Allylic Alkylation catalysed by Platinum Complexes; Structure and Reactivity of Intermediates, and the Overall Stereoselectivity

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η^3-Butenyl[(*R,R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane-*P,P'*]platinum tetrafluoroborate (**4**) has been synthesised and shown to exist as four diastereoisomers in solution. Their interconversion was shown to be promoted by added PPh_3 and to be rapid on the n.m.r. time-scale under appropriate conditions, with interconversion of *E*-isomers faster than that of *Z*-isomers and much faster than $E \rightleftharpoons Z$ interchange. The palladium analogue was unaffected by added PPh_3.

The platinum complex catalyses the *C*-alkylation of but-2-enyl acetate or trifluoroacetate by dimethyl sodiomalonate, giving dimethyl (1-methylprop-2-enyl)malonate and (*E*)-dimethyl but-2-enylmalonate in a 5:1 ratio, the former in 11% optical yield. For a number of related complexes of chiral biphosphines, the optical yield in allylic alkylation varied between 0 and 23%,

(*Z*)-But-2-enyl trifluoroacetate carrying ^{13}C enrichment at C-1 was synthesised and converted in part into the corresponding diop platinum allyl complex. A series of reactions involving dimethyl sodiomalonate together with labelled (**4**) and unlabelled substrate, or unlabelled (**4**) and labelled substrate, was carried out. The results clearly demonstrate that the platinum allyl is a true intermediate in catalytic allylic alkylation.

The extensive studies of Trost and his co-workers[1] have established catalytic allylic alkylation as a reaction of synthetic importance. In almost all cases palladium(0) phosphine complexes have been employed, although recent work has drawn attention to the potential of tungsten and molybdenum,[2] or platinum[3] complexes, which give different selectivity. In the palladium case, it has been claimed[4] that the catalytic cycle involves an η^3-allylbisphosphinepalladium cation which experiences exometallic nucleophilic attack by the stabilised carbanion nucleophile. This claim has been disputed.[5]

Platinum complexes offer manifest advantages for the study of mechanism in allylic alkylation. The structure and reactivity of platinum allyls is similar to that of the palladium analogues,[6] but platinum–olefin complexes are much more stable than their palladium analogues.[7] In addition, the ^{31}P n.m.r. spectra of platinum–phosphine complexes have the additional information content due to ^{195}Pt satellites, and P–Pt couplings reveal the identity of substituents *trans* to the phosphorus because of their close correlation with electronegativity.[8] We were interested in examining the correlation between stereospecificity in complexation and enantiomer excess in the catalytic allylic alkylation for which ^{31}P n.m.r. has proved informative in other cases.[9]

Synthesis of Platinum Complexes.—The first attempts involved preparation of hydrobis(triphenylphosphine)platinum tetrafluoroborate[10] and its reaction with butadiene *in situ*. This produced a single complex (**1**), the ^1H and ^{31}P n.m.r. spectra of which indicated that the butenyl ligand had *Z*-configuration (Table 1). A sharp non-fluxional ^{31}P n.m.r. spectrum was observed at room temperature with no trace of a second isomer. Addition of Ph_3P to the solution led to rapid equilibration with the *E*-isomer, which was then predominant. Similarly, (*E*)-penta-1,3-diene reacted under the same conditions to form η^3-[(*EZ*)-pent-2-enyl]bis(triphenylphosphine)platinum tetrafluoroborate (**2**), this also being the major product when vinylcyclopropane was employed as the olefinic substrate.[11] The stereochemistry implies that proton transfer occurs to a diene moiety which is *s-cis* co-ordinated as depicted in (**3**).

Reaction of the *Z*-complex (**1**) with (*R,R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (diop) in CH_2Cl_2 solution gave rise to a new complex, apparently of *E*-configuration, or predominantly so from the ^1H n.m.r. spectrum. The new species (**4**) could be isolated, but it proved very difficult to separate it from the displaced PPh_3 and so an alternative route was sought. Bis(cyclo-octa-1,5-diene)-platinum(0),[12] conveniently prepared by cobaltocene reduction of the corresponding dichloride,[13] was treated with *trans*-1-bromobut-2-ene to give (**5**),[14] and the product was treated

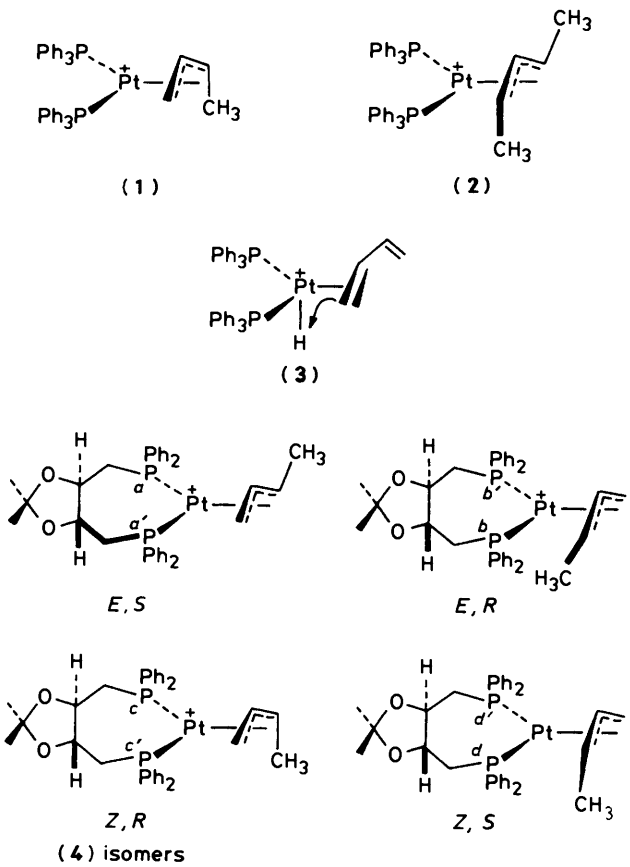


Table 1. ^{31}P N.m.r. parameters for η^3-butenylbisphosphine metal complexes (see Experimental section for relevant ^1H n.m.r. data)

Phosphine*			δ (^{31}P; CH_2Cl_2; relative to 85% H_3PO_4; J in Hz)			
2 PPh_3	*Z*		18.7	(J_{PPt} 3 986, J_{PP} 12)	27.2	(J_{PPt} 3 890)
	E[c]		21.4	(J_{PPt} 3 890, J_{PP} 9)	18.3	(J_{PPt} 4 150)
diphos[a,b]			48.6	(J_{PPt} 3 670, J_{PP} 8)	46.8	(J_{PPt} 3 760, J_{PP} 8)
diop	*E*	Species I	6.7	(J_{PPt} 3 874, J_{PP} 7)	1.98	(J_{PPt} 3 894)
		Species II	6.34	(J_{PPt} 3 850, J_{PP} 7)	1.40	(J_{PPt} 3 927)
	Z	Species I	5.27	(J_{PPt} 3 739, J_{PP} 7)	0.74	(J_{PPt} 3 798)
		Species II	3.63	(J_{PPt} 3 786, J_{PP} 7)	2.90	(J_{PA} 3 757)
(*R*,*R*)-dipamp[a,b]		Species I	42.1	(J_{PPt} 3 830, J_{PP} 11.0)	37.0	(J_{PPt} 3 856, J_{PP} 11.0)
		Species II	39.6	(J_{PPt} 3 859, J_{PP} 11.8)	39.15	(J_{PPt} 3 785, J_{PP} 11.8)
(*R*,*R*)-pampop[a,b]		Species I	5.5	(J_{PPt} 4 000, J_{PP} 8)	4.0	(J_{PPt} 3 850, J_{PP} 8)
		Species II	2.4	(J_{PPt} 4 040, J_{PP} 8)	1.3	(J_{PPt} 3 860, J_{PP} 8)
(*R*,*R*)-dbp-diop[a,b]		Species I	2.22	(J_{PPt} 3 800, J_{PP} 4)	−2.55	(J_{PPt} 3 723, J_{PP} 4)
		Species II	1.96	(J_{PPt} 3 760, J_{PP} 5)	−1.81	(J_{PPt} 3 805, J_{PP} 5)

* Abbreviations: diphos = 1,2-bis(diphenylphorphino)ethane; diop = 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane; dipamp = 1,2-bis-[*o*-methoxyphenyl(phenyl)phosphino]ethane; pampop = 4,5-bis[bis-(*o*-methylphenyl)phosphinomethyl]-2,2-dimethyl-1,3-dioxolane; dbp-diop = 4,5-bis(dibenzophospholomethyl)-2,2-dimethyl-1,3-dioxolane.

[a] Prepared *in situ* as described. [b] *E*-Isomers assumed to be predominant. [c] 3:1 *E*:*Z* at equilibrium.

sequentially with $AgBF_4$ and (*R*,*R*)-diop. By this route the complex (**4**) could be isolated in pure form. A related approach involved but-2-enyl trifluoroacetate, with ion-exchange against aqueous $NaBF_4$ in the final stage.

In other cases this route was employed to give bisphosphine-platinum η^3-butenyl complexes which were pure by ^{31}P n.m.r. but not isolated (Table 1).

Dynamic Behaviour of the Complex (**4**).—When this diop complex was prepared by displacement of PPh_3 from the corresponding butenyl complex, its ^{31}P n.m.r. spectrum at 30 °C (ambient probe) and 36.43 MHz suggested (incorrectly) that a single diastereoisomer was predominant. Conversely, preparation from bis(cyclo-octadiene)platinum gave a species which on initial dissolution in CD_2Cl_2 showed ^{31}P n.m.r. signals for two diastereoisomers, assigned *E*-stereochemistry on the basis of their ^1H n.m.r. spectra. The corresponding *Z*-isomers were apparent only in trace quantities, but an equilibrium mixture (*Z*:*E* 1:1.7) was quickly formed on addition of a trace of PPh_3. One of the two possible *E*-isomers predominated by 55:45 but the *Z*-isomers were present in equal amounts. Addition of further PPh_3 caused broadening and collapse of the separate signals in the ^{31}P n.m.r. spectrum, due to dynamic interchange, showing that this factor was responsible for the apparent simplicity of the spectrum of the product derived by the first route.

More accurate information on the various exchange processes was obtained. First, population inversion of the peak labelled P_B in Figure 1(*c*) and due to the phosphine *trans* to C-1 in one *E*-diastereoisomer (see later) by the DANTE technique[15] led to excitation transfer to P_A only. This is the related phosphine of the second *E*-diastereoisomer. The observation is readily explained if interchange takes place by a $\pi \rightleftharpoons \sigma \rightleftharpoons \pi$ mechanism[16] in which formation of the η^1-allyl always occurs at the primary terminus (Scheme 1). When more substantial quantities of PPh_3 were added, line broadening occurred at all sites and the spectra could be simulated using the program DNMR3.[17] Each spectrum was treated as containing separate and non-interconverting *Z*- and *E*-diastereoisomers so that the rate constants for (*Z*,*R*) ⟶ (*Z*,*S*) and (*E*,*R*) ⟶ (*E*,*S*) could be calculated. Equilibration of *Z*- and *E*-diastereoisomers by addition of a trace of PPh_3 to an *E*-enriched sample, prepared as above, proved too fast to be followed, but it is nevertheless much slower than the two evaluated processes.

The rate of interconversion of *E*-isomers is 21 times greater than the rate of interconversion of *Z*-isomers (Figure 2). This is explicable if the attack of PPh_3 leading to interconversion is stereospecific, such that the methyl group in the *Z*-form offers steric inhibition to reaction (Scheme 1). It can be seen that the two observed interconversions take place *via* the intermediacy of a primary η^1-allyl complex, which could not be detected in the ^{31}P n.m.r. spectrum. When the complex (**5**) was treated with bis-(2-diphenylphosphinoethyl)phenylphosphine in CH_2Cl_2, the ^{31}P n.m.r. spectrum showed that a single species was present [$\delta(P_A)$ 91.0 (t, J_{PPt} 1 530 Hz), $\delta(P_B)$ 43.0 (d, J_{PPt} 2 925 Hz)]. The low-field shift of the central phosphorus is characteristic of co-ordination *via* two chelate rings,[18] and a P–Pt coupling of *ca.* 1 500 Hz is typical for a square-planar complex with phosphorus *trans* to sp^3 carbon, thereby indicating that the new species has structure (**6**).

Exchange between *E*- and *Z*-stereoisomers was slow on the n.m.r. time-scale, even when a substantial excess of PPh_3 was added. Conversely, it could not be followed directly since addition of traces of PPh_3 to the initial, *E*-predominant product (**4**) led to isomerisation to the equilibrium mixture within 200 s. It appears that the reaction, which must proceed through a secondary η^3-allyl, is 10^2—10^3 times slower than $E \rightleftharpoons E$ or $Z \rightleftharpoons Z$ interconversion.

Stereochemistry of Catalytic Allylic Alkylation.—Examples of effective asymmetric induction in allylic alkylation are relatively rare,[19] and it was felt that a study of the stable isolated complex (**4**) would provide useful information. When its solution in CH_2Cl_2 was treated with a slight excess of $NaCH(CO_2Me)_2$ smooth dissolution occurred, and work-up revealed two products. These were shown to be the adducts (**7**) and (**8**) in 80:20 ratio by g.l.c. and n.m.r. comparison with authentic samples. The linear product is very predominantly *trans*, despite the near equal proportions of *E*- and *Z*-isomers in the equilibrated η^3-allyl (**4**).

Catalytic allylic alkylation was carried out in similar fashion by the reaction of equimolar amounts of but-2-enyl acetate and $NaCH(CO_2Me)_2$ in CH_2Cl_2 containing 5 mol % of platinum complex (**4**). During 0.5 h the mixture became yellow and some platinum metal was deposited. It was left overnight and then worked up, showing about 10 cycles of catalytic turnover. The ratio of products (**7**) and (**8**) was indistinguishable from that in the stoicheiometric reaction. The optical yield in (**7**) was determined by addition of the chiral shift reagent tris(hepta-fluorobutyrylcamphorato)europium, $Eu(hfc)_3$, in portions to

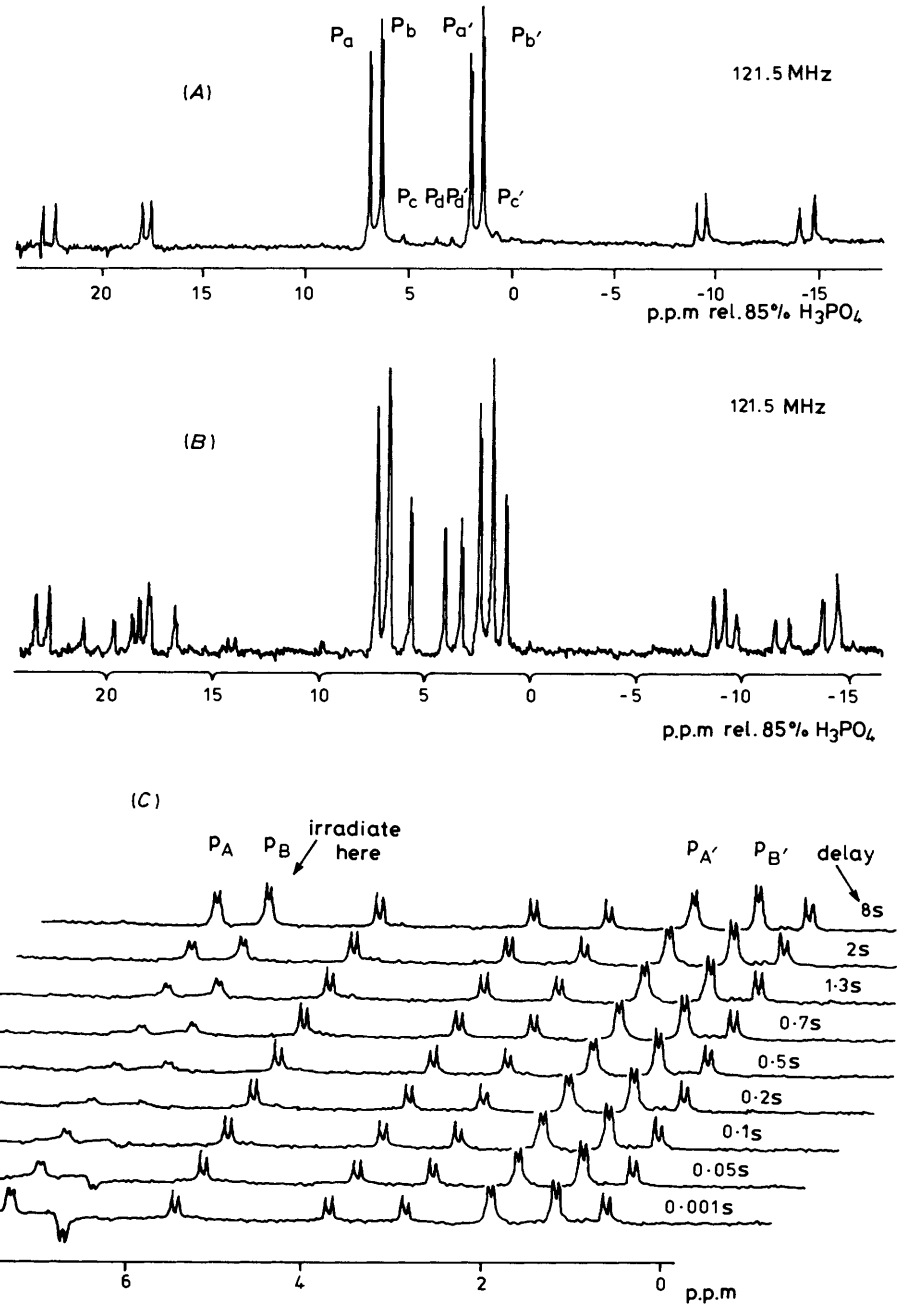
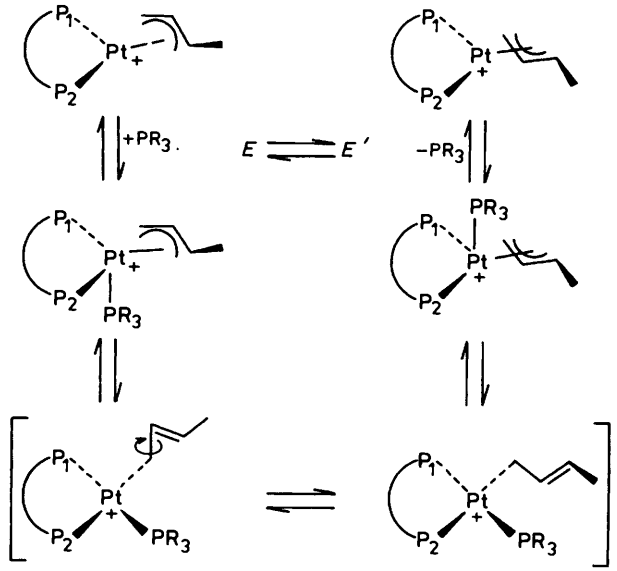


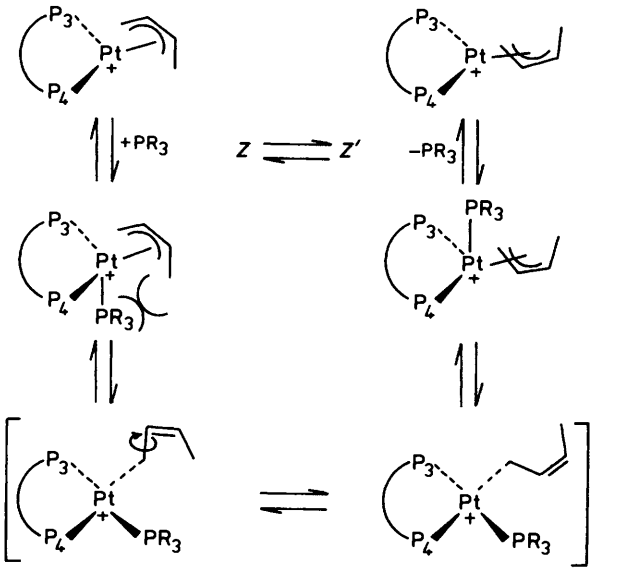
Figure 1. (A) The ^{31}P n.m.r. spectrum of the complex (**4**) in CH_2Cl_2 at ambient temperature, freshly prepared; (B) as (A) after isomer equilibration; (C) irradiation of the ^{31}P resonance at δ 6.34 and recovery at different delay times in the presence of a small quantity of added PPh_3

the mixture of alkylation products in $CDCl_3$ until the $-CHCH_3$ signals of the enantiomers of (**7**) were separated by *ca.* 10 Hz, with near-baseline resolution (10—15 mol% reagent). Computer simulation of this four-line spectrum showed an optical yield of 11%. The predominant enantiomer was shown to be *S* by hydrogenation of the double bond using nickel boride P2 catalyst,[20] and a further n.m.r. chiral shift experiment. The result was compared with that obtained from an authentic sample of (*R*)-(**9**), prepared from (*S*)-1-methylpropyl toluene-*p*-sulphonate by direct nucleophilic displacement employing $NaCH(CO_2Me)_2$ in MeOH.

A series of platinum bisphosphine complexes were prepared by treating the η^1-butenyl complex (**5**) with $AgBF_4$ and 1 mol equiv. of the bisphosphine. Samples of (**10**),[21] (**11**),[22] and (**12**)[23] thus obtained were shown to be diastereoisomeric mixtures by ^{31}P n.m.r. (Table 1), but no other species were apparent and the solutions were employed directly in catalysis. Results are recorded in Table 2, which shows that the highest enantioselectivity was obtained in the case of (**11**),[22] and also that the ratio of primary to secondary site attack is phosphine-dependent, with the former strongly favoured in the case of (**12**). This points to a correlation between the ring size of the bisphosphine chelate and regioselectivity.

Mechanism of Platinum-catalysed Allylic Alkylation.—(i) *Studies of the stoicheiometric rection.* Proton n.m.r. experiments were carried out by injecting an excess of $NaCH(CO_2Me)_2$ in $CDCl_3$, solubilised by 1 equiv. of 15-crown-5, into a solution of the platinum complex (**4**) in $CDCl_3$. Spectra were recorded at 100 s intervals. It was observed that the straight-chain product





Scheme 1. Mechanisms for diastereoisomer interconversion in the complex (**4**)

(**8**) [$\delta(CH_3)$ 1.66] was formed immediately, and did not accumulate further (presumably because the corresponding platinum complex is unstable and breaks down rapidly), whereas the amount of branched-chain isomer (**7**) [$\delta(CH_3)$ 1.11] increased steadily over 60 min. At the same time, four doublets were apparent in the region δ 0.4—0.65, the relative proportions of which changed slowly (Figure 3). These were ascribed to the C–CH_3 protons of the four possible isomers of (**13**). When the complex (diop)(ethylene)platinum[24] reacted with a ten-fold excess of the alkylmalonate (**7**) then the same four isomers were observed in different proportions. The fact that *four* complexes were observed in the initial phases of this stoicheiometric allylic alkylation strongly suggests that both *E*- and *Z*-isomers of (**4**) are reactive towards $NaCH(CO_2Me)_2$, as indicated by Scheme 2. In the achiral example of platinum-catalysed allylic alkylation studied by Kurosawa,[3] intermediate olefin complexes were observed.

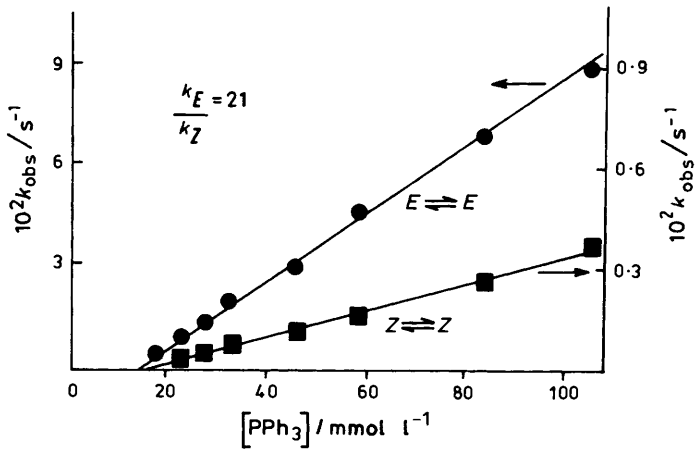
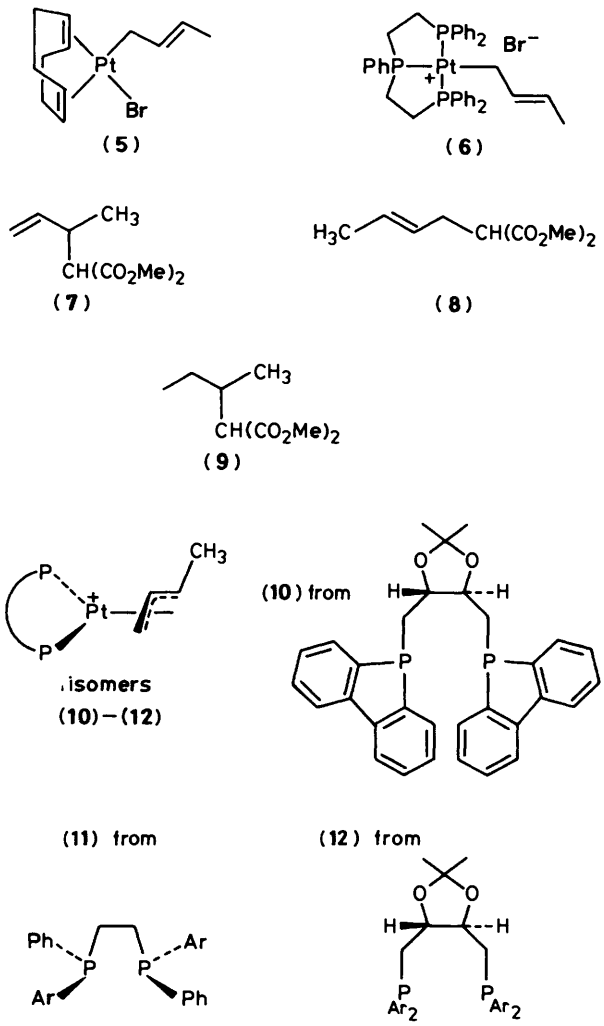
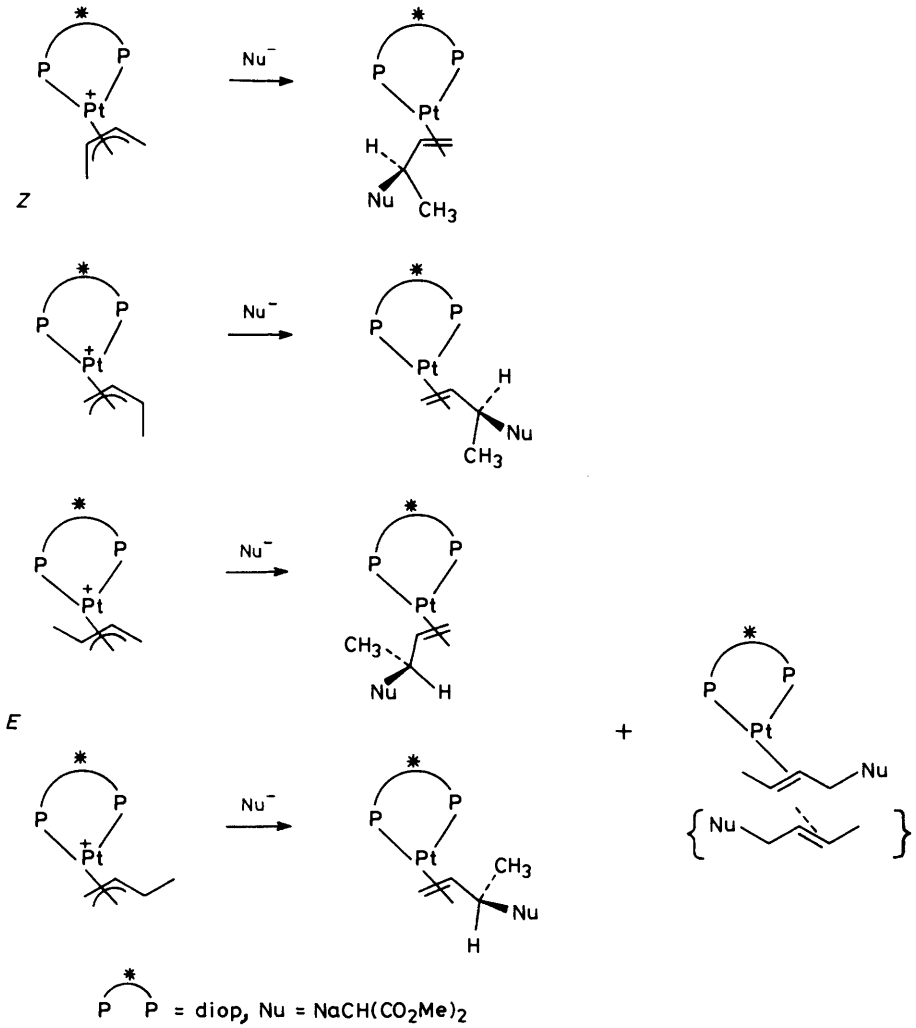


Figure 2. Rate of interconversion of *E*-isomers and of *Z*-isomers of the complex (**4**) as a function of PPh_3 concentration, by line-shape analysis employing the program DNMR3 to generate comparison spectra; the sample of (**4**) contained a trace impurity [colloidal Pt ⟶ $Pt(PPh_3)_3$?] so that the resonance due to free PPh_3 was deshielded and broadened. Line-shape analysis of the ^{195}Pt satellite spectra gave similar values and thus diop dissociation is not involved





Scheme 2. Exometallic attack of $NaCH(CO_2Me)_2$ on the complex (**4**)

Table 2. Catalytic allylic alkylation by η^3-butenyl-platinum and -palladium complexes; reactions conducted in CH_2Cl_2 solution as described in the Experimental section.

Complex	Product ratio (**7**):(**8**)	Enantiomer excess[b] in (**7**)
(**4**)	5:1	11 *S*
(**10**)[a]	1:1	0
(**11**)[a]	3:1	23 *S*
(**12**)[a]	1:4	13 *S*
(**17**)	1.3:1	13 *S*

[a] Complex prepared *in situ*, otherwise isolated. [b] Determined by the chiral shift n.m.r. method employing $Eu(hfc)_3$.

The complex (**4**) was then prepared enriched with ^{13}C at the 1-position. (*Z*)-1-Bromoprop-1-ene was treated with Mg in tetrahydrofuran,[25] and the organomagnesium reagent was carboxylated with $^{13}CO_2$. The acid (**14**) was >90% *Z*-isomer. It was esterified *in situ* with diazomethane and then reduced with $LiAlH_4$ in the presence of $AlCl_3$[26] giving (*Z*)-[1-^{13}C]but-2-en-1-ol (**15**). Initial attempts to convert the primary alcohol into a halide using Me_2S–*N*-chlorosuccinimide[27] or $(Cl_3C)_2CO$–PPh_3[28] did not work well; the alcohol (**15**) was therefore converted directly into its trifluoroacetate (**16**), which was treated with bis(cyclo-octadiene)platinum. The intermediate was converted directly into ^{13}C-labelled (**4**) by reaction with 1 equiv. of diop, and excess of $NaBF_4$. The product is an equilibrium mixture of *E*- and *Z*-isomers (since $CF_3CO^-{}_2$ was shown to cause rapid $\sigma \rightleftharpoons \pi$ interconversion). All four isomers are distinguishable in the ^{13}C n.m.r. spectrum, and show strong coupling to one phosphine, presumed to be *trans* to C-1. In three of the four cases this corresponds to the low-field ^{31}P resonance, but it is the more shielded nucleus in one of the *Z*-isomers.

When >1 equiv. of $NaCH(CO_2Me)_2$ was added, the ^{13}C n.m.r. signals due to (**4**) were lost immediately, to be replaced by those of (**8**) at δ 32 and those of (**7**) at δ 115. Whilst the intensity of the former remained constant, the latter increased with time, in keeping with earlier observations by ^1H n.m.r.

(ii) *Reactions under catalytic conditions.* When but-2-enyl acetate or trifluoroacetate was treated in $CDCl_3$ with excess of $NaCH(CO_2Me)_2$ (solubilised by 15-crown-5) in the presence of 5 mol % of the complex (**4**), the reaction was completely expended within 100 s. The ratio of branched to linear product was 4:1 in both cases but the acetate had only reacted to the extent of 30% whereas the trifluoroacetate was 55% consumed. Both allylic esters were 30:70 *Z*:*E* at the commencement of reaction, but the *E*-isomer became more predominant as it proceeded, to the extent of 85% for acetate and 93% for trifluoroacetate. This indicates that the *Z*-isomer is more reactive and selectively consumed.

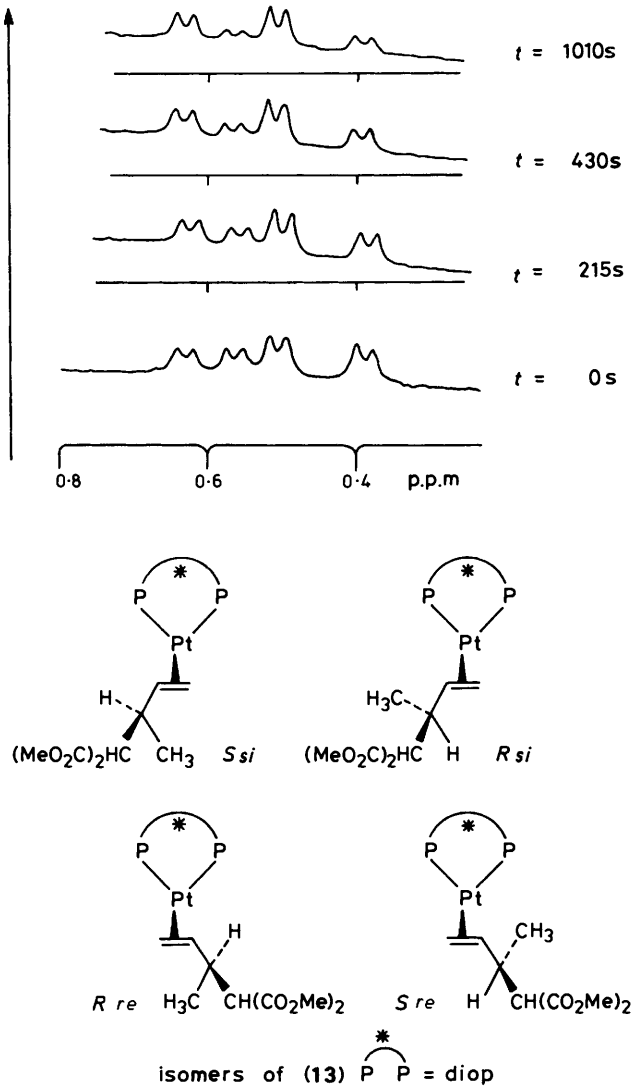
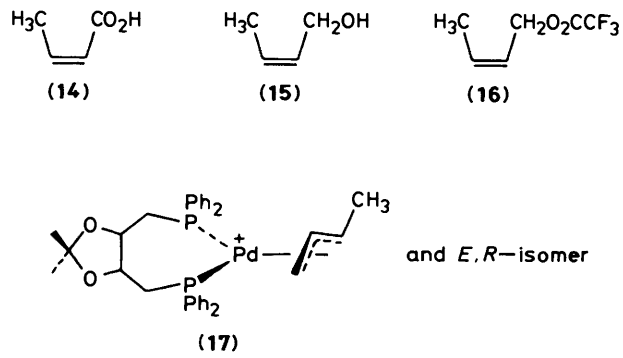


Figure 3. The high-field region of the ^1H n.m.r. spectrum of a reaction mixture containing the complex (**4**) and $NaCH(CO_2Me)_2$ in $CDCl_3$, showing the four diastereoisomers of the complex (**13**), $CHCH_3$ resonance, and changes in their proportion with time



The key experiments involved the ^{13}C-enriched trifluoroacetate and complex (**4**), and permit an evaluation of the role of the latter in catalysis. A set of experiments was carried out in which a defined quantity of ^{13}C-labelled complex (**4**) was treated with a defined quantity of unlabelled trifluoroacetate (**16**) in the presence of a slight deficiency of $NaCH(CO_2Me)_2$, or conversely unlabelled complex (**4**) was treated with ^{13}C-labelled trifluoroacetate (**16**), again in the presence of a slight deficiency of $NaCH(CO_2Me)_2$. The distribution of ^{13}C label between the various enriched species present at the end of the reaction was determined by ^{13}C n.m.r. In these spectra, any remaining complex (**4**) was shown to be at the fast-exchange limit for $(E,R) \rightleftharpoons (E,S)$ and $(Z,R) \rightleftharpoons (Z,S)$ because of reversible attack by CF_3CO_2Na and/or $NaCH(CO_2Me)_2$ at platinum. Results are recorded in Table 3, and are corrected for the effect of differential relaxation times.

The data may be compared directly with the predictions of a kinetic model in which the total flux of catalysis proceeds through an η^3-allyl (as opposed, for example, to mechanisms where a small amount of the available platinum complex is activated by electron-transfer and carries the bulk of the catalytic flux). This leads to the kinetic form delineated in Scheme 3 which predicts the distribution of ^{13}C label amongst starting material, platinum complex, and product at the termination of reaction. A computer program was written to test this model employing standard Runge–Kutta numerical integration techniques.[29] The outcome is insensitive to the values of k_1 and k_2 chosen, and these were set as $k_2 = 10$ mol l^{-1} s^{-1}. Since other experiments had demonstrated that reaction was not quantitative, allowance was made by introducing a side-reaction k_s leading to destruction of $NaCH(CO_2Me)_2$. This was set empirically, best results being obtained when $k_s = k_1/180$ mol l^{-1}. The program was run until the concentrations of all species remained constant; with the rate constants specified, this was the case after 50 s.

For all four runs, the agreement between theory and experiment is extremely close (Table 3), indicating that the η^3-allyl is a true reaction intermediate. In palladium chemistry, this idea has been challenged[5] and defended.[4] Given the close similarity between the palladium- and platinum-catalysed reactions, it is highly likely that they proceed by the same mechanism.

Analogous Palladium Chemistry.—The η^3-butenyl(diop)-palladium tetrafluoroborate complex (**17**) was readily prepared from the corresponding η^3-butenylpalladium chloride[30] and 1 equiv. of bisphosphine in CH_2Cl_2. Analysis of its ^{31}P and $^1H(^{31}P)$ n.m.r. spectra showed that it was predominantly (>9:1) two *E*-diastereoisomers in similar proportions. The much lower ratio of *Z*-isomers in the palladium case may reflect some stabilisation of the *endo*-methyl group by weak C–H • • • Pt bonding in the *Z*-complex (**4**). There is some precedent for agostic hydrogen bridges in *Z*-butenyl complexes,[31] and this would be more important for Pt than Pd because of the relative favouring of hydride complexes in the former case.

The ^{31}P n.m.r. spectrum of the complex (**17**) is unaffected by up to 2 equiv. of added PPh_3. Indeed the only experiment in which any appreciable line-broadening was effected involved addition of *ca.* 20 mol % of pyridine to the solution of (**17**). When this complex was employed in catalytic allylic alkylation, a rapid reaction gave the two products (**7**) and (**8**) in 1:1.3 ratio (*cf.* 4:1 in the Pt case), and the optical yield in the former was 13%, similar to that noted before.

A reaction was carried out in which the cationic complex (**17**) was not isolated but rather replaced by a mixture of η^3-butenylpalladium chloride and 2 equiv. of diop. The product distribution and optical yield were identical, suggesting that the intermediates involved are the same in both cases. This is in contrast to the conclusions of Åkermark for the amination of allylpalladium complexes.[32]

Table 3. Results of labelling experiments*

	Initial concentrations (mmol l^{-1})			Final distribution of ^{13}C-label (%)		
	Reactant (**16**)	Catalyst (**4**)	$NaCH(CO_2Me)_2$ [d]	Reactant (**16**)	Catalyst (**4**) [b]	Product (**7**) + (**8**)
A	16 U [a]	10.5 L [a]	13.6	−(0.7) [c]	48.1 (42.7)	51.9 (56.5)
B	40 U	10.1 L	34	−(1.9)	9.8 (11.8)	90.2 (86.3)
C	18 L	12.1 U	15.3	44.3 (43.3)	36.7 (36.9)	19.0 (19.7)
D	46 L	11.5 U	39	44.8 (48.0)	18.3 (20.4)	36.9 (31.6)

* Reactions were carried out in $CDCl_3$ (1.5 ml), with $NaCH(CO_2Me)_2$ added last, and the ^{13}C spectrum was recorded 5 min after addition. Conditions: sweep width 18 500 Hz, pulse width 12 μs, acquisition time 0.44 s, relaxation delay 0.4 s. Relative intensities did not change subsequently. Entry D was re-recorded with a relaxation delay of 60 s and a correction factor applied: complex (**4**) $I = 0.448\ I_{obs}$; compounds (**7**), (**8**) $I = 0.645\ I_{obs}$. Similar corrections were applied in the remaining cases.

[a] U refers to unlabelled (assumed 1%) and L to labelled (assumed 90%) species. [b] A single set of peaks was observed for *E*- and *Z*-isomers due to $CF_3CO_2^-$-induced equilibration; this was confirmed by examination of the ^{31}P n.m.r. spectrum. [c] Percentages in parentheses were calculated according to the model of Scheme 2. [d] Dimethyl sodiomalonate is present in deficiency [relative to reactant (**16**)] to suppress the formation of complex (**13**).

For unlabelled complex (**4**) reacting with ^{13}C-labelled substrate:

$$A + M \xrightarrow{k_1} AM$$

$$AM + S^* \xrightarrow{k_2} P + A^*$$

$$A^* + M \xrightarrow{k_1} A^*M$$

$$A^*M + S^* \xrightarrow{k_2} P^* + A^*$$

$$M \xrightarrow{k_s} M'$$

For ^{13}C-labelled complex (**4**) reacting with unlabelled substrate:

$$A^* + M \xrightarrow{k_1} A^*M$$

$$A^*M + S \xrightarrow{k_2} P^* + A$$

$$A + M \xrightarrow{k_1} AM$$

$$AM + S \xrightarrow{k_2} P + A$$

$$M \xrightarrow{k_s} M'$$

A is the platinum butenyl complex (**4**), M is dimethyl sodiomalonate, AM is the olefin complex (**13**), P is the mixed isomers of allylic alkylation product (**7**) and (**8**), and S is butenyl trifluoroacetate. Rate constants were set as $k_1 = 0.1$ mol l^{-1} s^{-1}, $k_2 = 10$ mol l^{-1} s^{-1}, with the side-reaction $k_s = k_1/180$ mol l^{-1}.

Scheme 3. Kinetic model for interpretation of the ^{13}C-labelling experiments, giving the results recorded in Table 3.

Experimental

N.m.r. spectra for ^1H and ^{13}C were recorded with a Bruker WH 300 instrument, and ^{31}P n.m.r. spectra either with this or with a Bruker WH 90 machine. Chemical shifts for ^1H and ^{13}C are recorded in p.p.m. relative to Me_4Si and ^{31}P chemical shifts relative to external 85% H_3PO_4. Mass spectra were recorded with a VG Micromass spectrometer operating in either electron-impact or field-desorption mode, as specified. Optical rotations were recorded with a Perkin-Elmer 241 polarimeter.

All reactions involving air- or moisture-sensitive materials were performed under pre-purified argon using Schlenk glassware and standard vacuum-line techniques. Solvents were dried and freshly distilled immediately prior to use.

Microanalyses were performed in the Dyson Perrins Laboratory by Dr. F. B. Strauss.

Preparation of (Z)-η³-*But-2-enylbis(triphenylphosphine)platinum Tetrafluoroborate.*—Buta-1,3-diene was bubbled through a solution of hydridochlorobis(triphenylphosphine)platinum [10] (100 mg, 0.13 mmol) in dichloromethane (1.5 ml) in a Craig tube. Silver tetrafluoroborate (30 mg, 0.15 mmol) was added and the mixture shaken vigorously to produce a copious precipitate of silver chloride. After centrifugation, the liquid was transferred to a Schlenk tube and the volume of dichloromethane was halved under reduced pressure. On addition of hexane (1.5 ml) an oil separated which crystallised on scraping against the sides of the tube with a spatula. The liquid was removed and the solid dried *in vacuo* to give *product* (80 mg, 73%) as a white powder, m.p. 240—244 °C (decomp.) (Found: C, 55.2; H, 4.3; P, 7.4. $C_{40}H_{37}BF_4P_2Pt$ requires C, 55.6; H, 4.3; P, 7.2%); $\nu_{max.}$(KBr) 3 080m, 3 060m, 1 590w, 1 575w, 1 480s, 1 440s, 1 315m, 1 070vs, 755vs, 745s, and 700s; δ (^1H; 300 MHz; CD_2Cl_2) 1.02 (m, 3 H), 2.59 (m, 1 H), 3.93 (br m, 1 H), 4.41 (br m, 1 H), 5.37 (m, 1 H), and 7.3 (Ar); *m/z* (field desorption) 773 (M^+, ^{194}Pt). On addition of a trace of PPh_3 to a solution of the complex in CH_2Cl_2 rapid epimerisation to the *E*-isomer (75% at equilibrium) occurred.

Preparation of (E,Z)-η³-*Pent-2-enylbis(triphenylphosphine)platinum Tetrafluoroborate.*—The foregoing procedure was followed, with (*E*)-penta-1,3-diene (50 μl), silver tetrafluoroborate (25 g, 0.13 mmol), and hydridochlorobis(triphenylphosphine)platinum (80 mg, 0.1 mmol). The product was obtained as a white powder (85 mg, 92%), m.p. 127—130 °C; δ (^1H; 300 MHz; CD_2Cl_2) 0.88 (m, 3 H), 1.18 (m, 3 H), 3.23 (br m, 1 H), 3.77 (m, 1 H), 3.81 (br m, 1 H), 5.32 (br m, 1 H), and 7.3 (m, Ar); δ (^{31}P; 36.43 MHz; CH_2Cl_2) 20.2 (d, J_{PPt} 3 858, J_{PP} 7 Hz), and 18.5 (J_{PP} 4 128 Hz). The same major product was formed when vinylcyclopropane was used in place of (*E*)-penta-1,3-diene.

Phosphine Displacement from η³-*But-2-enylbis(triphenylphosphine)platinum Tetrafluoroborate.*—(*R,R*)-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (0.014 g, 0.03 mmol) [33] was added to a solution of the complex (0.025 g, 0.03 mmol) in CH_2Cl_2 (1.5 ml). Aside from those due to displaced PPh_3, only one set of resonances was apparent in the ^{31}P n.m.r. spectrum: δ 6.6 (d, J_{PPt} 3 859 Hz, J_{PP} 7 Hz) and 3.1 (d, J_{PPt} 3 900 Hz).

Preparation of η³-*But-3-enyl*[(R,R)-4,5-*bis(diphenylphosphinomethyl)*-2,2-*dimethyl*-1,3-*dioxolane*-PP′]*platinum Tetrafluoroborate.*—Bis(cyclo-octadiene)platinum (20 mg, 0.049 mmol) [13] was added to a degassed solution of (*E*)-1-bromobut-2-ene (6.6 mg, 0.049 mmol) in diethyl ether (10 ml) at −78 °C. As the mixture warmed to room temperature the

bis(cyclo-octadiene)platinum dissolved. The solution was filtered under argon into a fresh Schlenk tube and solvent was removed *in vacuo* leaving pale yellow platelets of η^1-butenyl-(cyclo-octadiene)platinum(II) bromide, δ (^{1}H; 300 MHz; $CDCl_3$) 5.3 (2 H, m), 4.5 (4 H, br s, J_{HPt} 78 Hz), 2.67 (2 H, d, J_{HH} 9, J_{HPt} 95 Hz), 2.4 (8 H, m), and 1.68 (3 H, d, J 6 Hz).

This compound was not usually isolated but was immediately redissolved in dichloromethane (10 ml); to the solution was added silver tetrafluoroborate, with shaking. A copious precipitate of silver bromide formed which was removed by centrifugation, and the remaining liquid was transferred to a Schlenk tube containing the bisphosphine (24 mg, 0.049 mmol). The volume of solvent was reduced to *ca.* 2 ml; addition of pentane yielded the complex (**4**) which was washed with pentane (2 × 5 ml) and dried *in vacuo*. The *product* was thus obtained as a white powder (29 mg, 71%), m.p. 143—146 °C (Found: C, 50.5; H, 4.9. $C_{35}H_{39}BF_4O_2P_2Pt$ requires C, 50.3; H, 4.7%); δ (^{31}P; 121.49 MHz; CH_2Cl_2) major species 6.7 (d, J_{PP} 7, J_{PPt} 3 874 Hz) and 1.98 (d, J_{PP} 7, J_{PPt} 3 894 Hz), and 6.34 (d, J_{PP} 7, J_{PPt} 3 857 Hz) and 1.40 (d, J_{PP} 7, J_{PPt} 3 927 Hz); minor species 5.27 (d, J_{PP} 7, J_{PPt} 3 739 Hz) and 0.74 (d, J_{PP} 7, J_{PPt} 3 798 Hz), and 3.63 (d, J_{PP} 7, J_{PPt} 3 786 Hz) and 2.90 (d, J_{PP} 7, J_{PPt} 3 757 Hz); ^{1}H n.m.r. (300 MHz; $CDCl_3$) very complex, but with multiplets at δ 1.30 and 1.17 (allyl methyl groups of the major species) and at 0.83 and 0.68 (allyl methyl groups of the minor species); *m/z* ($M^+ - BF_4$).

General Procedure for Catalytic Allylic Alkylation.—(a) *Dimethyl sodiomalonate.* Sodium (0.5 g, 21.7 mmol) was dissolved in dry MeOH (10 ml) under Ar. Dimethyl malonate (2.87 g, 21.7 mmol) was added; the mixture was stirred for 5 min and then the solvent was removed *in vacuo*, giving a white powder (3.3 g, 99%) which was stored under Ar at −30 °C. Solutions in CH_2Cl_2 (CD_2Cl_2) were prepared freshly for each experiment. For n.m.r. work where homogeneity was required the solution was prepared by suspending dimethyl sodiomalonate (0.010 g, 0.065 mmol) in CD_2Cl_2 (100 μl) to which was added 1,4,7,10,13-pentaoxacyclopentadecane (0.016 g, 0.073 mmol), and the suspension was then sonicated for 15 s.

(b) *Alkylation procedure.* To a degassed solution of the η^3-but-2-enyl complex (0.03 mmol) in CH_2Cl_2 (3 ml) was added but-2-enyl acetate or but-2-enyl trifluoroacetate (0.6 mmol) followed by dimethyl sodiomalonate (0.6 mmol), and the mixture was stirred vigorously overnight at ambient temperature. Some metallic Pt was precipitated as the reaction proceeded. The mixture was filtered through 60 μ silica gel and solvent was then removed under reduced pressure. Products were analysed by ^{1}H n.m.r. spectroscopy by comparison with authentic samples, prepared as described later.

(c) *Authentication of components.* Sodium (0.9 g, 0.04 mol) was cautiously dissolved in a solution of dimethyl malonate (4.7 g, 0.036 mol) in dry MeOH (35 ml). To the resulting solution was added 1-bromobut-2-ene (5.0 g, 0.037 mmol), and the mixture was heated under reflux for 2 h. MeOH was then removed under reduced pressure. The remaining oil was distilled at 10 mmHg (b.p. 60—80 °C, bath temp.) and monoalkylation products were then separated from the six-component mixture by preparative g.l.c. (Carbowax 20M): dimethyl (1-methylprop-2-enyl)malonate,[34] δ (300 MHz; $CDCl_3$) 5.77 (1 H, =CH, m), 5.05 (2 H, $=CH_2$, dd), 3.75 (6 H, s), 3.33 (1 H, d, α-H, J 9 Hz), 2.96 (1 H, C*H*Me, dq), and 1.11 (3 H, Me, d, J 7 Hz); *m/z* 127 (89), 126 (52), 111 (31), 67 (36), and 55 (100).

(*E*)-Dimethyl but-2-enylmalonate,[34] δ (300 MHz; $CDCl_3$) 5.56 (1 H, m, $=CHCH_3$), 5.38 (1 H, m, =CH), 3.73 (6 H, s), 3.42 (1 H, t, α-H, J 7.5 Hz), 2.58 (2 H, dd, CH_2), and 1.66 (3 H, dd, CH_3, J *ca.* 7 and 1.5 Hz); *m/z* 186 (11, M^+), 126 (71), 111 (100), 67 (85), and 55 (86).

Absolute Configuration of the Alkylation Product.—An air-free solution (25 μl) of sodium borohydride (12 mg, 0.32 mmol) in ethanol (0.25 ml) was added to an air-free solution of nickel(II) acetate tetrahydrate (9 mg, 0.036 mmol) in ethanol (1 ml). There was immediate precipitation of black colloidal nickel, the hydrogenation catalyst.[20] The apparatus was flushed with hydrogen and a solution (50 μl; *ca.* 0.27 mmol) of the products of (*R*)-diop-platinum-catalysed alkylation of but-2-enyl acetate with dimethyl sodiomalonate (see later) were added. The mixture was stirred for 1.5 h under hydrogen, after which it was filtered through a bed of charcoal to remove nickel. The charcoal was washed several times with acetone, and the combined organic filtrate was dried ($MgSO_4$). Removal of solvent under reduced pressure was followed by direct analysis of the products by ^{1}H n.m.r. spectroscopy (5 mg to 0.5 ml; $CDCl_3$). This showed the presence of expected alkylation products, including (**8**). Addition of the chiral shift reagent Eu(hfc)$_3$ (*ca.* 12 mol %) caused deshielding and clean separation of the $CHCH_3$ signals of *R*- and *S*-enantiomers, corresponding to an optical yield of 11%. Comparison with authentic (*R*)-(**8**) [from (+)-(*S*)-butan-2-ol (Fluka)] demonstrated that the predominant isomer in the alkylation product is *S*.

In subsequent experiments the optical yield was determined directly on the alkylation product by chiral shift n.m.r. experiments, in similar manner.

Preparation of (Z)-[1-^{13}C]*But-2-enoic Acid* (cf. *ref.* 35).—Magnesium turnings (0.6 g, 25 mmol) were suspended under argon in dry, degassed tetrahydrofuran (THF) (10 ml) contained in a Schlenk tube fitted with a water condenser. To this was added a few drops of a solution of (*Z*)-1-bromopropene (3.025 g, 25 mmol) in THF (10 ml). After a few minutes, reaction set in and the remaining (*Z*)-1-bromopropene was added, with stirring, at a rate sufficient to maintain gentle reflux. The Grignard reagent thus formed was heated to 70 °C for 15 min, after which virtually no magnesium remained. The brown solution was cooled to −196 °C and the condenser was replaced by a glass connection to a 100 ml three-necked flask containing a magnetic stirrer and ^{13}C-labelled barium carbonate (5.0 g, 25.2 mmol), and fitted with a manometer and septum cap. The whole apparatus was evacuated to 0.1 mmHg, the connection to vacuum pump was closed, and the Grignard solution was allowed to warm to −20 °C, thus permitting any gas trapped on freezing to escape. The mixture was refrozen (−196 °C) and the system was re-opened to vacuum until the pressure was again reduced to 0.1 mmHg. The connection to vacuum was closed and the Grignard reagent again allowed to reach −20 °C. ^{13}C-Labelled carbon dioxide was generated by cautiously dropping 98% sulphuric acid onto barium [^{13}C]-carbonate *via* a syringe through the septum cap. Gas was generated at a rate sufficient to maintain a pressure of 10—40 mmHg.

When generation of carbon dioxide was complete, the reaction vessel was once more cooled to freezing to transfer any remaining carbon dioxide to it, and then warmed to −20 °C. After 5 min, water was added to quench the reaction, followed by hydrochloric acid (*ca.* 2 ml; 25%) and the product was extracted into dichloromethane (4 × 10 ml). Drying the organic layer ($MgSO_4$), followed by removal of solvent under reduced pressure, yielded a brown oil which was purified by 'trap-to-bucket' distillation (oil-bath temp. 110 °C). The product (1.23 g, 57% based on $Ba^{13}CO_3$) was [1-^{13}C]but-2-enoic acid (*Z*:*E* 9:1), which crystallised just below room temperature (lit.,[36] *Z* 16 °C), δ (^{1}H; 300 MHz; $CDCl_3$) *Z* 10.9, (br s, 1 H, CO_2H), 6.40 (1 H, m), 5.68 (1 H, m), and 2.15 (3 H, dd, J 1.8 and 7.5 Hz), *E* 7.09 (1 H, m), 5.91 (1 H, m), and 1.94 (3 H, d, J 7.1 Hz); δ (^{13}C; 75.47 MHz; $CDCl_3$) *Z* 172.1 (ddq, $^2J_{CH}$ 14.6, $^3J_{CH}$ 3.9, $^4J_{CH}$ 1.9 Hz).

Preparation of (Z)-[1-^{13}C]*But-2-en-1-ol*.—To a solution of the labelled acid (0.70 g, 8.1 mmol) in Et_2O (5 ml) was added a slight excess of a cold solution of diazomethane in ether. Excess of reagent was removed by addition of a small quantity of AcOH and the solution was dried ($MgSO_4$ and then 4 Å molecular sieves). $LiAlH_4$ (0.31 g, 8.2 mmol) was suspended in dry Et_2O under Ar and heated under reflux for 45 min to aid dissolution. The suspension was cooled to 0 °C and to it was added solid aluminium chloride (1.09 g, 8.2 mmol). A vigorous reaction ensued. The mixture was stirred for 30 min at room temperature, then a solution of methyl [1-^{13}C]but-2-enoate (8.1 mmol) in ether was added dropwise. Fifteen min after addition was complete, water was added **very** cautiously (0.5 ml), followed by aqueous 15% potassium hydroxide (0.5 ml) and a second portion of water (0.5 ml). A grey precipitate appeared over 5 min, after which the ethereal liquid was decanted and washed with brine (12 ml). The brine was back-washed with ether (3 × 5 ml) and the combined organic extracts were dried ($MgSO_4$ followed by 3 Å molecular sieves). Ether was removed by fractional distillation and the residue transferred to a microdistillation apparatus. The product was collected as a colourless liquid (271 mg, 46%), b.p. 120—123 °C (lit.,[37] 121 °C); δ (^{1}H; 300 MHz; $CDCl_3$) *Z* 5.63 (2 H, m), 4.29 (2 H, dd, *J* 4.5, J_{CH} 140 Hz), 1.69 (3 H, d, *J* 6 Hz), and 1.59 (1 H, br s, OH), *E* 4.08 (2 H, d, *J* 4.5, J_{CH} 141 Hz); ratio of labelled to unlabelled material 93:7, ratio of labelled *Z*-isomer to labelled *E*-isomer 94:6; δ (^{13}C; 75.47 MHz; $CDCl_3$) *Z* 58.3 (t, $^1J_{CH}$ 140 Hz), *E* 63.7 (t, $^1J_{CH}$ 141 Hz); *m/z* 73 (M^+).

(Z)-[1-^{13}C]*But-2-enyl Trifluoroacetate*.—Trifluoroacetic anhydride (0.20 ml, 1.37 mmol) was added with caution to a cooled solution of (*Z*)-[1-^{13}C]but-2-en-1-ol (100 mg, 1.37 mmol) in dichloromethane (5 ml) with stirring. The mixture was allowed to warm to room temperature over 2 h, after which the reaction was quenched with water (10 ml). The organic phase was separated, washed with a second portion of water, dried ($MgSO_4$), and distilled using a 'trap-to-bucket' distillation apparatus (oil-bath temp. 100 °C). This gave the title comound as a colourless liquid (180 mg, 78%), δ (^{1}H; 300 MHz; $CDCl_3$) 5.91 (1 H, m), 5.63 (1 H, m), 4.95 (2 H, dd, $^1J_{CH}$ 150, $^2J_{HH}$ 7 Hz), and 1.78 (3 H, d, *J* 7.5 Hz); δ (^{13}C; 75.47 MHz; $CDCl_3$) *Z* 63.7 (t, $^1J_{CH}$ 150 Hz), *E* 64.2 (t, $^1J_{CH}$ 150 Hz); *m/z* 169 (M^+). An unlabelled sample of (*Z*)-but-2-enyl trifluoroacetate was prepared from the alcohol from but-2-yn-1-ol (Lindlar) in similar manner.

η^3-[^{13}C]*But-2-enyl*[(R,R)-4,5-*bis*(*diphenylphosphinomethyl*)-2,2-*dimethyl*-1,3-*dioxolane*-PP′]*platinum Tetrafluoroborate*.—This was prepared from bis(cyclo-octadiene)platinum (0.020 g) and (*E*)-[1-^{13}C]but-2-enyl trifluoroacetate (0.0082 g) in Et_2O at −78 °C with the bisphosphine (0.025 g) added subsequently below 0 °C. Ion-exchange was effected by washing with an excess of aqueous $NaBF_4$. Solvent was removed *in vacuo* and the product characterised by ^{13}C and ^{31}P n.m.r.; δ (^{31}P; 121.49 MHz; CD_2Cl_2) *E* 6.7 (J_{CP} 25 Hz); *E′* 6.34 (J_{CP} 25 Hz); *Z* 0.74 (J_{CP} 29 Hz); *Z′* 3.63 (J_{CP} 29 Hz) (other peaks unaffected); δ (^{13}C of labelled atom; 75.0 MHz; CD_2Cl_2) *E* 65.6 (J_{CPt} 103.1, J_{CP} 25 Hz); *E′* 65.1 (J_{CPt} 103.7, $J_{C,P}$ 25 Hz); *Z* 62.4 (J_{CPt} 94.6, J_{CP} 29 Hz); *Z′* 61.5 (J_{CPt} 93.8, J_{CP} 29. Hz). Allylic alkylation experiments were carried out as described in Table 3.

Preparation and Reactions of η^3-*But-2-enyl*[(R,R)-4,5-*bis*-(*diphenylphosphinomethyl*)-2,2-*dimethyl*-1,3-*dioxolane*-P,P] *palladium Tetrafluoroborate*.—(−)-diop (85 mg, 0.17 mmol) was added to an oxygen-free solution of di-μ-chlorobis(1-methylallylpalladium chloride) (35 mg, 0.075 mmol)[30] in dichloromethane (10 ml). Silver tetrafluoroborate was added with shaking and after 5 min the resulting precipitate of silver chloride was removed by centrifugation. The volume of solvent was reduced to 2 ml; trituration with pentane yielded a white solid which was dried *in vacuo*. The product was thus obtained as a white powder, m.p. 130—132 °C; δ (^{1}H; 300 MHz; CD_2Cl_2) 1.16 and 0.97 (*E*,*E′* CH_3, ddd) (otherwise complex); δ (^{31}P; 121.49 MHz; CD_2Cl_2) *E* 9.0 (d, J_{PP} 44 Hz) and 8.71 (d); *E′* 8.6 (d, J_{PP} 44 Hz) and 7.8 (d) (*Z*-isomers < 10%); *m/z* (field desorption) 646 ($M^+ - BF_4$). Allylic alkylation experiments were performed as follows:

Method A. To a degassed solution of preformed η^3-1-methylallyl[(−)-diop]palladium tetrafluoroborate (20 mg, 0.027 mmol) in CH_2Cl_2 (3 ml) was added but-2-enyl acetate (0.54 mmol), followed by dimethyl sodiomalonate (0.54 mmol), and the mixture was stirred vigorously overnight. Reaction was accompanied by precipitation of palladium metal. The organic products were isolated by filtration through silica gel and removal of solvent under reduced pressure. ^{1}H N.m.r. showed that the ratio of linear to branched-chain products was 1.3:1, and the optical yield in the branched-chain compound was 13%.

Method B. Di-μ-chlorobis[(η^3-1-methylallyl)palladium] (5 mg, 0.013 mmol) and (−)-diop (13 mg, 0.026 mmol) were dissolved in degassed CH_2Cl_2 (3 ml). The colour of the resulting solution was yellow, characteristic of the palladium chloride dimer. To this was added (*E*)-but-2-enyl acetate (65 μl, 0.52 mmol), followed by dimethyl sodiomalonate (80 mg, 0.52 mmol). The mixture was stirred vigorously overnight, during which time it became bright red. The organic products were isolated by filtration as before, and ^{1}H n.m.r. spectroscopy showed that both the product ratio and the optical yield were identical with those obtained using method A.

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