

Synthesis and characterization of platinum(0) alkene complexes; X-ray crystal structure determinations on [Pt(*trans*-PhCH=CHCHO)(PPh₃)₂] and [Pt(*trans*-PhCH=CHCOMe)(PPh₃)₂]

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Abstract—Reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with a range of alkenes gave the complexes $[Pt(alkene)(PPh_3)_2]$. Complexes of alkenes bearing electron-withdrawing ligands were, predictably, more stable than those of electron-rich alkenes. The complexes were characterized by multinuclear (¹H, ¹³C, ³¹P and ¹⁹⁵Pt) NMR spectroscopy and the structures of the derivatives of *trans*-PhCH=CHCHO and *trans*-PhCH=CHCOMe were established by X-ray diffraction studies. The complexes reacted with PCy₃ to give $[Pt(alkene)(PCy_3)(PPh_3)]$, usually as a mixture of regioisomers. Copyright © 1996 Elsevier Science Ltd

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We have been interested for some time in the substitution chemistry of platinum(0), and have shown that the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with bulky phosphines at low temperature results in substitution of the phosphine rather than the ethene [1]. 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 [2]. Alkene complexes isolated by this method include derivatives of ketenes [3], cumulenes [4], allenes [5], $C_2H_{4-n}X_n$ (X = CN or COOMe, n = 0-4 [6], styrene [7], strained cycloalkenes [8], Dewar benzenes [9], cyclooctene [10] and others [11]. The reaction of $[Pt(C_2H_4)(DIOP)]$ with chiral alkenes has been used to indicate the enantiometric purity of the alkene [12], and alkynes have also been shown to displace ethene [13]. We have recently reported the preparation and characterization of a range of complexes in which the added alkene is a propenoate or a 2-methylpropenoate ester [14], and we now extend this to more varied alkenes.

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RESULTS AND DISCUSSION

Reaction of alkenes with $[Pt(C_2H_4)(PPh_3)_2]$

Addition of a wide range of alkenes [15] to a toluene solution of $[Pt(C_2H_4)(PPh_3)_2]$ resulted in clean conversion to the complexes 1-7, which were generally isolated by reduction of the volume of toluene and precipitation with light petroleum (b.p. 30-40°C) to give white or cream powders. Analytically pure material was obtained in this way in several cases. However, the complexes decomposed when attempts were made to recrystallize them. The yields were generally good, except for 2a, which was rather unstable and decomposed completely in solution at room temperature in less than 1 h. Since bonding in these complexes is dominated by metal to ligand back-bonding, we would expect that complexes of electron-rich alkenes would be less stable than those of alkenes bearing electron-withdrawing groups.

³¹P NMR spectra (Table 1)

It proved possible (vide infra) to establish which phosphorus atom was which, and the structures show



the labelling convention used. The presence of electron-withdrawing substituents on the alkenes causes a decrease in the coupling constant ${}^{1}J(Pt-P_{a})$ and an increase in ${}^{1}J(Pt-P_{b})$ relative to $[Pt(C_{2}H_{4})(PPh_{3})_{2}]$. This follows the trend previously established for the propenoates, and may be attributed to the *trans* influence of the electron-withdrawing group. The substitution of an α -methyl group on the double bond (compare complexes **6a**, and **6b**, and **7a** and **7b**) causes an increase in ${}^{1}J(Pt-P_{a})$ and a decrease in ${}^{1}J(Pt-P_{b})$. The methyl group is an inductive donor, and might be expected to weaken the Pt-P bond *trans* to it; hence ${}^{1}J(Pt-P_{b})$ is decreased.

For complexes 1a-c, ${}^{1}J(Pt-P_{a})$ increases with substitution at nitrogen, but the effect is small. This parallels the results with propenoate ester complexes; we can postulate that as the alkene becomes more hindered, bonding to it is weakened and there is a concomitant increase in the strength of the platinumphosphorus bonds [16].

Complexes of alkenes bearing electron-donating groups, 2, show a decrease in both phosphorus-platinum coupling constants relative to $[Pt(C_2H_4)(PPh_3)_2]$, whilst ²J(PP) increases to 50-52 Hz. The complex of *trans*-PhCH==CHPh gave data comparable with the ethene complex. In the less symmetrical styrene derivative, however, the α -phenyl substitution decreases the value of ¹J(Pt-P_b) by approximately 40 Hz; the phenyl might appear to be acting as a donor of electron density into the platinum-phosphorus bond *trans* to it. However, it is more likely that the phenyl substituent has an effect on the position of the

| Complex | $\delta(\mathbf{P}_{\mathbf{a}})$ (ppm) | $^{1}J(\text{Pt-P}_{a})$ (Hz) | $\delta(\mathbf{P}_{\mathrm{b}})$ (ppm) | $^{1}J(Pt-P_{b})$ (Hz) | $^{2}J(\mathbf{P}_{a}-\mathbf{P}_{b})$ (Hz) |
|---------|---|-------------------------------|---|------------------------|---|
| 1a | 32.3 | 3626 | 32.5 | 4012 | 45 |
| 1b | 32.8 | 3673 | 32.1 | 3939 | 46 |
| 1c | 33.4 | 3686 | 30.4 | 3989 | 46 |
| 2a | 32.0 | 3349 | 34.8 | 3717 | 50 |
| 2b | 34.8 | 3572 | 33.9 | 3562 | 52 |
| 3 | 30.4 | 3578 | 33.7 | 3642 | 35 |
| 4a | 31.8 | 3749 | 33.7 | 3790 | 56 |
| 4b | 35.6 | 3731 | _ | | _ |
| 5a | 27.9 | 3650 | 28.9 | 4245 | 38 |
| 5b | 29.2 | 3659 | 28.0 | 4173 | 40 |
| 5c | 28.5 | 3648 | 29.5 | 4249 | 40 |
| 5d | 27.4 | 3674 | 29.8 | 4234 | 37 |
| 6a | 32.1 | 3624 | 31.7 | 4169 | 40 |
| 6b | 33.2 | 3748 | 30.0 | 3959 | 44 |
| 7a | 30.5 | 3496 | 31.3 | 3947 | 34 |
| 7b | 29.4 | 3600 | 30.4 | 3685 | 40 |

Table 1. ³¹P NMR spectra of platinum(0) alkene complexes 1–7

 ${Pt(PPh_3)_2}$ moiety relative to the carbon–carbon double bond. The steric bulk of the phenyl group could cause slippage of the platinum towards the less hindered terminus, which would have the same effect on the observed coupling constant.

¹⁹⁵Pt NMR spectra (Table 2)

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 [17]. The chemical shifts of compounds 1–7 confirm that they are platinum(0) complexes. The appearance of each spectrum is a doublet of doublets,

Table 2. ¹⁹⁵Pt NMR spectra of platinum(0) alkene complexes 1–7

| Compound | $\delta({ m Pt})~({ m ppm})$ | $^{i}J(Pt-P_{a})$ (Hz) | $^{1}J(\text{Pt}-\text{P}_{b})$ (Hz) |
|-----------|------------------------------|------------------------|--------------------------------------|
| 1a | - 5094 | 3609 | 4006 |
| 1b | - 5090 | 3665 | 3957 |
| 1c | -5131 | 3692 | 3988 |
| 2a | - 5030 | 3354 | 3718 |
| 2b | - 5085 | 3590 | 3723 |
| 3 | - 4694 | 3562 | 3610 |
| 4a | - 5023 | 3749 | 3788 |
| 4b | - 5050 | 3742 | 3742 |
| 5a | - 5087 | 3650 | 4246 |
| 5b | - 5100 | 3656 | 4177 |
| 5c | - 5039 | 3634 | 4261 |
| 5d | - 5076 | 3667 | 4239 |
| 6a | - 5098 | 3621 | 4167 |
| 6b | - 5123 | 3750 | 3957 |
| 7a | - 5042 | 3496 | 3950 |
| 7b | - 5053 | 3604 | 3681 |

since coupling to the two phosphorus atoms is distinct in each case (Fig. 1).

¹³C NMR spectra (Table 3)

The alkene carbons in the complexes resonate at higher fields than in the free alkenes (upfield shift ca 80 ppm), as is common in metal alkene complexes [18]. A typical spectrum is shown in Fig. 2. The notation for the labelling of the carbon atoms is shown in structures 1–7.

The effect of a methyl substituent on the double bond is to change the chemical shift of the carbon atom to which it is bonded, C_b . Thus, in the free alkene the shift moves downfield; δ for C_b in CH₂==CHCHO is 138.6, whereas for CH₂==C(Me)CHO it is 145.6. In the complexes this effect is accentuated. An α -phenyl substituent causes a downfield shift of the resonance of the carbon atom to which it is bonded by 20 ppm relative to a proton. For example, in **6a** $\delta(C_a) = 39.8$ whereas for **5c** $\delta(C_a) = 60.7$.

Each carbon atom has one large (ca 24-30 Hz) and one small (ca 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. These are significantly smaller than those reported for highly strained and pyramidalized alkenes, but are comparable with that in $[Pt(C_2H_4)(PPh_3)_2]$ [9]. As the signals were relatively weak, ¹⁹⁵Pt satellites could be identified only in one complex, that of PhCH=CHCOPh, 5a, viz. $^{1}J(\text{Pt---C}_{b}) = 149$ Hz. This is smaller than the coupling found in $[Pt(C_2H_4)(PPh_3)_2] [^1J(PtC) = 194 Hz].$ This may suggest that the steric hindrance in 5a results in a longer Pt--C distance, and hence a smaller coupling constant, but more examples would be needed for a definitive answer. An α -methyl or an α -phenyl group



Fig. 1. ¹⁹⁵Pt NMR spectrum of [Pt(trans-PhCH=CHCHO)(PPh₃)₂] 5c.

| Compound | $\delta(C_a)^a$ (ppm) | $\delta(C_b)^a$ (ppm) | $\delta(C_a)$ (ppm) | $\delta(\mathrm{C_b})$ (ppm) | $^{2}J(C_{a}-P_{a})$ (Hz) | $^{2}J(C_{a}-P_{b})$ (Hz) | $^{2}J(C_{b}-P_{b})$ (Hz) | $^{2}J(C_{b}-P_{a})$ (Hz) |
|------------|--------------------------|-----------------------|------------------------|------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 1b | 132.8 | 137.6 | 53.0 | 40.8 | 25.7 | 2.9 | 32.4 | 2.9 |
| 1c | 137.8 | 144.3 | 49.0 | 42.1 | 30.3 | 6.4 | 33.2 | 5.7 |
| 2b | 137.9 | 114.6 | 58.5 | 40.9 | 29.1 | 4.3 | 28.6 | 3.8 |
| 4 a | 137.3 | 137.8 | 59.1 | 39.8 | 29.0 | 5.3 | 26.7 | 4.7 |
| 4b | 137.3 | 137.3 | 59.3 | 52.0 | 20.5 | 5.3 | 26.7 | 4.7 |
| 5a | 138.8 | 144.3 | 57.7 | 61.2 | 24.7 | 5.6 | 29.3 | 3.3 |
| 5b | 137.6 | 142.4 | 60.2 | 63.0 | 32.0 | 3.3 | 24.8 | 5.7 |
| 5c | 134.4 | 152.4 | 60.7 | 64.5 | 32.4 | 1.9 | 22.8 | 4.3 |
| 5d | 137.5 | 142.7 | 60.1 | 64.9 | 32.4 | 3.8 | 23.8 | 5.7 |
| 6a | 138.0 | 138.6 | 39.6 | 62.4 | 28.6 | 1.0 | 16.2 | 1.9 |
| 6b | 137.1 | 145.6 | 46.5 | 72.0 | nd | nd | 22.9 | 5.7 |
| 7a | 137.7 | 117.5 | 39.8 | 23.8 | 29.2 | 3.0 | 38.6 | 4.5 |
| 7b | 137.7 | 130.6 | 44.5 | 33.5 | 38.0 | 5.5 | 35.6 | 4.9 |

Table 3. ¹³C NMR spectroscopic data for complexes 1-7

^a Data for the uncomplexed alkenes.

nd: not determined; the signal was broad.

increases ${}^{2}J(C_{a}P_{a})$ and decreases ${}^{2}J(C_{b}P_{b})$. No significant effect was found on ${}^{2}J(C_{a}P_{b})$ or ${}^{2}J(C_{b}P_{a})$. We suggest that this is a result of the fact that the α substituent causes some slippage of the platinum towards the less hindered end of the double bond.



Fig. 2. Alkene region of the ¹³C NMR spectrum of [Pt(*trans*-PhCH=CHCOPh)(PPh₃)₂], **5a**.

¹H NMR spectra (Tables 4 and 5)

The chemical shift of the protons attached to the carbon-carbon double bond is moved upfield by 3-4 ppm up on coordination, as is typical for this type of complex [20]. An expansion of the alkene region of the spectrum of **6a** is shown in Fig. 3; this illustrates the complexity of the assignments. The coupling constants were determined by ¹H $\{^{31}P\}$ decoupling experiments followed by simulation using PANIC [21], but even this did not allow complete assignment in every case (the spectra of **1a**, **1b**, **2a**, **2b**, **6a** and **7a** were not assigned).

The interproton coupling is very different from that in the free alkenes. Both *trans* and *cis* couplings are reduced and the geminal coupling is increased. These data are all consistent with the lowering of the carbon– carbon bond order in the complex. For each proton there is a large coupling to one phosphorous atom, and a smaller one to the other. The ${}^{3}J(PH)$ couplings are similar to those in related complexes. For example, in [Pt{MeOCH=C(CN)₂}(PPh₃)₂] ${}^{3}J(HP_{a}) = 6.9$ Hz and ${}^{3}J(HP_{b}) = 3.6$ Hz [22]. As it is known which phosphorus has the larger coupling to each proton (from the decoupling experiments) and we know which phosphorus was decoupled, we can tell which phosphorus was which. The significance of the coupling of the alkene protons to 195 Pt was not analysed in detail, but varied between 38 and 66 Hz. ${}^{2}J(Pt-H_{a})$ is typically 60–66 Hz.

Structure of [Pt(trans-PhCH=CHCHO)(PPh₃)₂], 5c

A number of platinum(0) complexes of the type $[Pt(alkene)(PPh_3)_2]$ have been characterized crystallographically including those for which the alkene was *trans*-4-O₂NC₆H₄CH=CHC₆H₄-4-NO₂ [23], *trans*-Ph(CN)C=C(CN)Ph [24], (NC)₂C=C(CN)₂ [25], (MeO₂C)₂C=CHCO₂Me [26], Cl₂C=CCl₂ [27], *trans*-NCCH=CHCN [28] and **8** [29]. The geometry of these complexes is characterized 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 PtP₂ and PtC₂ planes.



Crystals of 5c were grown by slow evaporation of a perdeuterotoluene solution. The molecular structure is shown in Fig. 4, and selected bond lengths and angles are given in Table 6. The Pt-P bond lengths [2.252(3), 2.272(4) Å] are slightly shorter than those in $[Pt{(MeO_2C)_2C=CHCO_2Me}(PPh_3)_2]$ [26] [2.283(4), 2.286(3) Å], reflecting lower steric hindrance, but the carbon-carbon bond length of the bound alkene [1.43(1) Å versus 1.44(2) Å] is essentially identical. The P-Pt-P bond angle [113.5(1)°] is larger than is usually found in this type of complex. For example P—Pt—P is $100.6(2)^{\circ}$ in [Pt(Cl₂C=CCl₂)(PPh₃)₂] [27], 104.4(2)° in $[Pt(trans-NCCH=CHCN)(PPh_3)_2]$ [30] and $103.90(3)^{\circ}$ in [Pt{trans-Ph(CN)C=C (CN)Ph}(PPh₃)₂] [24]. The reason for this unusually high value is not immediately apparent, except that

Table 4. ¹H NMR spectroscopic data for complexes 1-7

| ² J(H _b H _c) (Hz) | 3.16 | 4.92 | | | 4.0 4.51 |
|---|--------------|----------|--------------|--------------|--------------|
| ³ J(H _a H _c) (Hz) | 10.40 | 10.52 | 8.75 9.30 | 8.71 9.17 | |
| $^{3}J(H_{a}H_{b})$ (Hz) | 8.61 | 8.48 | | | |
| ² J(H _b H _c) ^a (Hz) | 2.0 | 1.0 | | | 0.97 0.8 |
| ${}^{3}J(\mathrm{H_{a}H_{c}})^{a}$ (Hz) | 16.9 | 17.6 | 15.7 16.3 | 15.9 15.9 | |
| $^{3}J(\mathrm{H_{a}H_{b}})^{a}$ (Hz) | 10.1 | 10.9 | | | |
| δ(H _c) (ppm) | 3.05 4 41 | 3.86 | 4.66 | 4.00 4.30 | 2.41 2.46 |
| δ(H _b) (ppm) | 2.13 | 2.90 | | | 2.36 1.99 |
| $\delta(H_a)$ (ppm) | 3.51 | 2.74 | 4.79 4.33 | 4.14 4.61 | |
| $\delta(H_c)^a$ | 6.4 4 42 | 5.5 | 7.2 | 7.1 7.6 | 6.15 5.0 |
| $\delta(H_b)^a$ | 5.1 | 5.1 | | | 5.85 5.2 |
| $\delta(H_a)^a$ (ppm) | 5.9 | 6.5 | 7.25 6.4 | 6.5 6.7 | |
| Complex | 1c 3 | 4a 4h | ើលីលី | ς. Σ | 6b 7b |

Data for the uncomplexed alkenes.

Table 5. ¹H-³¹P coupling constants for 1-7

| Complex | $^{3}J(\mathrm{H_{a}P_{a}})$ (Hz) | $^{3}J(H_{a}P_{b})$ (Hz) | $^{3}J(\mathrm{H_{b}P_{a}})$ (Hz) | $^{3}J(H_{b}P_{b})$ (Hz) | $^{3}J(\mathrm{H_{c}P_{a}})$ (Hz) | $^{3}J(\mathrm{H_{c}P_{b}})$ (Hz) | $^{3}J(\mathrm{H_{a}Pt})$ (Hz) | $^{3}J(\mathrm{H_{b}Pt})$ (Hz) | ³ J(H _c Pt) (Hz) |
|-----------|--------------------------------------|--------------------------|-----------------------------------|-----------------------------|-----------------------------------|--------------------------------------|--------------------------------|-----------------------------------|---|
| 1c | 8.80 | 4.18 | 8.31 | 4.68 | 8.52 | 5.68 | 66 | 48 | 48 |
| 3 | | | | | | nd | | | 60 |
| 4a | 7.60 | 4.89 | 8.53 | 4.35 | 9.51 | 8.90 | 64 | 58 | nd |
| 4b | | | | | | nd | | | 60 |
| 5a | 8.77 | 3.23 | | | 8.78 | 5.00 | 60 | | 50 |
| 5b | 9.10 | 3.40 | | | 8.78 | 5.33 | 60 | | 52 |
| 5c | 8.26 | 3.77 | | | 8.69 | 5.37 | 56 | | 52 |
| 5d | 9.38 | 3.46 | | | 9.03 | 5.63 | 62 | | 58 |
| 6b | | | 8.10 | 4.7 | 10.4 | 7.4 | | nd | 50 |
| 7b | | | 7.53 | 4.36 | 7.43 | 5.24 | | 46 | 56 |

nd: not determined.



Fig. 3. Alkene region of the ¹H NMR spectrum of [Pt(CH₂=CHCHO)(PPh₃)₂], 5c.

the Pt—P bond lengths are short in comparison with related complexes, so that the bond angle is opened to minimize steric repulsions. The angle between the PtC₂ and PtP₂ planes is $5(3)^{\circ}$, in the expected range.

Structure of [Pt(trans-PhCH=CHCOMe)(PPh₃)₂], 5b

Crystals of **5b** were grown by evaporation of a perdeuterotoluene solution. The structure is shown in Fig. 5, and selected bond lengths and angles are given in Table 7. The structure is quite similar to that of **5c**. The Pt—P bond lengths are a little longer, as are the Pt—C bond distances, and the P—Pt—P angle has been closed to $109.87(3)^\circ$. These changes all reflect the increased steric demand of the alkene. Strain is also alleviated by twisting the PtC₂ and PtP₂ planes relative to each other; the dihedral angle in this case is $12.2(4)^{\circ}$.

In the complex of PhCH=CHCHO there is little or no slippage [31] of the platinum away from the midpoint of the carbon-carbon double bond. However, in **5b** the platinum has slipped towards the less hindered end of the bond [Pt--C_a = 2.124(3) Å, Pt--C_b = 2.139(4) Å]. The reason is unclear, since study of a model reveals no severe interactions on moving the platinum to the midpoint of the double bond.

Reactions of the complexes with PCy₃

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,



Fig. 4. Structure of [Pt(trans-PhCH=CHCHO)(PPh₃)₂], 5c.



Fig. 5. Structure of [Pt(*trans*-PhCH=CHCOMe)(PPh₃)₂], **5b**.

the one with PCy_3 was the most stable. PCy_3 has a large cone angle [32], and since it is appreciably more basic than PPh₃, the chemical shift is sufficiently different from that for PPh₃ that the ³¹P NMR spectra should be readily interpreted. PCy₃ was therefore added to complexes 1–7 at -50° C. The ³¹P NMR spectra of the products show one or more AB quartets, and the reaction appears to go to completion in most cases, 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 as 9a and 9b for a monosubstituted alkene complex. The reaction mixture was stored at -20° C for 1–2 weeks and any equilibration monitored by ³¹P NMR spectroscopy.

Details of the complexes formed and the ratios between the regioisomers are given in Table 8. In some cases (1a, 4b, 5c, minor isomers from 5d, 6b) complete data were not obtained owing to the low solubility of the complexes. The reaction of 2a was unsuccessful because of decomposition; this was not surprising as this was much the least stable of the complexes prepared. Complex 7b did not appear to react. The complexes of CH2=CHCONH2, trans-PhCH=CH CHO, HC=CCH₂OH and CH₂=CHCHO gave a single regioisomer on reaction with PCy₃, and the complex of PhCH=CHPh gave a single product because of its symmetry. It seems that the selective production of a single regioisomer is confined to complexes of ligands with low steric demand. This suggests that only in these complexes is there no barrier to PCy₃, the bulkier and more basic ligand, taking up the electronically favourable site.

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 ³¹P NMR spectroscopy. One molar equivalent of a second alkene was added at -50° C to [Pt(alkene)(PPh₃)₂] prepared *in situ*. The resulting solution was warmed slowly in the NMR probe, and the ³¹P NMR spectrum recorded. The solu-

| Table 6. Selected bond lengths | (Å) |) and angles | (°) |) for | [Pt(trans-PhCH | =CHCHO) | $(\mathbf{PPh}_3)_2],$ | 5c |
|--------------------------------|-----|--------------|-----|-------|----------------|---------|------------------------|----|
|--------------------------------|-----|--------------|-----|-------|----------------|---------|------------------------|----|

| Pt—M(1) | 2.037 | Pt—P(1) | 2.252(3) |
|---------------------|-----------|-----------------|-----------|
| Pt-P(2) | 2.272(4) | PtC(38) | 2.159(14) |
| Pt-C(39) | 2.158(14) | C(37)-C(38) | 1.44(2) |
| C(38)C(39) | 1.43(2) | O-C(37) | 1.21(2) |
| M(1) - Pt - P(1) | 121.2 | M(1)PtP(2) | 125.3 |
| P(1)— Pt — $P(2)$ | 113.5(1) | OC(37)C(38) | 126(1) |
| C(37)—C(38)—C(39) | 122(1) | C(38)C(39)C(40) | 121(1) |
| | | | |

M(1) is the midpoint of the C(38)-C(39) bond.

| PtM(1) | 2.008 | Pt—P(1) | 2.270(1) |
|---------------------|-----------|-----------------------|----------|
| Pt—P(2) | 2.275(1) | Pt-C(39) | 2.139(4) |
| Pt—C(40) | 2.124(3) | O-C(38) | 1.228(4) |
| C(37) - C(38) | 1.508(5) | C(38)-C(39) | 1.472(5) |
| C(39)—C(40) | 1.437(5) | | |
| M(1)— Pt — $P(1)$ | 121.7 | M(1)PtP(2) | 128.3 |
| P(1)— Pt — $P(2)$ | 109.87(3) | O-C(38)-C(37) | 120.2(3) |
| O-C(38)-C(39) | 123.3(3) | C(37) - C(38) - C(39) | 116.5(3) |
| C(38)—C(39)—C(40) | 118.9(2) | C(39) - C(40) - C(41) | 122.6(3) |
| | | | |

Table 7. Selected bond lengths (Å) and angles (°) for [Pt(trans-PhCH=CHCOMe)(PPh₃)₂], 5b

M(1) is the midpoint of the C39-C40 bond.

Table 8. ³¹P NMR spectroscopic data for the products of the reactions of 1-7 with PCy₃

| Starting complex | $\delta(\text{PPh}_3)$ (ppm) | ¹ J(Pt-PPh ₃) (Hz) | $\delta(PCy_3)$ (ppm) | ¹ J(Pt-Pcy ₃) (Hz) | ² <i>J</i> (PP) (Hz) | Ratio ^a |
|------------------|------------------------------|--|-----------------------|--|---|--------------------|
| 1a | 30.8 | b | 41.6 | b | 46 | 100:0 |
| 1b | 25.2 | 3551 | 35.1 | 3855 | 48 | 57:43 |
| | 25.1 | 3806 | 34.9 | 3855 | 46 | |
| 1c | 27.5 | 3662 | 34.2 | 3894 | 49 | 57:43 |
| | 25.5 | 4014 | 28.5 | 3666 | 47 | |
| 2b | 34.3 | 3476 | 42.1 | 4267 | 57 | 67:33 |
| | 33.2 | 3364 | 39.4 | 3993 | 53 | |
| 3 | 30.6 | 4462 | 38.7 | 3488 | 37 | 100:0 |
| 4 a | 32.3 | 3724 | 41.2 | 3651 | 57 | 63:27 |
| | 29.8 | 3592 | 40.4 | 3694 | 55 | |
| 4b | 29.9 | b | 36.9 | ь | 40 | |
| 5a | 21.5 | 3354 | 32.7 | 3989 | 35 | 67:33 |
| | 26.8 | 4179 | 33.9 | 3534 | 35 | |
| 5b | 31.8 | 4229 | 39.1 | 3961 | 37 | 58:42 |
| | 30.5 | 3652 | 38.6 | 3517 | 42 | |
| 5c | 29.9 | b | 36.9 | b | 40 | 100:0 |
| 5d | 25.5 | 3749 | 38.6 | 4045 | 34 | 71:29 |
| | 37.1 | ь | 44.7 | b | 38 | |
| 6 a | 30.5 | 4213 | 35.4 | 3461 | 40 | 100:0 |
| 6b | 28.6 | 3939 | 36.6 | 3647 | 43 | 74:26 |
| | 30.3 | ь | 38.0 | ь | 46 | |
| 7a | 29.6 | 3929 | 38.7 | 3433 | 34 | 60:40 |
| | 28.7 | 3435 | 39.7 | 3821 | 37 | |

"The date for the major complex is given first in each case.

^b Not determined owing to low solubility.

tion was then kept at 25° C and the ³¹P 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. The spectra for a typical experiment involving the reaction of [Pt(*trans*-Ph CH=CHCOMe)(PPh₃)₂] with CH₂=CHCO₂Me are shown in Fig. 6. Some of the data obtained are shown in Table 9. This allowed us to construct a stability series for the platinum(0) alkene complexes as follows:

 CH_2 =CHCN ~ CH_2 =CHCHO > CH_2 =CHCO₂ $CH_2Ph > CH_2$ =CHCO₂ $Me > CH_2$ =CHCO₂Bu' >
$$\label{eq:hc} \begin{split} HC &= CCH_2OH \sim CH_2 == C(Me)CN \sim \\ CH_2 &= C(Me)CHO > trans-PhCH == CHCHO > \\ trans-PhCH == CHCOCH == CHPh > \\ CH_2 &= CHCONH_2 > CH_2 == CHCONMePh > \\ trans-PhCH == CHCOMe > trans-PhCH == CHCOPh : \\ CH_2 &= C(Me)COOR > CH_2 == CHCH_2OH > \\ CH_2 &= CHPh > trans-PhCH == CHPh > \\ CH_2 &= CHOCOMe \end{split}$$

It can be clearly seen that two factors are important.



Fig. 6. ³¹P NMR spectra of the products of the reactions between [Pt(*trans*-PhCH=CHCOMe)(PPh₃)₂] **5b**, and CH₂=CHCO₂Me.

The most stable complexes are those bearing alkenes with the most electron-withdrawing groups; thus CH_2 — $CHCHO > CH_2$ — $CHCO_2Me > CH_2$ — $CHCONH_2 > CH_2$ — $CHCH_2OH$. However, steric factors are also important. The substitution of an α -methyl group contributes to both effects, and the phenyl group is even bulkier. Bulky groups tend to cause twisting of the alkene, which decreases orbital overlap. The results described here have parallels in the work of Tolman [33]. He determined the equilibrium constants for the reaction of [Ni(alkene){P(OC_6H_4-2-Me)_3}_2]

with 38 alkenes. He concluded that the most important contribution to bonding was back-bonding from the metal into the π^* orbital of the alkene, and that steric effects were less significant than electronic ones.

CONCLUSIONS

Spectroscopic parameters for complexes 1–7 may be rationalized in terms of steric and electronic effects. The bonding to the metal is strongest, and the com-

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| Alkene 1 | Alkene 2 | Final ratio of alkene 1 : alkene 2 |
|------------------------------|-------------------------------|------------------------------------|
| CH ₂ =CHCN | СН2=СНСНО | 56:44 |
| CH2—CHCN | CH ₂ =CHCOOMe | 75:25 |
| CH2==CHCN | $CH_2 = C(Me)CN$ | 100:0 |
| CH2=CHCHO | CH ₂ ==CHCOOMe | 62:38 |
| CH2=CHCHO | HC≡CCH₂OH | 50:50 |
| CH2=CHCHO | CH ₂ ==C(Me)CHO | 100:0 |
| CH ₂ =CHCOOMe | $HC \equiv CCH_2OH$ | 50:50 |
| CH ₂ =CHCOOMe | trans-PhCH=CHCHO | 79:21 |
| CH ₂ ==CHCOOMe | $CH_2 = CHCONH_2$ | 80:20 |
| CH2=CHCOOMe | CH2==CHCONHCMe2CH2COCH3 | 67:33 |
| CH ₂ =CHCOOMe | trans-PhCH=CHCOPh | 75:25 |
| CH ₂ ==CHCOOMe | trans-PhCH=CHCOMe | 71:29 |
| CH2=CHCOOBut | trans-PhCH—CHCOPh | 83:17 |
| CH2=CHCOOBu ^t | trans-PhCH=CHCOMe | 80:20 |
| $CH_2 = C(Me)CN$ | trans, trans-PhCH=CHCOCH=CHPh | 83:17 |
| $CH_2 = C(Me)CN$ | CH2==CHPh | 100:0 |
| HC=CCH ₂ OH | CH ₂ ==CHPh | 100:0 |
| CH ₂ ==C(Me)CHO | trans, trans-PhCH=CHCOCH=CHPh | 83:17 |
| CH ₂ ==C(Me)CHO | CH2=CCONHCMe2CH2COCH3 | 50 : 50 |
| CH ₂ =C(Me)CHO | trans-PhCH=CHCOMe | 100:0 |
| trans-PhCH=CHCHO | trans, trans-PhCH=CHCOCH=CHPh | 72:28 |
| trans-PhCH=CHCHO | $CH_2 = CHCONH_2$ | 67:33 |
| trans-PhCH=CHCHO | CH ₂ =CHCON(Me)Ph | 64:36 |
| trans-PhCH=CHCHO | trans-PhCH=CHCOMe | 67:33 |
| trans,trans-PhCH=CHCOCH=CHPh | trans-PhCH=CHCOPh | 60:40 |
| trans,trans-PhCH=CHCOCH=CHPh | trans-PhCH=CHCOMe | 67:33 |
| trans,trans-PhCH_CHCOCH_CHPh | CH ₂ ==C(Me)COOEt | 86:14 |
| trans,trans-PhCH=CHCOCH=CHPh | CH ₂ ==CHPh | 83 : 17 |
| CH2=CHCONH2 | trans-PhCH=CHCOMe | 78:22 |
| trans-PhCH=CHCOPh | trans-PhCH=CHCOMe | 50:50 |
| trans-PhCH=CHCOPh | CH ₂ ==CHPh | 50:50 |

plexes are most stable, when the alkene bears electronwithdrawing groups, and has a low steric demand; the major component of the bonding is back-donation from platinum(0) to the π^* orbital of the alkene. When PCy₃ is reacted with 1–7 two regioisomers are generally formed, but a few complexes, usually of unhindered alkenes, gave a single regioisomer.

EXPERIMENTAL

All preparations were carried out under nitrogen using standard Schlenk line techniques. Solvents were dried, distilled and degassed prior to use. NMR spectra were recorded using a Bruker ACP250 FT spectrometer operating at 250 (¹H), 62.82 (¹³C), 101.20 (³¹P) or 53.78 MHz (¹⁹⁵Pt). Chemical shifts are reported relative to external TMS (¹H, ¹³C), 85% H₃PO₄ (³¹P) or Na₂[PtCl₆] (¹⁹⁵Pt). Microanalyses were performed using a Perkin–Elmer 400 CHN analyser. Melting points were determined using a Stuart melting point apparatus and are uncorrected.

Synthesis of cis-[Pt(PPh₃)₂Cl₂]

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

Synthesis of [Pt(C₂H₄)(PPh₃)₂]

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

Synthesis of complexes of the type [Pt(alkene)(PPh₃)₂]

In a typical synthesis $[Pt(C_2H_4)(PPh_3)_2]$ (0.1483 g, 19.8 mmol) was placed in a Schlenk line and dissolved in dry degassed toluene (3 cm³). 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 cm³) was added and the complex was precipitated. The precipitate was collected by filtration under nitrogen, washed (light petroleum, b.p. 30-40°C, 10 cm³) and dried *in vacuo*. In many cases analytically pure material was obtained in this way. However, recrystallization proved difficult as all the complexes deteriorated slowly in solution. Details of the preparations and the microanalytical data (where available) are given in Table 10.

Structure of [Pt(trans-PhCH=CHCHO)(PPh₃)₂], 5c

Data were collected using a crystal grown by slow perdeuterotoluene. evaporation from ca $0.15 \times 0.15 \times 0.10$ mm³ on an Enraf-Nonius CAD4 diffractometer operating in the θ -2 θ mode with $\Delta \theta = (0.8 + 0.35 \tan \theta)$ and a maximum scan time of 1 min, monochromated Mo- K_{α} radiation, $\lambda = 0.71069$ Å, $\mu = 39.9$ cm⁻¹. Unit-cell parameters were obtained from a least-square fit of 25 reflections, $7.3 < \theta < 10.4^{\circ}$. A total of 3635 independent reflections were measured for $2 < \theta < 25^{\circ}$ and h 0-39, k 0-15, l 0-13. 2236 observed reflections with $|F^2| > 3\sigma(F^2), \quad \sigma(F^2) = \{\sigma^2(l) + (0.04l)^2\}^{1/2}/Lp \text{ were}$ used in the refinement. Two reference reflections were remeasured every 60 min and showed a maximum deviation of 0.2%. Lorentz and polarization corrections and absorption correction by DIFABS [36] (max. 1.12, min. 0.92) were applied. The structure was solved by routine heavy-atom methods and nonhydrogen atoms refined anisotropically by full-matrix least squares. The phenyl hydrogen atoms were fixed at calculated positions ($B_{iso} = 1.4B_{eq}$ for parent atom) and the other hydrogen atoms were freely refined. The

absolute structure was determined by refinement of a $\Delta F''$ multiplier. The weighting scheme was $w = 1/\sigma^2(F)$, $\Sigma w(|F_o|-|F_c|)^2$ minimized, and the final residuals were R = 0.031, wR = 0.037. C₄₅H₃₈OP₂Pt, $M_w = 851.8$, orthorhombic, *Pna2*₁ (No. 33), a = 24.513(3), b = 13.292(2), c = 11.227(4) Å, V = 3657.8 Å³, Z = 4, $D_x = 1.55$ g cm⁻³, F(000) = 1696, 453 variables, S = 1.24, $\Delta/\sigma_{max}0.05$, $\Delta\rho_{max,min} = +0.81$, -0.83 eÅ³.

Structure of [Pt(trans-PhCH=CHCOMe)(PPh₃)₂], 5b

Data were collected using a crystal grown by slow evaporation from perdeuterotoluene, ca $0.35 \times 0.25 \times 0.20$ mm³ on an Enraf-Nonius CAD4 diffractometer operating in the θ -2 θ mode with $\Delta \theta = (0.8 + 0.35 \tan \theta)$ and a maximum scan time of 1 min, monochromated Mo- K_{α} radiation, $\lambda = 0.71069$ Å, $\mu = 38.8 \text{ cm}^{-1}$. Unit-cell parameters were obtained from least squares fit of 25 reflections, $7.3 < \theta < 10.3^{\circ}$. A total of 6616 independent reflections were measured for $2 < \theta < 25^{\circ}$ and h 0–11, k -15 to 15, l - 19 to 19. 5926 observed reflections with $|F^2| > 3\sigma(F^2), \quad \sigma(F^2) = \{\sigma^2(l) + (0.04l)^2\}^{1/2}/Lp \text{ were}$ used in the refinement. Two reference reflections were remeasured every 60 min and showed a maximum deviation of 0.7%. Lorentz and polarization corrections and absorption correction by DIFABS [36] (max 1.19, min 0.89) were applied. The structure was solved by routine heavy-atom methods and non-

| | | | Found (Calc.) (%) | | | |
|------------|-----------|--|-------------------|-------|-------|--|
| Complex | Yield (%) | M .p. (° C) ^{<i>a</i>} | С | Н | N | |
| 1a | 84 | 188-194 | | | | |
| 1b | 85 | 136-140 | 60.7 | 5.3 | 1.5 | |
| | | | (60.8) | (5.1) | (1.6) | |
| 1c | 24 | 138-146 | | | | |
| 2a | 10 | 118-130 | | | | |
| 2b | 78 | 94-102 | | | | |
| 3 | 82 | 120-124 | 60.5 | 4.6 | | |
| | | | (60.7) | (4.4) | | |
| 4a | 70 | 105-108 | | · · · | | |
| 4b | 83 | 118-124 | | | | |
| 5a | 92 | 190-196 | 65.1 | 4.7 | | |
| | | | (66.0) | (4.6) | | |
| 5b | 60 | 178-182 | 63.0 | 4.6 | | |
| | | | (63.8) | (4.7) | | |
| 5c | 92 | 182-188 | 64.2 | 4.7 | | |
| | | | (63.5) | (4.5) | | |
| 5d | 94 | 172-184 | . , | | | |
| 6a | 96 | 139–143 | | | | |
| 6b | 81 | 126-134 | 60.3 | 4.7 | | |
| | | | (60.8) | (4.6) | | |
| 7 a | 96 | 150-160 | | . / | | |
| 7b | 63 | 124-128 | | | | |

Table 10. Yield, melting point and analyses for complexes 1-7

^a All the complexes decompose on melting, hence the long melting ranges.

hydrogen atoms refined anisotropically by full-matrix least squares. The phenyl hydrogen atoms were fixed at calculated positions ($B_{iso} = 1.3B_{eq}$ for parent atom) and the other hydrogen atoms were freely refined. The weighting scheme was $w = 1/\sigma^2(F)$, $\Sigma w |F_0| - |F_c|)^2$ minimized, and the final residuals were R = 0.019, wR = 0.026. C₄₆H₄₀OP₂Pt, $M_w = 865.9$, triclinic, $P\overline{1}$, $a = 9.667(1), \quad b = 12.859(2), \quad c = 16.571(3)$ Ă. $\beta = 84.13(1)^{\circ},$ $\alpha = 76.62(1),$ $\gamma = 70.04(1)^{\circ}$, V = 1883.0 Å³, Z = 2, $D_x = 1.53$ g cm⁻³, $F(000) = 864, \ \Delta/\sigma_{max} \ 0.4, \ \Delta\rho_{max,min} = +0.85, \ -0.83$ eÅ³.

Reactions of complexes 1-7 with PCy₃

The complexes 1–7 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 C₆D₅CD₃ (0.5 cm³) in an NMR tube. The tube was then cooled to -70° C and a solution of PCy₃ (1:1 molar ratio with platinum) in C₆D₅CD₃ (0.5 cm³) was added. The NMR tube was shaken carefully and the ³¹P NMR spectrum recorded at -70 and -50° C, and then allowed to equilibrate at 5°C over 2–3 weeks.

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REFERENCES

- Chaloner, P. A. and Broadwood-Strong, G. T. L., J. Organomet. Chem., 1989, 362, C21.
- Chicote, M. T., Green, M., Spencer, J. L., Stone F. G. A. and Vicente, J., J. Organomet. Chem., 1977, 137, C8.
- 3. Schorpp, K. and Beck, W., Z. Naturforsch., 1973, 28B, 738.
- White, M. R. and Stang, P. J., Organometallics, 1983, 2, 1654; Sharp, T. R., White, M. R., Davis, J. F. and Stang, P. J., Org. Mass Spectrom., 1984, 19, 107.
- 5. Osborn, J. A., J. Chem. Soc., Chem. Commun., 1968, 1231.
- Pellizer, G., Graziani, M., Lenarda, M. and Heaton, B. T., *Polyhedron*, 1983, 2, 657; Cenini, S., Ugo, R. and La Monica, G., *J. Chem. Soc.*, *A*, 1971, 409; Cenini, R., Ugo, R., Bonati, F. and La Monica, G., *Inorg. Nucl. Chem. Lett.* 1967, 3, 191.
- Chatt, J., Shaw, B. L. and Williams, A. A., J. Chem. Soc., 1962, 3269.
- Visser, J. P., Schipperijn, A. J. and Lukas, J., J. Organomet. Chem., 1973, 47, 433.
- Cook, D. J., Green, M., Mayne N. and Stone, F. G. A., J. Chem. Soc., A, 1968, 1771; Booth, B. L., Haszeldine R. N. and Tucker, N. I., J. Organomet. Chem., 1968, 11, P5.
- Gilchrist, T. L., Graveling F. J. and Rees, C. W., J. Chem. Soc., Chem. Commun., 1968, 821; Sanders, W. D., Laird, B. B. and Davies, R. E., J. Am. Chem. Soc., 1981, 103, 970.

- Gassman, P. G. and Cesa, I. G. Organometallics, 1984, 3, 119; Godleski, S. A., Gundlach K. B. and Valpey, R. S., Organometallics, 1985, 4, 296.
- Parker D. and Taylor, R. J., J. Chem. Soc., Chem. Commun., 1987, 1781; Tetrahedron, 1988, 44, 2241.
- Halpern, J. and Weil, T. A., J. Chem. Soc., Chem. Commun., 1973, 631; Nelson, J. H., Jonassen, H. B. and Roundhill, D. M., Inorg. Chem., 1969, 8, 2591; Tripathy, P. B. and Roundhill, D. M., J. Organomet. Chem., 1970, 24, 247; Newkome, G. R. and McClure, G. L., J. Am. Chem. Soc., 1974, 96, 617; Bennett, M. A. and Yoshida, T. J. Am. Chem. Soc., 1978, 100, 1750; Smart, L. E., Browning, J., Green, M., Laguna, A., Spencer, J. L. and Stone, F. G. A., J. Chem. Soc., Dalton Trans., 1977, 1777.
- 14. Chaloner, P. A., Davies, S. E. and Hitchcock, P. B., J. Organomet. Chem., in press.
- We thank Chris DeArmitt for a sample of CH₂=CHCONMcPh.
- Mason R. and Meek, D. W., Angew. Chem., Int. Ed. Engl., 1978, 17, 183.
- Pregosin, P. S., Ann. Rep. NMR Spec., 1986, 17, 285.
- Pellizer, G., Lenarda, M., Ganzerla, R. and Graziani, M., *Gazz. Chim. Ital.*, 1986, **116**, 155.
- Nicolaides, A., Smith, J. M., Kumar, A., Barnhart D. M. and Borden, W. T., Organometallics, 1995, 14, 3475.
- Hall, P. W., Puddephatt, R. J. and Tipper, C. F. H., J. Organomet. Chem., 1974, 71, 145.
- Castellano, S. and Bothney-By, A. A., J. Chem. Phys. 1964, 41, 3863.
- Lenarda, M., Ganzerla, R., Lisini, A., Graziani, M. and Boschi, T., *Trans. Met. Chem.*, 1981, 6, 199.
- 23. Barbaran, J. M. and McGinnety, J. A., Inorg. Chem., 1974, 13, 2864.
- 24. Osborne, R. B., Lewis, H. C. and Ibers, J. A., J. Organomet. Chem., 1981, 208, 125.
- Cheng, P.-T. and Nyberg, S. C., Can. J. Chem., 1972, 50, 912.
- Caruso, F., Camalli, M., Pellizer, G., Asaro, F. and Lenarda, M., *Inorg. Chim. Acta*, 1991, 181, 167.
- Francis, J. N., McAdam, A. and Ibers, J. A. J. Organomet. Chem., 1971, 29, 131.
- Pannattoni, C., Graziani, R., Bandoli, G., Clements, D. A. and Belluco, U., J. Chem. Soc., B, 1970, 371.
- Choi, H., Hershberger, J. W., Pinhas, A. R. and Ho, D. M., Organometallics, 1991, 10, 2930.
- Jason, M. E. and McGinnety, J. A., *Inorg. Chem.*, 1975, 14, 3025.
- Albright, T. A., Hoffmann, R., Thibeault, J. C. and Thorn, D. L., J. Am. Chem. Soc., 1979, 101, 3801.
- 32. Tolman, C. A., Chem. Rev. 1977, 77, 313.
- 33. Tolman, C. A., J. Am. Chem. Soc., 1974, 96, 2780.
- Gillard, R. D. and Pilbrow, M. F., J. Chem. Soc., Dalton Trans., 1974, 2320.
- 35. Nagel, U., Chem. Ber., 1982, 115, 1998.
- Walker, N. and Stuart, D., Acta Cryst. 1983, A39, 158.