	F(5)-P(4)-F(6)	90.1(8)
Fe-C(4)-O(1)	178.9(8)		
C(6)-C(5)-C(9)	108.7(11)		
C(5)-C(6)-C(7)	107.9(11)		
C(6)-C(7)-C(8)	107.4(9)		
C(7)-C(8)-C(9)	107.4(10)		
C(8)-C(9)-C(5)	108.6(9)		
Fe-Cp-Cp	69.4(5)-71.3(7)		

in the present compound. In all these latter compounds Pt-C distances are variable and somewhat inaccurately determined with a typical range of values from 2.07-2.24 Å. The cant of the allyl groups in these and analogous Pd compounds are typically 116 ± 10° [17].

The C-C bond lengths in the allyl fragment of **2b** (1.421(10) and 1.464(13) Å) are essentially equal although the CCFe angles are non-equivalent (123.8(5) and 127.6(7)°) presumably due to differences in the interactions between the *syn* H atoms and the Cp and CO groups on the Fe. These C-C bond lengths are significantly elongated over typical C-C bond lengths in other η^3-allyl complexes (1.357-1.359(15) Å) [17].

The observed Pt-P distances (2.281(2) and 2.287(2) Å) are significantly shorter than those observed in (η^3-allyl)bis(tricyclohexylphosphine)platinum hexafluorophosphate (2.330(3) Å, ave.) [12] and other *cis*-$Pt(PCx_3)_2$ complexes as well as that in (η^3-allyl)chloro(tri-t-butylphosphine)platinum (2.333(2) Å) [14]. Surprisingly, the Pt-P bond in (η^3-allyl)chloro(tri-*p*-tolylphosphine)platinum is slightly shorter at 2.272(4) Å [15]. Other Pt^{II}-P distances are generally within the range 2.218-2.362 Å. In the present compound the PPtP angle (104.17(8)°) is significantly smaller than that observed in (η^3-allyl)bis(tricyclohexylphosphine)platinum hexafluorophosphate (111.2(1)°) which is attributable to severe steric crowding amongst the cyclohexyl rings in the latter compound. In the PPh_3 groups of **2b** disorder amongst the phenyl rings results in a pair of ring orientations (12,14) separated by a CPC angle of 15(2)° and inter-plane angle of 14° for P(1) and two pairs of ring orientations (21, 25) and (23, 24) separated by CPC angles and inter-plane angles of 8.8(7) and 14(1)° and 2.6 and −24.8° respectively for P(2). The resultant average CPC angles are then 104.0° (P(1)) and 102.5° (P(2)). Further evidence of steric effects between the phenyl rings involve displacements of the P atoms from the mean planes of the rings by up to 0.142(2) Å (0.072(2) Å for ring 31) and variable PCC angles of 115–126(1)° (Supplementary Tables).

If the Cp ring is considered to occupy three vertices, then the coordination geometry of the Fe atom is distorted octahedral with C(2)–Fe–C(4), C(2)–Fe–P(3) and C(4)–Fe–P(3) angles of 96.0(4), 86.2(3) and 90.2(4)° respectively and *trans* angles involving the Cp of 153.9(3) (P(3)), 157.2(4) (C(2)) and 158.8(5)° (C(4)). The Fe–Cp bond lengths (2.101(12)–2.127(14)Å) and Fe...centroid distance (1.730(1) Å) are comparable to those observed for $(\eta^5C_5H_5)Fe(CO)(PPh_3)(COOC_{10}H_{15})$ and related compounds [18]. The present Fe–C(≡O) and Fe–allyl distances are however significantly longer than the Fe–C(≡O) (1.670(7) Å) and Fe–C(=O)R (1.825(6) Å) distances observed in the above ester. In other compounds tabulated in the same paper, Fe–C(≡O) distances are generally > 1.73 Å in length. Similarly, with two exceptions, other Fe–C(=O)–R distances were 1.98–2.04 Å. The Fe–allyl distance is, however, the same as the σ-Fe-1-allyl distance (1.968(12)Å) observed in a bridging η^1,η^3-allyldiiron complex. Notably the C–C distances in this latter complex are 1.433(18) and 1.457(17) Å, [19].

The observed Fe–P bond length (2.188(3) Å) is significantly shorter than the $Fe–PPh_3$ bond length (2.214(2) Å) in the ester above. Other Fe–P bond lengths in five coordinate carbonyltriphenylphosphineiron complexes have been found to vary from 2.188–2.264 Å and to correlate well with the stretching frequency of the carbonyl group [20]. In a six coordinate *trans*-bis(dimethylphenylphosphine) complex the Fe–P distances were 2.260 and 2.264(2) Å [21]. The short Fe–P distance in **2b** results in an opening out of the FePC angles (av. 115.6°) and compression of the CPC angles at P(3) (av. 102.7°).

The hexafluorophosphate anion is a distorted octahedron with ⟨P–F⟩ 1.51 Å.

Experimental

All manipulations were carried out under an atmosphere of dry N_2, using dry, degassed solvents. IR spectra (as CH_2Cl_2 solutions) were recorded on a Nicolet 10DX spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2) were obtained on a Varian XL 200 spectrometer and are referenced to TMS and 85% H_3PO_4, respectively. The cations $[\eta^5\text{-}Cp(OC)(PR_3)Fe(\eta^2\text{-allene})]PF_6$ (**1a**, $PR_3 = PPh_2H$; **1b**, $PR_3 = PPhMe_2$) were prepared following the procedure described by Reger et al. for the synthesis of $[\eta^5\text{-}Cp(OC)(PPh_3)Fe(\eta^2\text{-allene})]PF_6$ [6]. Complexes **1** were isolated in 50% yield as yellow powders. Their IR ν(CO) region and ^1H NMR data were similar to those reported for $[\eta^5\text{-}Cp(OC)(PPh_3)Fe(\eta^2\text{-}C_3H_4)]PF_6$.

*$[2\text{-}\{\eta^5\text{-}Cp(OC)(PPh_2H)Fe\}C_3H_4Pt(PPh_3)_2]PF_6$ (**2a**)*

$Pt(C_2H_4)(PPh_3)_2$ (0.159 g, 0.213 mmol) was added to a CH_2Cl_2 solution (10 ml) of **1a** (0.098 g, 0.215 mmol). After 30 min the yellow solution was filtered and concentrated to 5 ml. Addition of n-octane (5 ml) precipitated a yellow oil which, upon replacement of the mother liquor with neat n-octane (5 ml) followed by rapid stirring, afforded complex **2a** as a yellow solid (0.210 g, 0.178 mmol, 84% yield).

Complex **2b** was similarly prepared in 80% yield. Recrystallization from CH_2Cl_2/pentane at $-20\,^\circ C$ gave yellow crystals suitable for X-ray diffraction. Spectroscopic data **2a**: $\nu(CO)$ 1942 cm^{-1}. ^1H NMR (ppm) C_5H_5 4.41(s); allylic ligand H_{syn} 3.43 (broad) and 4.05 (broad) $\{^2J(^{195}Pt-^1H)$ was small and not resolved$\}$, H_{anti} 2.48 ($^2J(^{195}Pt-^1H)$ 46 and $^3J(^{31}P-^1H)$ ca. 7 Hz) and 3.34 ($^2J(^{195}Pt-^1H)$ 48, $^3J(^{31}P-^1H)$ ca. 7 Hz). The Ph_2P-H resonance is partly masked by the phenyl resonance. ^{31}P NMR $\delta(PPh_2H)$ 64.8 ($^3J(^{195}Pt-^{31}P)$ 152 Hz) $\delta(PPh_3)$ 19.3 ($^1J(^{195}Pt-^{31}P)$ 3600 Hz) and 18.9 ($^1J(^{195}Pt-^{31}P)$ 3708 Hz).

Spectroscopic data **2b**: $\nu(CO)$ 1932 cm^{-1}. ^1H NMR (ppm) C_5H_5 4.27(d) ($^2J(^{31}P-^1H)$ 1.5 Hz); allylic ligand H_{syn} 3.61 (broad) and 4.5 (broad), H_{anti} 2.96 ($^2J(^{195}Pt-^1H)$ 51, $^3J(^{31}P-^1H)$ 7.5 Hz) and 3.71 ($^2J(^{195}Pt-^1H)$ 51, $^3J(^{31}P-^1H)$ 7.5 Hz); PMe_2Ph (diastereotopic CH_3 groups) 1.55(d) and 1.70(d) ($^2J(^{31}P-^1H)$ 9.5 Hz). ^{31}P NMR $\delta(PMe_2Ph)$ 46.7 ($^3J(^{195}Pt-^{31}P)$ 116 Hz) $\delta(PPh_3)$ 19.5 (^1J ($^{195}Pt-^{31}P$) 3582 Hz), 18.9 ($^1J(^{195}Pt-^{31}P)$ 3710 Hz). ^{13}C NMR C_5H_5 85.25; CO 219 ($^2J(^{31}P-^{13}C)$ 31 Hz. $J(^{195}Pt-^{13}C)$ not resolved) allylic carbons C(1) and C(3) 81.5 and 80.9 ($^1J(^{195}Pt-^{13}C)$ 116, $^2J(^{31}P-^{13}C)$ 5.5 Hz) central allyl carbon C(2) 219 ($^1J(^{195}Pt-^{13}C)$ 80, $J(^{31}P-^{13}C)$ 28 Hz), PMe_2Ph 17.5 ($^1J(^{31}P-^{13}C)$ 34 Hz), 15.9 ($^1J(^{31}P-^{13}C)$ 30 Hz).

X-Ray crystallography

Large yellow prisms and rhombs of **2b** were cleaved into smaller fragments. One approximately needle shaped fragment used throughout. D_m not measured. Unit cell dimensions were obtained by least-squares refinement of diffracting positions of 25 reflections ($12.2 < \theta < 16.3°$) on an Enraf–Nonius CAD4 diffractometer by the use of graphite monochromatized Mo-K_α radiation. Intensity data collected using $\omega-2\theta$ scans over ω scan ranges $(0.65 \pm 0.35 \tan\theta)°$. Scan rates conditional on information collected in prescans (at 10 deg min^{-1}) selected to give $I/\sigma(I) > 25$ within a max. scan time of 80 s. Backgrounds by extending scan by 25% on either side of peak measured for half the time taken to collect peak. The crystal was recentred or reoriented regularly to compensate for slight crystal movements as indicated by the measured intensities of 3 standard reflections collected every 9000 s of exposure time. Several small sections of data recollected after large shifts in the intensities of the standards. A total of 11733 reflections (inc. standards) in the quadrants h, $\pm k$, $\pm l$ with $2\theta \leq 50°$ measured. Lorentz, polarization and corrections for crystal decay (max. loss in intensities of standards ca. 19%) applied to all data. 696 reflections with $F_{obs} = 0.0$ rejected and a further 815 symmetry equivalent or duplicated data then averaged ($R_{merge}(F) = 0.022$) to give a final data set of 9885 reflections.

The statistical distribution of the normalized structure factors favored the acentric space group $P1$ and the initial structure solution in this space group (by the use of the Patterson function for 2Pt atoms, least-squares and Fourier calculations) revealed two independent molecules and the presence of several solvent molecules. However, the majority of the heavy atoms were related by a centre of symmetry and further refinement was in the centric space group. In both space groups several residual peaks in ΔF maps were close to some of the rings with large thermal parameters in the triphenyl phosphine groups *. The (common) population parame-

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* High thermal parameters for atoms in the phosphine ligands of several allyl-platinum and -palladium complexes have frequently been observed and attributed to unresolved disorder [23].

ters of atoms in these alternative ring orientations were then allowed to refine with no constraints on geometry (with the exception of ring 25 which was refined as a rigid group) nor on the sum of the population parameters for alternative orientations. Significant improvements in the residual and reasonable ring geometries and population parameter sums were obtained. Final least-squares refinement in 3 blocks and minimizing $\Sigma w \Delta F^2$ (Pt, Fe, P and F anisotropic) then converged (max. $\Delta/\sigma = 0.153$) to final agreement indices $R = 0.0527$ ($R_w = 0.0575$) for 7731 observed data with $I > 3\sigma(I)$. Weights given by $w = [\sigma^2(F) + 0.00191\ F^2]^{-1}$. Most significant features in a final ΔF map were some peaks up to 1.3 eÅ^{-3} in height near Pt.

Programs: Enraf–Nonius SDP package and SHELX76 [22] on PDP 11/23 and Gould 9705 computers respectively. Atomic scattering factors were taken from International Tables for X-ray Crystallography.

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