Synthesis and characterisation of platinum(0) complexes of propenoates: X-ray diffraction study of [Pt(CH₂=CHCO₂CH₂Ph)(PPh₃)₂]

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Abstract

Reaction of [Pt(C₂H₄)(PPh₃)₂] with propenoate or 2-methylpropenoate esters gave the complexes [Pt(propenoate)(PPh₃)₂] in good yield. These have been characterised by ¹H, ¹³C, ³¹P and ¹⁹⁵Pt NMR spectroscopy. The complex of benzyl propenoate has been characterised in a diffraction study. Reaction of the complexes produced with tricyclohexylphosphine, PCy₃, gave [Pt(propenoate)(PCy₃)(PPh₃)]. The propenoate complexes were shown to be more stable than those of the 2-methylpropenoates.

Keywords: Platinum; Alkene; X-ray diffraction; Nuclear magnetic resonance

1. Introduction

We have been interested for some time in the substitution chemistry of platinum(0), and have shown that the reaction of [Pt(C₂H₄)(PPh₃)₂] with bulky phosphines at low temperature results in substitution of the phosphine rather than the ethene [1]. The stability of platinum(0) alkene complexes is improved by the presence of electron-withdrawing groups on the alkene, since these allow for better metal to ligand backbonding [2]. A number of platinum alkene complexes have been prepared by displacement of ethene by another alkene. The reactions are clean, as the only by-product is gaseous ethene which is easily removed [3]. Alkene complexes isolated by this method include derivatives of ketenes [4], cumulenes [5], allenes [6], $C_2H_{4-n}X_n$ (X = CN or COOMe, n = 0–4) [7], styrene [8], strained cycloalkenes [9], Dewar benzenes [10], cyclooctene [11] and others [12]. The reaction of [Pt(C₂H₄)(DIOP)] (DIOP = *trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolan) with chiral alkenes has been used to indicate the enantiomeric purity of the alkene [13], and alkynes have also been shown to displace ethene [14]. We now report the preparation of a series of complexes of propenoates and 2-methylpropenoates by displacement of ethene from [Pt(C₂H₄)(PPh₃)₂].

2. Reaction of propenoates with [Pt(C₂H₄)(PPh₃)₂]

Addition of one molar equivalent of the propenoate to a toluene solution of [Pt(C₂H₄)(PPh₃)₂] resulted in the elimination of ethene to give [Pt(alkene)(PPh₃)₂]. The complexes 1a–c, 2a–f and 3a–e were isolated by reduction of the volume of toluene and precipitation with light petroleum (b.p. 30–40 °C) to give white or cream powders. The complexes were reasonably stable

Table 1
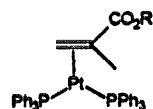³¹P NMR spectroscopic parameters for platinum(0) propenoate derivatives (25 °C, C₇D₈)

Complex	δP_a (ppm)	δP_b (ppm)	$J(PtP_a)$ (Hz)	$J(PtP_b)$ (Hz)	$J(P_aP_b)$ (Hz)
1a	32.4	31.2	3586	4060	43
1b	33.8	31.3	3691	3990	46
1c	33.5	31.4	3624	4052	44
2a	32.5	29.6	3744	3812	46
2b	32.9	29.7	3763	3792	46
2c	32.9	29.7	3760	3787	46
2d	33.9	29.5	3735	3812	48
2e	32.9	29.7	3760	3792	48
2f	32.8	29.6	3748	3804	46
3a	31.7	29.6	3684	3932	42
3b	32.4	29.4	3728	3818	45
3c	32.5	29.4	3726	3810	45
3d	32.7	29.4	3748	3816	45
3e	31.9	29.1	3619	3881	39

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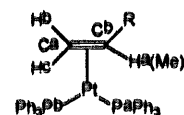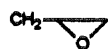at 0°C in the solid state, but decomposed over a few hours at room temperature in solution.

CO₂R structure and complexes 1a, 1b, 1c:
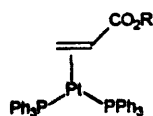
1a   R = Me
1b   R = tert-Bu
1c   R = CH₂Ph

2a   R = Me   3a   R = H
2b   R = Et   3b   R = CH₂CH₂OH
2c   R = n-Bu   3c   R = CH₂CH(OH)CH₃
2d   R = tert-Bu   3d   R =

2e   R = C₁₂H₂₅
2f   R = CH₂Ph   3e   C(=O)C(CH₃)=CH₂

structure 4

2.1. ³¹P NMR spectra

The ³¹P NMR spectra of the complexes are detailed in Table 1 and a typical spectrum is shown in Fig. 1. It proved possible (vide infra) to establish which phospho-

rus atom should be assigned to which site, and the structure 4 shows the labelling conventions used. For 1a–c the values of the coupling constant $^1J(PtP_a)$ and $^1J(PtP_b)$ both increase as the steric bulk of R increases. Since it has been noted that shorter Pt–P bond lengths give rise to higher platinum–phosphorus couplings [15], we might suggest that bonding to the alkene is weakened as the alkene becomes more bulky, with a concomitant strengthening of the phosphorus–platinum bonds.

The substitution of an α-methyl group on the double bond, in 2, causes an increase in the value of $^1J(PtP_a)$ and a decrease in the value of $^1J(PtP_b)$. The methyl group is an inductive donor, and might be expected to weaken the Pt–P bond trans to it; hence $^1J(PtP_b)$ is decreased. This argument may also be extended to explain the observation that the chemical shift of P_b in 2 is upfield by about 1.5 ppm relative to 1. Changing the ester substituent in 2 has relatively little effect on either the chemical shift or coupling constants in the phosphorus spectrum.

The other 2-methylpropenoates used in this study all have oxygen-containing side chains, giving rise to 3a–e. The ³¹P NMR spectra of these complexes show higher values of $^1J(PtP_a)$ and lower values of $^1J(PtP_b)$ relative to 2. Both 3c and 3d, which contain a chiral centre in the side chain, are formed as a mixture of two diastereoisomers in approximately equal amounts, but their phosphorus spectra are barely distinguishable.

2.2. ¹⁹⁵Pt NMR spectra

In platinum NMR spectroscopy chemical shifts are relatively insensitive to small changes in molecular structure, but they are indicative of the oxidation state of platinum [16]. The chemical shifts of compounds 1–3 confirm that they are platinum(0) complexes. Table 2
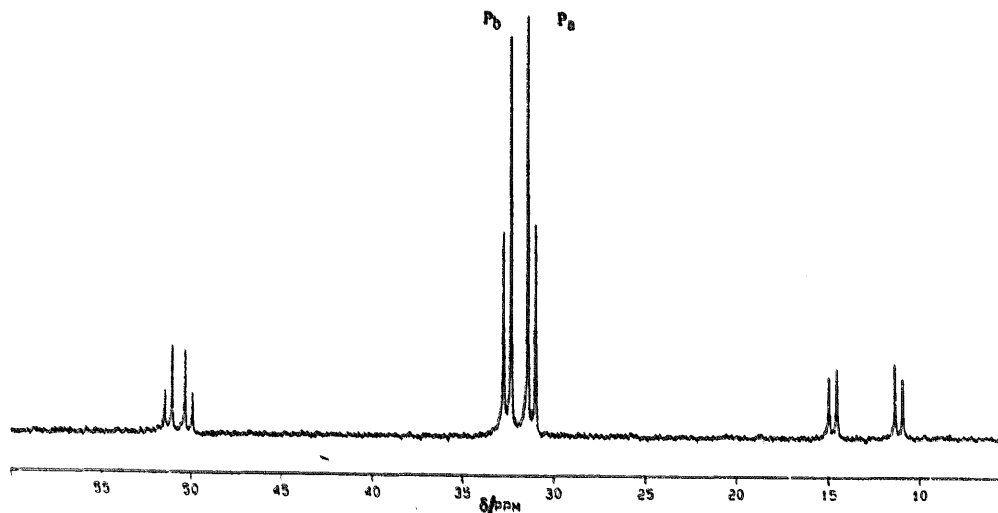

Fig. 1. ³¹P NMR spectrum (25°C, C₇D₈) of [Pt(CH₂=CHCOOMe)(PPh₃)₂] 1a.

Table 2
^{195}Pt NMR spectroscopic parameters for platinum(0) propenoate complexes (21 °C, C₇D₈)

Compound	δPt (ppm)	$^1J(PtP_a)$ (Hz)	$^1J(PtP_b)$ (Hz)
1a	−5108	3610	4067
1b	−5162	3694	3987
1c	−5110	3622	4054
2a	−5126	3742	3812
2b	−5131	3765	3794
2c	−5128	3760	3787
2d	−5143	3734	3811
2e	−5128	3761	3791
2f	−5127	3749	3804
3a	−5128	3680	3944
3b	−5129	3721	3829
3c	−5128	3719	3816
3d	−5130	3745	3815
3e	−5140	3689	3948

gives the spectroscopic data. The appearance of the spectra is a doublet of doublets, since the two values of $^1J(PPt)$ are quite distinct in all cases.

2.3. ^{13}C NMR spectra

The alkene carbons in the complexes resonate at higher fields ($\Delta\delta \approx 80$ ppm) than the free alkenes, as is common in metal alkene complexes [17]. ^{13}C NMR spectroscopic parameters for the bound carbon atoms are given in Table 3. C_a is the unsubstituted carbon atom of the propenoate, and C_b is that which bears the ester and, in 2 and 3, the methyl group. A methyl substituent on the double bond affects the chemical shift for the carbon atom to which it is bonded. In the free alkene δ is moved downfield. Thus the signal for C_b in methyl propenoate is at δ 130.6 ppm, but that in methyl 2-methylpropenoate resonates at δ 137.2 ppm. This ef-

fect is accentuated in the complexes with a change from δ 40.4 in 1a to δ 55.6 in 2a.

Each carbon atom shows one large (approximately 24–30 Hz) and one small (approximately 3–7 Hz) coupling constant associated with the two phosphorus atoms. The large coupling constant is assumed to be that associated with the pseudo-*trans* phosphorus atom. The signals were relatively weak and thus the ^{195}Pt satellites could not be observed. The α-methyl group increases $^2J(C_aP_a)$ and decreases $^2J(C_bP_b)$, but there is little effect on $^2J(C_aP_b)$ or $^2J(C_bP_a)$. The α-substituent could have an effect on the position of the platinum relative to the double bond, causing slippage towards the less congested terminus. Thus the platinum would be closer to C_a than to C_b. This would be predicted to have the effect of increasing $^2J(C_aP_a)$ and decreasing $^2J(C_bP_b)$, as is observed.

2.4. ^1H NMR spectra

Typically the chemical shift of the protons attached to the carbon–carbon double bond is moved upfield by 3–4 ppm on coordination [18]. The signals are complex as the protons are coupled to both phosphorus atoms, and to platinum, as well as to each other. The coupling constants were determined by decoupling the protons from each phosphorus in turn, and computer simulations using PANIC [19]. A typical decoupling experiment, for 2f, is shown in Fig. 2. When both phosphorus atoms are irradiated, both H_b and H_c appear as doublets with $^2J(H_bH_c) = 3.82$ Hz. When P_a is irradiated they appear as triplets, since $^3J(H_bP_b)$ at 3.93 Hz and $^3J(H_cP_b)$ at 3.22 Hz are very similar to $^2J(HH)$. Decoupling of P_b completes the data set with $^3J(H_bP_a) = 5.15$ Hz and $^3J(H_cP_b) = 3.67$ Hz. Fig. 3 shows an expansion of the alkene region of the spectrum, and a PANIC simulation

Table 3
^{13}C NMR spectroscopic parameters for platinum(0) propenoate complexes (21 °C, C₇D₈)

Compound	δC$_a$ * (ppm)	δC$_b$ * (ppm)	δC$_a$ (ppm)	δC$_b$ (ppm)	$^2J(C_aP_a)$ (Hz)	$^2J(C_aP_b)$ (Hz)	$^2J(C_bP_b)$ (Hz)	$^2J(C_bP_a)$ (Hz)
1a	129.0	130.6	47.6	40.4	26.3	6.2	33.0	4.7
1b	128.9	130.9	48.9	41.6	28.1	6.2	33.9	5.2
1c	130.3	135.5	47.5	40.5	27.3	6.4	34.4	5.4
2a	125.1	137.2	46.2	55.6	33.9	6.5	28.5	5.8
2b	124.6	137.2	46.3	55.6	33.9	6.2	30.0	6.2
2c	124.6	137.2	46.4	55.7	33.9	6.2	30.5	5.7
2d	123.8	138.4	46.9	56.5	33.9	6.2	30.5	6.7
2e	124.4	137.1	46.5	55.8	33.4	6.2	30.0	7.6
2f	127.7	135.6	46.5	55.5	33.9	6.2	30.0	6?
3a	127.7	136.4	46.4	55.3	32.8	4.9	27.6	5.7
3b	125.9	136.7	46.6	54.6	34.3	5.7	30.1	7.0
3c	125.8	136.6	46.3	55.0	32.4	1.9	29.6	5.7
3d	125.8	136.6	46.0	54.6	34.3	5.7	29.6	6.2
3e	128.3	137.5	45.6	55.4	35.7	5.2	27.6	5.7

* NMR spectroscopic parameters for the free alkenes.

(the [195]Pt satellites are omitted). Complete ^{1}H NMR spectroscopic data are given in Tables 4 and 5. The analysis of the spectrum of 2f gave starting parameters

for the more complex spectrum of the related 1c. The decoupling experiment is shown in Fig. 4.
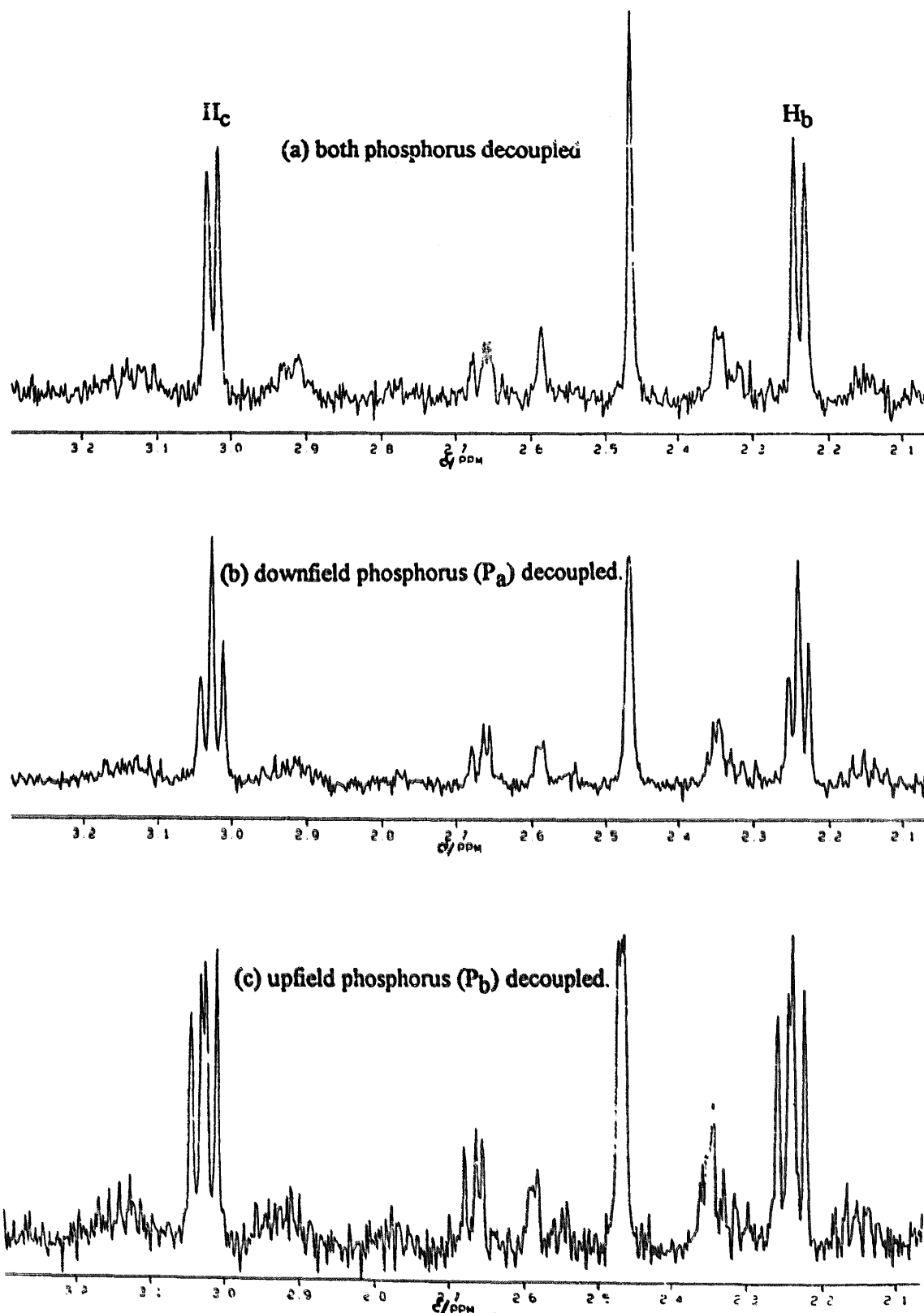
Proton–proton coupling in the complexes is substan-

Fig. 2. The decoupled ^{1}H{^{31}P} NMR spectra of [Pt{CH$_2$=C(Me)COOCH$_2$Ph}(PPh$_3$)$_2$] (25 °C, C$_7$D$_8$) 2f showing the alkene region only.

Table 4
¹H NMR chemical shifts for the alkene protons in the complexes of propenoates and 2-methylpropenoates

Compound	δH_a * (ppm)	δH_b * (ppm)	δH_c * (ppm)	δH_a (ppm)	δH_b (ppm)	δH_c (ppm)
1a	5.90	5.50	6.20	3.48	2.32	2.93
1b	6.07	5.36	5.80	3.52	2.28	2.89
1c	6.43	5.73	6.15	3.57	2.33	2.94
2a		5.20	5.80		2.23	3.01
2b		5.22	5.90		2.20	3.05
2c		5.21	5.91		2.21	3.02
2d		5.17	5.87		2.16	2.94
2e		5.20	5.93		2.22	3.03
2f		5.40	6.10		2.25	3.03
3a		5.30	6.04		2 23	3.02
3b		5.30	5.98		2.20	2.95
3c		5.30	5.97		2.19	2.92
3e		5.20	5.85		2.18	2.70

* NMR spectroscopic parameters for the free alkenes.

tially different from that in the free alkenes. The *trans*-coupling across the alkene has decreased from 17 to 10.5 Hz for 1a. The *cis*-coupling has decreased from 10.32 to 8.83 Hz, and the *geminal*-coupling has increased from 1.7 to 3.8 Hz. These data are as expected, owing to the decrease in C–C bond order, but also suggest that the molecules may possess some cyclopropane character [20] (vide infra). The $^3J(PH)$ couplings are similar to those noted for related species. Thus for $[Pt\{MeOCH=C(CN)_2\}(PPh_3)_2]$, $^3J(HP_a) = 6.9$ Hz and $^3J(HP_b) = 3.6$ Hz [21]. As it is known which phosphorus has the larger coupling to each proton (from

the decoupling experiments), and we know which phosphorus was decoupled each time, we can tell which phosphorus atom is which. The coupling of the alkene protons to platinum varies from 38 to 66 Hz, with $^2J(H_aPt)$ typically 60–66 Hz.

3. Structure of $[Pt(CH_2=CHCOOCH_2Ph)(PPh_3)_2]$

A number of platinum(0) complexes of the type $[Pt(alkene)(PPh_3)_2]$ have been characterised crystallographically, including those for which the alkene was *trans*-4-$O_2NC_6H_4CH=CHC_6H_4$-4-NO_2 [22], *trans*-Ph(CN)C=C(CN)Ph [23], $(NC)_2C=C(CN)_2$ [24], $(MeO_2C)_2C=CHCO_2Me$ [25], $Cl_2C=CCl_2$ [26], *trans*-NCCH=CHCN [27] and 5 [28]. The geometry of these complexes is characterised by a trigonal planar arrangement of the ligands with the alkene in the plane of the triangle. There is a non-zero angle between the PtP_2 and PtC_2 planes.

Crystals of 1c were grown by slow evaporation of a toluene solution. The molecular structure is shown in Fig. 5, and atomic positions and selected bond lengths and angles in Tables 6 and 7 respectively. The Pt–P bond lengths (2.261(2) and 2.296(1) Å) are significantly different, and the shorter Pt–P bond is found for the phosphorus *trans* to the -CHCOOCH₂Ph, as would be expected both from steric and electronic arguments. The Pt–C bond lengths are also distinct (2.098(8) and 2.133(8) Å). The bond to the less hindered carbon is the
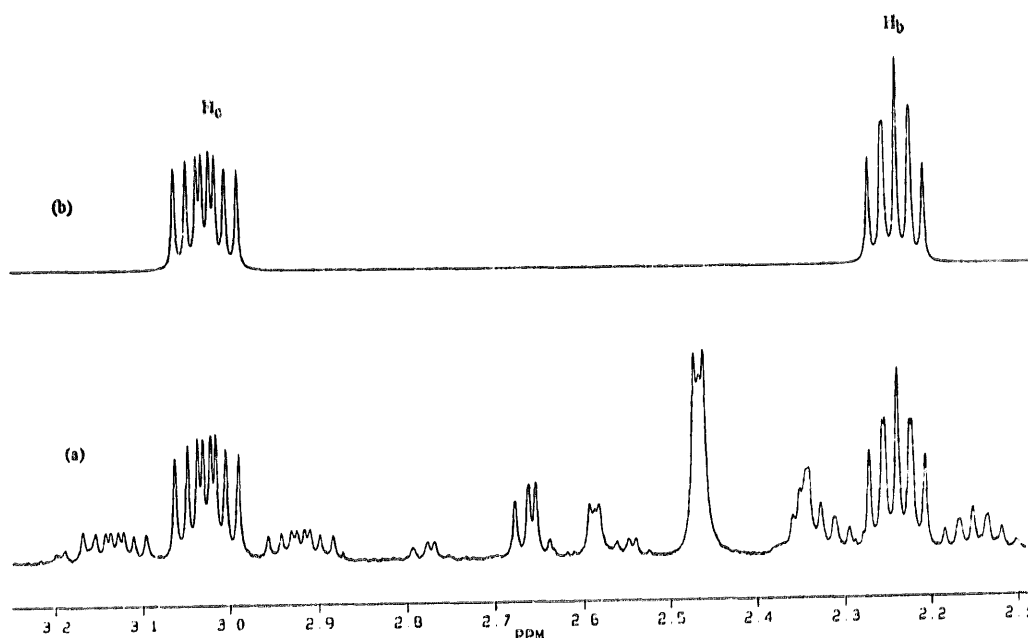

Fig. 3. (a) ¹H NMR spectrum of the alkene region of $[Pt(CH_2=CH(Me)COOCH_2Ph)(PPh_3)_2]$ (25 °C, C_7D_8) and (b) the PANIC simulation of the corresponding region.

shorter one, and the platinum has 'slipped' along the carbon–carbon double bond [29]. The dihedral angle between the PtP_2 and PtC_2 planes is $7(2)°$. This angle seems to reflect the level of steric hindrance; it is $1.6°$ in $[Pt(C_2H_4)(PPh_3)_2]$ [30], $10.8(7)°$ in $[Pt\{trans-(CF_3)CF=CF(CF_3)\}(PPh_3)_2]$ [31] and $22.1°$ in the complex of **6** [32].

6

6

7a

7b
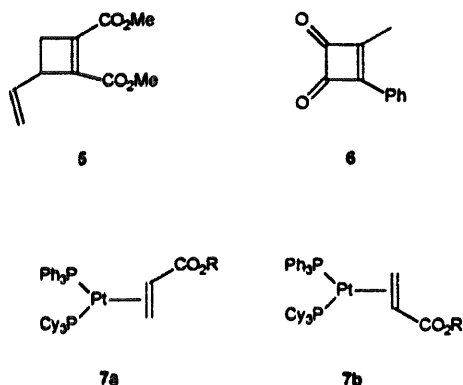
4. Reactions of the complexes with PCy_3

It was known that reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with bulky phosphines at low temperature gave $[Pt(C_2H_4)(PPh_3)(PR_3)]$, and that, of these complexes, the one with PCy_3 was the most stable. PCy_3 has a large cone angle [33], and since it is appreciably more basic than PPh_3, the chemical shift is sufficiently different from that for PPh_3 for the ^{31}P NMR spectra to be readily interpreted. PCy_3 was therefore added to complexes **1–3** at $-50°C$. The ^{31}P NMR spectra of the products show one or more AB quartets, and the reaction appears to go to completion in each case, although

some of the products were very insoluble. The same reaction products were obtained by addition of the relevant alkene to $[Pt(C_2H_4)(PCy_3)(PPh_3)]$, formed in situ. In each case there are two possible regioisomers, which are shown for the product of **1** in structures **7a** and **7b**. The reaction mixture was stored at $-20°C$ for 1–2 weeks and any equilibration monitored by ^{31}P NMR spectroscopy.

Reaction of **1a** with PCy_3 yielded a single regioisomer, for which the ^{31}P coupling constants were similar to those in the starting material. With **1b** two regioisomers were obtained in the ratio 1:1. Similar results (Table 8) were obtained for **2** and **3**, except that good spectra of the products of the reaction of **2a**, **3a** and **3e** could not be obtained due to solubility problems, and those from **3c** and **3d** (where the starting materials were a mixture of diastereoisomers) were too complex for complete interpretation.

5. Equilibration studies on alkene complexes

In order to gain some insight into the relative stabilities of the complexes, the displacement of one alkene by another was followed by ^{31}P NMR spectroscopy. One molar equivalent of a second alkene was added at $-50°C$ to $[Pt(alkene)(PPh_3)_2]$ prepared in situ. The resulting solution was warmed slowly in the NMR probe, and the ^{31}P NMR spectrum recorded. The solution was then kept at $25°C$ and the ^{31}P NMR spectrum recorded at intervals until no further change was observed. It was shown that it did not matter in which order the reaction was carried out; the same ratio of final products was obtained. It was thus shown that all of the unsubstituted propenoates displaced all of the 2-methylpropenoates, irrespective of the nature of the ester group. Of the three propenoates, methyl propenoate

Table 5
Proton–proton coupling constants for complexes of propenoates and 2-methylpropenoates

Compound	$^3J(H_aH_b)$ [a] (Hz)	$^3J(H_aH_c)$ [a] (Hz)	$^2J(H_bH_c)$ [a] (Hz)	$^3J(H_aH_b)$ (Hz)	$^3J(H_aH_c)$ (Hz)	$^2J(H_bH_c)$ (Hz)
1a	10.32	17.33	1.77	8.83	10.47	3.78
1b	10.21	17.29	1.91	8.73	10.27	4.06
1c	10.30	17.30	1.60	8.93	10.36	3.97
2a			1.70			3.59
2b			0.90			3.64
2c			0.90			3.69
2d			1.05			3.46
2e			0.98			3.60
2f			0.85			3.65
3a			0.97			3.95
3b			0.76			3.86
3c			0.95			3.41
3e			nd			4.24

[a] NMR spectroscopic data for the uncomplexed alkenes.
nd = not determined.
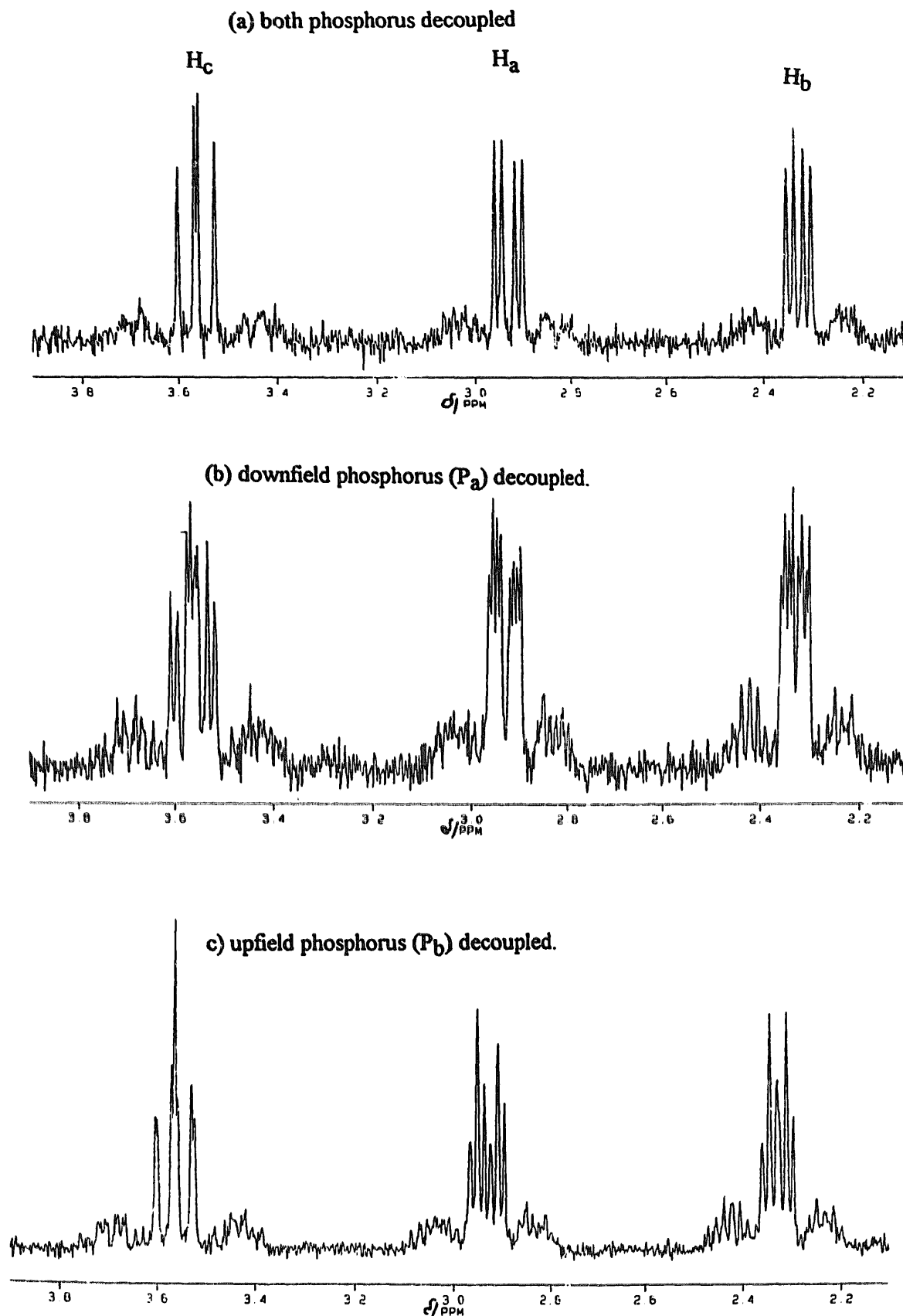
Fig. 4. The decoupled $^1H\{^{31}P\}$ NMR spectra of $[Pt(CH_2=CHCOOCH_2Ph)(PPh_3)_2]$ (25 °C, C_7D_8) 1c showing the alkene region only.

formed the most stable complex and the *tert*-butyl ester the least stable, but the differences, presumably entirely steric in origin, were not great. Thus the methyl propenoate complex predominated in any equilibrium mixture of the propenoate complexes, whilst the deriva-

Table 6
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Pt	1788.7(2)	3219.1(2)	2174.8(2)	34.7(1)
P1	3084.0(15)	1929.6(11)	1445.6(11)	35(1)
P2	−357.4(15)	2900.0(11)	2855.9(11)	38(1)
O1	798(5)	5856(4)	1283(4)	69(5)
O2	−144(5)	5773(4)	2891(3)	70(5)
C1	3863(6)	862(4)	2270(4)	43(5)
C2	3424(7)	797(5)	3274(5)	53(6)
C3	4030(9)	−28(7)	3924(5)	79(8)
C4	5014(8)	−751(6)	3552(6)	78(7)
C5	5501(7)	−703(6)	2559(6)	72(7)
C6	4929(6)	93(5)	1915(5)	52(5)
C7	2244(5)	1425(4)	813(4)	37(4)
C8	2499(6)	430(5)	754(5)	52(5)
C9	1910(7)	137(5)	181(6)	68(6)
C10	1037(7)	835(5)	−336(5)	63(6)
C11	746(7)	1823(5)	−269(5)	57(6)
C12	1352(7)	2117(5)	291(4)	52(5)
C13	4589(6)	2203(4)	466(4)	39(5)
C14	4825(7)	2066(5)	−484(5)	51(5)
C15	5974(8)	2312(5)	−1196(5)	62(6)
C16	6866(7)	2693(5)	−982(6)	64(7)
C17	6656(7)	2835(5)	−36(6)	61(6)
C18	5529(6)	2582(5)	679(5)	49(5)
C19	−1071(6)	2961(5)	4160(4)	45(5)
C20	−999(8)	3797(5)	4451(5)	66(7)
C21	−1607(9)	3938(6)	5411(5)	80(8)
C22	−2267(10)	3251(7)	6078(5)	87(9)
C23	−2336(9)	2419(7)	5822(6)	89(9)
C24	−1750(8)	2271(6)	4855(5)	66(7)
C25	−755(6)	1727(5)	2818(5)	48(5)
C26	−1749(8)	1691(6)	2408(6)	85(7)
C27	−2026(10)	784(6)	2426(7)	119(9)
C28	−1345(9)	−77(6)	2872(7)	94(8)
C29	−324(9)	−75(6)	3270(8)	93(9)
C30	−31(7)	835(6)	3234(7)	76(7)
C31	−1608(6)	3857(4)	2270(4)	41(5)
C32	−2965(6)	4115(6)	2773(5)	58(6)
C33	−3912(6)	4801(6)	2295(5)	60(6)
C34	−3509(7)	5216(5)	1307(5)	62(6)
C35	−2177(8)	4993(6)	821(5)	66(7)
C36	−1235(7)	4315(5)	1307(5)	51(6)
C37	3078(6)	4229(5)	1823(5)	57(6)
C38	1833(6)	4603(5)	2478(5)	53(5)
C39	832(7)	5447(5)	2126(5)	52(6)
C40	−1288(10)	6556(7)	2685(6)	87(8)
C41	−2219(8)	6690(5)	3639(5)	65(7)
C42	−1895(8)	7072(6)	4298(6)	76(8)
C43	−2783(10)	7137(7)	5228(6)	84(8)
C44	−3958(10)	6863(8)	5460(6)	92(10)
C45	−4317(10)	6511(8)	4812(7)	104(11)
C46	−3466(10)	6417(7)	3917(7)	84(9)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.
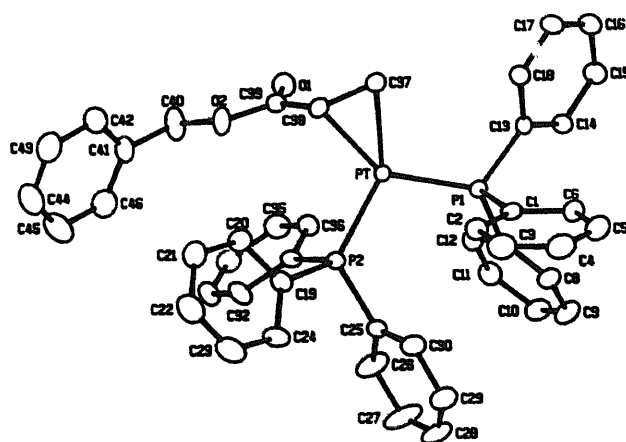
Fig. 5. Molecular structure of $Pt(CH_2 = CHCOOCH_2Ph)(PPh_3)_2]$ 1c, 20% thermal ellipsoids.

tive of the *tert*-butyl ester was the least abundant component. We would expect the 2-methylpropenoates to form less stable complexes, as backbonding is inhibited by the electron-donating effect of the methyl group, as well as its steric effect. The 2-methylpropenoate complexes all had approximately the same stability.

6. Conclusions

Spectroscopic parameters for complexes 1–3 may be readily rationalised in terms of a combination of steric and electronic effects. The bonding is strong in these complexes due to significant backbonding from platinum(0) to the π^*-orbital of the alkene; these alkenes are poor σ-donors. When PCy_3 is reacted with 1–3, two regioisomers are generally observed, mostly in more or less equal amounts. As found for the parent complexes, the phosphine *trans* to the electron-withdrawing group has the higher $^1J(PPt)$ value. This appears in general to be PCy_3, but unequivocal confirmation could not be

Table 7
Selected bond lengths (Å) and angles (°) for $[Pt(CH_2 = CHCOOCH_2Ph)(PPh_3)_2]$

Bonds			
Pt–P1	2.261(1)	Pt–P2	2.296(2)
Pt–C37	2.098(8)	Pt–C38	2.133(8)
O1–C39	1.208(8)	O2–C39	1.354(8)
O2–C40	1.435(10)	C37–C38	1.431(8)
C38–C39	1.445(8)	Pt–M	1.991(8)

Angles			
P1–Pt–M	123.8(2)	P2–Pt–M	128.4(2)
P1–Pt–P2	107.75(6)	P1–Pt–C37	104.0(2)
P1–Pt–C38	143.3(2)	P2–Pt–C37	147.0(2)
P2–Pt–C38	108.9(2)	C37–Pt–C38	39.5(2)
Pt–C37–C38	71.6(4)	Pt–C38–C37	68.9(4)

M is the midpoint of the C37–C38 bond.

Table 8
^{31}P NMR spectroscopic parameters of the products [Pt(alkene)(PCy$_3$)(PPh$_3$)] of the reaction of complexes 1–3 with tricyclohexylphosphine

Starting complex	δ(PPh$_3$) (ppm)	^1J(PtPPh$_3$) (Hz)	δ(PCy$_3$) (ppm)	^1J(PtPCy$_3$) (Hz)	^2J(PP) (Hz)	Ratio [a]
1a	28.0	3566	29.9	4059	42	100:0
1b	30.8	3117	38.1	3858	46	82:18
	32.7	3311	40.6	4114	46	
1c	32.5	4031	39.3	3525	44	50:50
	31.1	3918	39.5	3929	45	
2b	31.0	3134	38.6	3909	44	50:50
	28.6	2898	37.4	3789	46	
2c	28.6	2892	38.6	3906	47	50:50
	31.0	3141	37.0	3712	46	
2d	34.3	3477	41.6	4218	57	100:0
2e	28.6	2893	38.6	3908	47	50:50
	31.0	3143	37.4	3781	46	
2f	28.3	3725	38.6	3621	46	50:50
	29.5	3769	37.5	3715	45	
3b	30.5	3029	38.6	3907	44	50:50
	28.4	2880	37.3	3773	51	

[a] In each case the first quoted isomer is the more abundant one.

obtained as the complexes could not be isolated or separated. The relative stability of the complexes depends on both steric and electronic factors.

7. Experimental

All preparations were carried out under an atmosphere of nitrogen using standard Schlenck line techniques. Solvents were dried, distilled and degassed prior to use. NMR spectra were recorded using a Bruker ACP250 FT spectrometer operating at 250 MHz (^{1}H), 62.82 MHz (^{13}C), 101.20 MHz (^{31}P) or 53.78 MHz (^{195}Pt). Chemical shifts are reported to external TMS (^{1}H, ^{13}C), 85% H$_3$PO$_4$ (^{31}P) or Na$_2$[PtCl$_6$] (^{195}Pt). Microanalyses were performed using a Perkin–Elmer 400 CHN analyser. Melting points were determined using a Stuart melting point apparatus and are uncorrected.

7.1. Synthesis of cis-[Pt(PPh$_3$)$_2$Cl$_2$]

The synthesis was carried out as described by Gillard and Pilbrow [34] in 87% yield.

7.2. Synthesis of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$]

The synthesis was carried out as described by Nagel [35] in 90% yield.

7.3. Synthesis of complexes of the type [Pt(CH$_2$ = CHCOOR)(PPh$_3$)$_2$] and [Pt-{CH$_2$ = C(Me)COOR}(PPh$_3$)$_2$]

In a typical synthesis, [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (0.1483 g, 19.8 mmol) was placed in a Schlenck tube and dissolved in dry degassed toluene (3 ml). The alkene (1:1 molar

ratio with platinum) was added to the solution, which was then stirred for 2 h. After cooling to 0 °C, light petroleum (b.p. 30–40 °C, 10 ml) was added and the complex precipitated. The precipitate was collected by filtration under nitrogen, washed (light petroleum, b.p. 30–40 °C, 10 ml) and dried in vacuo. In many cases analytically pure material was obtained in this way. However, recrystallisation proved difficult as all the complexes deteriorated slowly in solution. Details of the preparations and the microanalytical data (where available) are given in Table 9.

7.4. Structure of [Pt(CH$_2$ = CHCOOCH$_2$Ph)(PPh$_3$)$_2$] 1c

Data were collected using a crystal grown by slow evaporation from toluene, ca. 0.2 × 0.2 × 0.15 mm^3 on

Table 9
Preparations of complexes 1–3

Complex	Yield (%)	M.p. (°C) [a]	Colour	%C Found (theoret.)	%H Found (theoret.)
1a	95	140–144	cream	59.01 (59.53)	4.53 (4.50)
1b	87	118–122	cream	61.38 (60.90)	5.12 (5.00)
1c	90	158–168	white	62.03 (62.65)	4.58 (4.57)
2a	80	158–162	white	60.32 (60.07)	5.02 (4.67)
2b	90	130–136	white		
2c	88	130–136	beige		
2d	89	118–120	cream	61.01 (61.32)	5.10 (5.15)
2e	83	110–116	cream		
2f	88	112–120	cream		
3a	86	190–200	white	59.41 (59.63)	5.05 (4.50)
3b	84	140–150	cream		
3c	85	136–140	white		
3d	92	138–142	white	58.02 (59.93)	4.70 (4.68)
3e	93	106–116	white		

[a] All complexes decomposed at or around the melting point, hence the long melting ranges.

an Enraf–Nonius CAD4 diffractometer operating in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of 1 min, monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 37.8\,\text{cm}^{-1}$. A total of 6790 unique reflections were measured for $2° < \theta < 25°$ and $h\ 0 \to 12$, $k\ -16 \to 16$, $l\ -17 \to 17$. 5469 reflections with $|F^2| > 3\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$. Two reference reflections were remeasured every 60 min and showed a maximum deviation of -6.3%. Absorption (DIFABS [36] max, min: 1.18, 0.77) and decay corrections were applied. The structure was solved by routine heavy-atom methods and non-hydrogen atoms refined anisotropically by full-matrix least-squares. The phenyl hydrogen atoms were fixed at calculated positions and all other hydrogen positions were refined. All B_{iso} were fixed at $1.3B_{eq}$ for the atoms to which they are bonded. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were $R = 0.037$ and $wR = 0.041$. Programs from the Enraf–Nonius SDP-Plus package were run on a microVAX computer. $C_{46}H_{40}O_2P_2Pt$, MW = 881.9, triclinic, $P\bar{1}$, $a = 10.520(2)$ Å, $b = 14.131(5)$ Å, $c = 14.494(3)$ Å, $\alpha = 74.27(2)°$, $\beta = 72.72(1)°$, $\gamma = 73.98(2)°$, $Z = 2$, $V = 1935$ Å^3, $D_{calc} = 1.51\,\text{g cm}^{-3}$, $F(000) = 880$, 475 variables, $\Delta/\sigma_{max} = 0.08$, $\Delta\rho_{max,min} = 1.16$, $-0.22\,\text{e Å}^{-3}$.

8. Reactions of complexes 1–3 with PCy$_3$

The complexes 1–3 were formed in situ by addition of the relevant alkene (1:1 molar ratio) to a dry, degassed solution of $[Pt(C_2H_4)(PPh_3)_2]$ in $C_6D_5CD_3$ (0.5 ml) in an NMR tube. The tube was then cooled to $-70°C$ and a solution of PCy$_3$ (1:1 molar ratio with platinum) in $C_6D_5CD_3$ (0.5 ml) was added. The NMR tube was shaken carefully and the ^{31}P NMR spectrum recorded at $-70°C$ and $-50°C$.

Acknowledgements

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