Platinum-Catalysed Allylic Alkylation: Reactivity, Enantioselectivity, and Regioselectivity

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Abstract: The use of platinum complexes as catalysts for allylic substitution has been studied. A variety of different complexes catalyse the reaction, and several substrates have been tested. In the alkylation of mono(alkyl)-substituted allylic acetates, regioselectivity is highly dependent on ligand choice. By using tricyclohexylphosphine as the ligand, almost complete formation of branched products is observed. The development of a highly enantioselective (ca. 80–90% *ee*) reaction that makes use of chiral diphenylphosphinooxazoline ligands (abbreviated as (*S*)-P^N) is also described. The enantioselectivity is highly dependent on the ratio of ligand to platinum (when the ratio ligand/Pt is greater than 1:1, the *ee* drops off dramatically). This is in contrast to palladium and is interpreted in terms of differing coordination chemistry for the two metals ((*S*)-P^N is hemilabile when complexed to platinum) and should be of significance to future systems that utilise heterobidentate ligands. The crystal structures of two isoelectronic platinum and palladium complexes [{(*S*)-P^N}MCl_2] are also described.

Keywords: alkylations · asymmetric catalysis · platinum · regioselectivity

Introduction

Allylic substitution reactions that are catalysed by transition metals are an area of considerable research interest. The palladium-catalysed reaction has been well studied and constitutes an important tool in organic synthesis.[1] The use of other transition metal catalysts is now gaining increasing importance. Nickel catalysts have received considerable attention and allowed the use of Grignard reagents and organoborates as nucleophiles.[2, 3] Tungsten,[4] molybdenum[5] and iridium[6] catalysts are particularly interesting as these give different selectivities to palladium. There are now examples of highly enantioselective reactions catalysed by these metals. Molybdenum catalysts additionally allow the use of electron-rich aromatics as nucleophiles.[7] There are also reports on rhodium-,[8] ruthenium-,[9] copper-[10a] and cobalt-catalysed[10b] allylic substitution. Given the periodic relationship of platinum to palladium, it is surprising that the potential of platinum as a catalyst for this important reaction has not been fully investigated. [$(Ph_3P)_4Pt$] has been shown to catalyse the alkylation of propenyl and butenyl acetates,[11] while [(*R*,*R*-diop)Pt(η^3-C_4H_8)]BF_4 (DIOP = [(2,2-dimethyl-1,3-dioxalane-4,5-diyl)bis(methylene)]bis(diphenylphosphine) catalyses the alkylation of but-2-enyl acetate with low enantioselectivity, but with better regioselectivity than with palladium.[12] Murai and co-workers have also reported that substitution at both vinyl and allylic positions may be possible when 2-chloroallyl acetate is used as the substrate.[13] As far as we know, no other studies have been carried out. We therefore wished to find out if the use of a platinum catalyst could expand the scope of this reaction still further. Herein we describe the first highly enantioselective allylic alkylations catalysed by platinum complexes.[14] In addition, the scope of platinum-catalysed allylic substitutions has been explored by studying a variety of pro-catalysts and substrates.

The platinum catalysts show important differences when compared with palladium, thus providing information about the different coordination chemistry of the two metals.

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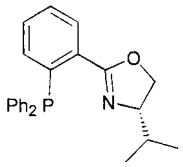
Results and Discussion

As a starting point, we tested the readily available precursors [$(Ph_3P)_4Pt$], [$(PPh_3)_2$Pt-ethylene] and [Pt(dba)$_2$][15] in the

presence of the chiral ligand (4*S*)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline (**1**) (here on abbreviated as (*S*)-P^N). This ligand is one of the most successful ligands for allylic substitution reactions when catalysed by palladium, iridium or tungsten.[4b, 6b, 16]



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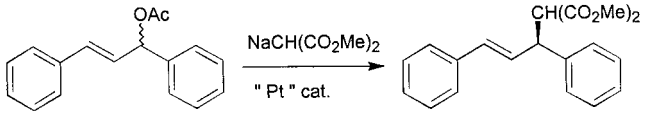
The reaction chosen was the alkylation of diphenylprop-2-enyl acetate (**2**) with dimethyl malonate to produce **3** (Scheme 1). This reaction is often used as a standard to assay the effectiveness of a new ligand or catalyst.



2 3

Scheme 1. Allylic alkylation of diphenylprop-2-enyl acetate.

The first two catalyst systems proceeded readily, giving complete conversion to product after 16 hours at room temperature (Table 1: entries 1, 2). However, enantioselectivity is low. It is our contention that during these reactions the major catalytic species does not contain a chelating phosphino-oxazoline ligand. This is possible as the excess triphenylphosphine present could compete with the nitrogen donor of the oxazoline group for a coordination site on the platinum. It is assumed that (*S*)-P^N needs to chelate in order to achieve high selectivity. The low enantioselectivity is somewhat in contrast to palladium, as Gais and co-workers have successfully used a combination of $[(Ph_3P)_4Pd]$ and ligand **1** as a highly enantioselective catalyst.[17]

Table 1. Allylic alkylation catalysed by readily available precursors in the presence of (*S*)-P^N.[a]

	Catalyst	*T* [°C]	*t* [h]	yield [%]	*ee*[b]
1	$[(Ph_3P)_4Pt]$	20	16	85	8(*S*)
2	$[(Ph_3P)_2Pt\text{-}C_2H_4]$	20	16	90	28(*S*)
3	$[Pt(dba)_2]$	20	24	trace	95(*S*)
4	$[Pt(dba)_2]$[c]	65	44	trace	–

[a] All reactions were carried out in dry CH_2Cl_2 with 5 mol% of catalyst, 3 equiv of dimethyl malonate and BSA as base. [b] Determined by HPLC using Daicel Chiralcel® OD column (Hexane/*i*PrOH 99:1) Abs. Configuration by comparison with known Pd-catalysed products.[16] [c] 10 mol% $[Pt(dba)_2]$ used.

When $[Pt(dba)_2]$ and (*S*)-P^N were used as the catalyst system (Table 1: Entry 3), a highly enantioselective reaction was realised, but only a trace amount of product was obtained. This catalytic system was tested again under many different conditions, but we never found a system that gave good turnover. It has recently been reported that palladium-dba complexes are less active catalysts than the combination of palladium(II) and a reducing agent.[18] In order for allylic alkylation reactions to proceed, the dba has to be replaced by the allylic acetate, and studies on diphosphine-platinum complexes, [(P^P)Pt(dba)], have revealed that dba is not easily displaced, even by phosphine ligands.[19]

After further studies, it became clear that we needed to determine which complex types would catalyse the reaction with maximum efficiency. To this end, the seven catalysts in Table 2 were prepared. The complexes in entries 1–5 and 7 (Table 2) were either prepared by a literature procedure or purchased. $[(dppe)PtC_3H_5]BF_4$ (Entry 6) was prepared as for $[(PPh_3)Pt(C_3H_5)]BF_4$.[20] Each of these compounds was tested under identical conditions in the standard reaction (Scheme 1) shown.

Table 2. Types of platinum complexes that catalyse allylic alkylation at room temperature.

	Catalyst	Conversion (TLC)	Isolated yield[a,b]
1	$[(Ph_3P)_4Pt]$	100	82
2	$[(Ph_3P)_2Pt\text{-ethylene}]$	100	88
3	$[(dppe)_2Pt]$	0	0
4	$[(Ph_3P)_2Pt\text{-stilbene}]$	100	NA[c]
5	$[\{(PhO)_3P\}_4Pt]$	0	0
6	$[(dppe)PtC_3H_5]BF_4$	100	78
7	$[(Ph_3P)_2PtCl_2]$ and $NaBH(OMe)_3$	100	85

[a] Conditions: 5 mol% Pt catalyst, 1.7 equiv $NaCH(CO_2Me)_2$, 16 h at 20 °C in dry THF. [b] After purification by column chromatography. [c] NA = not applicable.

In the platinum-catalysed reaction, it appears that the source of zerovalent platinum is crucial to the high reactivity of the system. The lower reactivity of zerovalent bis(diphosphine) complexes (Entry 3) is not observed in the Pd-catalysed reaction, and it has been suggested that $[(dppe)_2Pd]$ is a more reactive catalyst than $[(Ph_3P)_4Pd]$. Complexes that do not act as catalysts at 20 °C are thought to be less prone to dissociation into a coordinatively unsaturated species. It is therefore plausible that the oxidative addition step of the reaction does not occur at room temperature for these compounds.

Having found out more about the type of procatalyst required, we returned to the enantioselective reaction. In order to avoid contamination from less enantioselective reaction pathways during the reactions, it seemed most sensible to synthesise a procatalyst that contains a single phosphino-oxazoline ligand which chelates to the platinum. This should also fulfil the requirement of having a coordinatively unsaturated species that undergoes the oxidative addition reaction.

As $[(Ph_3P)_2Pt\text{-}trans\text{-stilbene}]$ was a convenient and active catalyst, we attempted to prepare the enantiomerically pure analogue [{(*S*)-P^N}Pt-*trans*-stilbene] (**6**). Enantiomerically pure platinum complexes of *trans*-stilbene are of considerable interest in their own right as models for enantioface recognition of alkenes.[21, 22] Complexes of this type are typically prepared by reduction of the corresponding dichloro complex, $[LPtCl_2]$, in the presence of the alkene. [{(*S*)-P^N}$PtCl_2$] (**4**) was prepared by the route shown in Scheme 2.

The crude product from this reaction contains the two Pt complexes **4** and **5**. The major product, **4**, is readily separated

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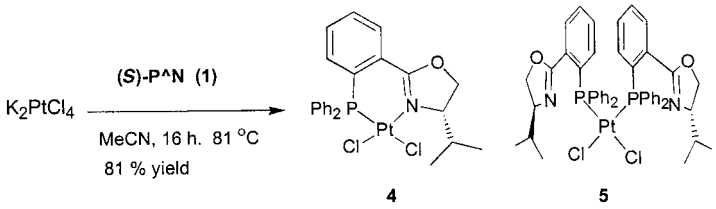
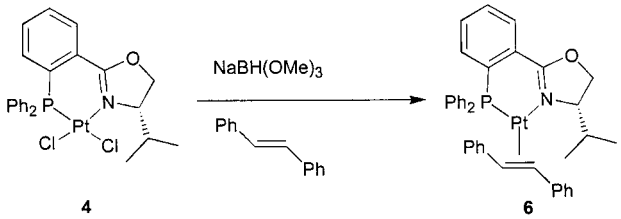


4 5

Scheme 2. Synthesis of [{(*S*)-P^N}$PtCl_2$] (**4**).

by column chromatography and can be obtained in high yield under the conditions described in the Experimental Section. The minor product was assigned as **5** by ^{31}P and ^{195}Pt NMR spectroscopy. The ^{31}P NMR spectrum shows the complex to have two identical phosphorus atoms in *trans* position to the chloride. ^{195}Pt NMR spectroscopy confirms that there are two phosphines bound to the platinum.

Reduction of **4** in the presence of stilbene was carried out by using $NaBH(OMe)_3$ as the reducing agent, giving an orange-brown solid, which is suggested to contain the desired product **6** (Scheme 3). However, the complex was impure, and



4 6

Scheme 3. Attempted synthesis of [{(*S*)-P^N}Pt-stilbene].

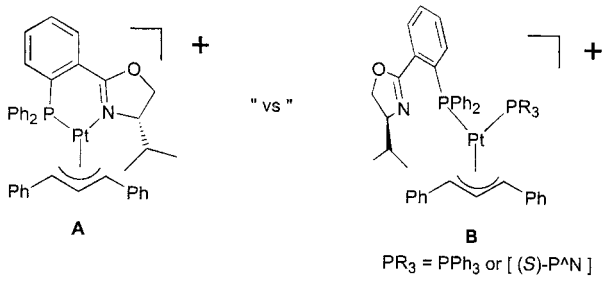
all attempts at recrystallisation resulted in decomposition. Importantly, the use of impure **6** as the allylic substitution catalyst gave a moderate yield of enantiomerically enriched product **3**, providing that the reaction was carried out at reflux temperature (42% yield; 75% *ee*; 72 h, 65 °C). It is noteworthy that complexes of the P,N bidentate ligand make less active catalysts than those derived from triphenylphosphine. A combination of [{(*S*)-P^N}$PtCl_2$] and $NaBH(OMe)_3$ was also tested as catalyst (Table 3). Good yields and enantioselectivities were observed when this system was used at 65 °C (entries 3 and 4).

Table 3. Enantioselective allylic alkylation of **2** using 5 mol% of complex **4** and 10 mol% $NaBH(OMe)_3$ co-catalyst.

	Additive	*T* [°C]	*t* [h]	Conversion[b] (yield)	*ee*[b]
1	None	20	20	–	–
2[c]	None	65	90	48	77 (*S*)
3	None	65	44	65 (–)	77 (*S*)
4	**5% ligand (1)**	**65**	**35**	**100 (93)**	**83 (*S*)**
5	10% ligand (**1**)	65	44	100 (–)	61 (*S*)
6	5% PPh_3	20	16	100 (91)	2 (*S*)
7	stilbene	65	24	43 (–)	49 (*S*)
8[d]	none	65	50	25 (–)	48 (*S*)

[a] All reactions carried out in THF, with 1.7 equiv $NaCH(CO_2Me)_2$ as nucleophile. [b] Determined by HPLC with a Daicel Chiralcel® OD column (Hexane/*i*PrOH 99:1) Abs. Configuration by comparison with known Pd-catalysed products.[16] [c] Reaction carried out in acetonitrile. [d] Allylic acetate added prior to $NaBH(OMe)_3$.

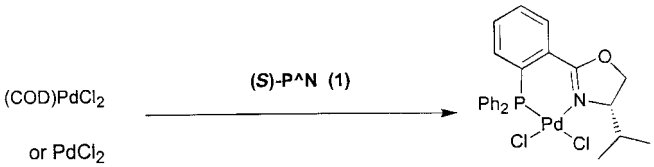
Whereas **4**/$NaBH(OMe)_3$ requires 44 hours at 65 °C to obtain high conversion, **4**/$NaBH(OMe)_3$/PPh_3 gives a high yield (of racemic material) after 16 hours at 20 °C. The presence of triphenylphosphine, far from inhibiting the reaction, speeds it up dramatically. In addition, running the reaction with 10 mol% of excess ligand (Entry 5) reduces the enantioselectivity considerably. It seems that when excess ligands are present, the reaction proceeds via intermediate **B** and that **B** can be more reactive than intermediate **A**.



A B

$PR_3 = PPh_3$ or [(*S*)-P^N]

In order to make a strict comparison with the palladium-catalysed reaction, palladium analogue **7** was also prepared, as shown in Scheme 4, and tested as a catalyst. If the palladium catalyst is used with an excess of ligand, the enantiomeric excess goes up slightly; this is in complete



7

Scheme 4. Synthesis of the palladium complex, [{(*S*)-P^N}$PdCl_2$].

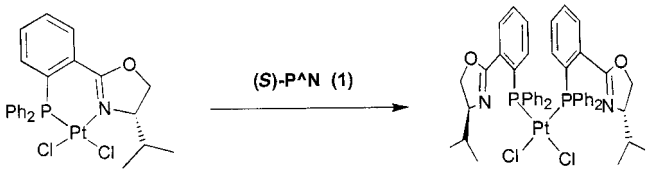
contrast to platinum (Table 4). If the palladium complex is reduced in the presence of triphenylphosphine, enantiomerically enriched products are still formed. The reactivity of the palladium catalyst is significantly reduced when it is used with excess ligand; this is also in complete contrast to platinum.

We have proposed that the more variable enantiomeric excess associated with Pt is due to the ligand being hemilabile when complexed to platinum. To support this, we added excess ligand to the complexes **4** and **7** and characterised the resultant products by ^{31}P and ^{1}H NMR spectrsocopy. In the case of platinum, **4** is instantly converted into **5** on addition of one equivalent of ligand (Scheme 5). Even after extended

Table 4. Enantioselective allylic alkylation of **2** using 5 mol% of palladium complex **7** and 10 mol% $NaBH(OMe)_3$ co-catalyst.

	Additive	*T* [°C]	*t* [h]	Conversion[b]	*ee*[b]
1	none	20	20	100	91 (*S*)
2	5% (*S*)PN	20	20	38	93 (*S*)
3	5% PPh_3	20	20	58	56 (*S*)

[a] All reactons carried out in THF, with 1.7 equiv $NaCH(CO_2Me)_2$ as nucleophile. [b] Determined by HPLC using Daicel Chiralcel® OD column (Hexane/*i*PrOH 99:1) Abs. Configuration by comparison with known Pd-catalysed products.[16]



4 5

Scheme 5. (*S*)-P^N is hemilabile when complexed to platinum as evidenced by the synthesis of **5**.

reaction times, the palladium complex gives a mixture of free ligand, unchanged starting material (**7**) and a new complex, presumably the palladium analogue of **5**, as it shows one peak in the ^{31}P NMR spectrum. Thus, compounds **4** and **7** show different behaviour in the presence of excess ligand.

Coordination chemistry of the type described here has the potential to occur in any metal complex that contains heterobidentate ligands and has considerable effects on the catalytic properties. Very recently, another research group has observed similar chemistry for another set of heterobidentate ligands coordinated to palladium.[23] Measurement of enantiomeric excess as a function of metal:ligand ratio should be an essential experiment in the testing of catalysts derived from chiral heterobidentate ligands.

Crystal structures of [{(*S*)-P^N}PtCl$_2$] (4) and [{(*S*)-P^N}PdCl$_2$] (7): In order to fully establish the conformation of the two catalysts, the crystal structures of [{(*S*)-P^N}PtCl$_2$] (**4**) and [{(*S*)-P^N}PdCl$_2$] (**7**) were determined by X-ray diffraction. ORTEX[36] views of the structures of **4** and **7** are shown in Figures 1 and 2, respectively. Selected geometric data are given in Tables 5 and 6, respectively.

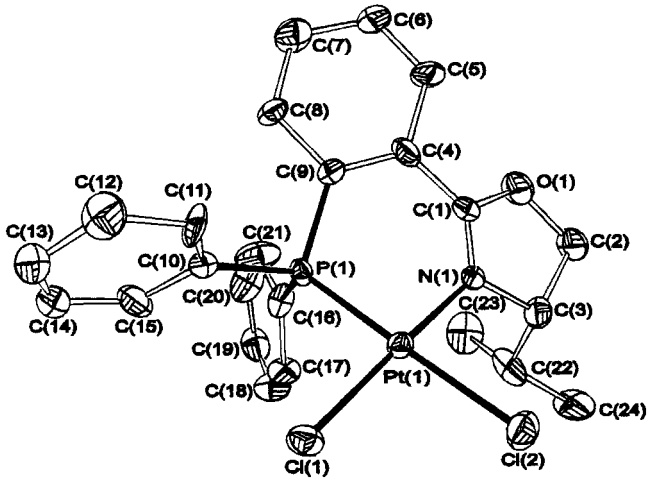


Figure 1. Asymmetric unit of **4** showing labelling scheme used. Thermal ellipsoids are drawn at 30% probability level.

Table 5. Selected bond lengths [Å] and angles [°]for [{(*S*)-P^N}PtCl$_2$] (**4**).

Pt(1)−N(1)	2.01(2)	N(1)-Pt(1)-P(1)	90.0(5)
Pt(1)−P(1)	2.192(5)	N(1)-Pt(1)-Cl(1)	176.1(5)
Pt(1)−Cl(1)	2.284(6)	P(1)-Pt(1)-Cl(1)	90.8(2)
Pt(1)−Cl(2)	2.363(6)	N(1)-Pt(1)-Cl(2)	90.2(5)
C(1)−N(1)	1.29(3)	P(1)-Pt(1)-Cl(2)	176.6(2)
		Cl(1)-Pt(1)-Cl(2)	89.2(2)

Both structures show that the ligand is bidentate and that it forms a six-membered, puckered chelate ring with the metal. All three carbon atoms in this ring reside above the plane of the complex with respect to the isopropyl group [C(23), C(22), C(24) for **4**].

This conformation, common to other metal complexes of this ligand, forces the diphenylphosphine group to adopt an edge-on/face-on array. The overall shape and coordination environment surrounding the metal centres is similar within both crystal structures, despite the fact that the asymmetric unit in **7** incorporates one molecule of recrystallisation solvent (CH_2Cl_2). The metal–phosphorus bonds are approximately

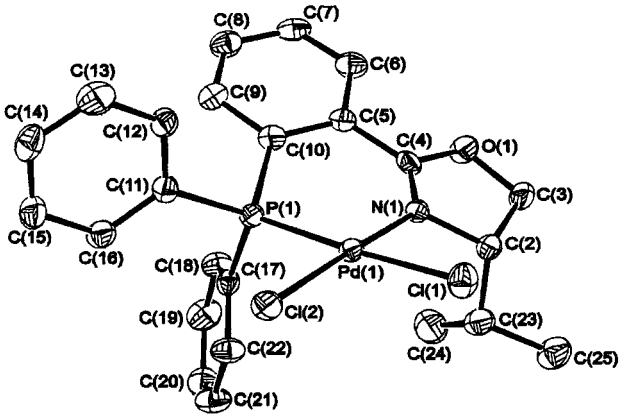


Figure 2. Asymmetric unit of **7** showing labelling scheme used. Thermal ellipsoids are drawn at 30% probability level.

Table 6. Selected bond lengths [Å] and angles [°]for [{(*S*)-P^N}PdCl$_2$] (**7**).

Pd(1)−N(1)	2.034(8)	N(1)-Pd(1)-P(1)	88.6(2)
Pd(1)−P(1)	2.217(3)	N(1)-Pd(1)-Cl(2)	174.6(2)
Pd(1)−Cl(2)	2.294(3)	P(1)-Pd(1)-Cl(2)	89.16(10)
Pd(1)−Cl(1)	2.379(3)	N(1)-Pd(1)-Cl(1)	92.4(2)
C(4)−N(1)	1.254 (13)	P(1)-Pd(1)-Cl(1)	175.17(12)
		Cl(2)-Pd(1)-Cl(1)	90.26(10)

0.2 Å longer than the metal–nitrogen bond lengths. The C=N bond, which is 1.26 Å in the crystal structure of the free ligand,[25] is 1.254(13) Å for the Pd complex and 1.29(3) Å for [{(*S*)-P^N}PtCl$_2$]. In both complexes, the greater *trans* influence of the phosphine relative to the oxazoline is reflected in the significantly differing M−Cl bond lengths.

The Pt−Cl bond *trans* to phosphorus is 2.363(6) Å, whereas the corresponding Pd−Cl bond is 2.379(3) Å. As such, these metal–chlorine bond lengths are, as expected, 0.1 Å longer than the M−Cl bond lengths *trans* to the nitrogen atom.

We also looked at the use of readily available [(η^3-C_3H_5)PtCl]$_4$ in the presence of (*S*)-P^N as a catalyst for this reaction (Table 7). The highest *ee* (90%) was observed at room temperature (when conversion was low). When the reaction was carried out in THF at reflux, high conversion into product could be observed (74% yield: 84% *ee*). The enantioselectivity of the product is constant throughout the reaction. The *ee* of the starting material gradually increases as the reaction progresses and reaches 72% at 81% conversion. When the metal to ligand ratio is 1:2, the enantiomeric excess of the product formed drops to 57%.

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Table 7. Allylic alkylation of **2** with 1.25 mol % $[(C_3H_5)PtCl]_4$ and (*S*)-P^N as catalyst.[a]

	Ligand **1** added [%]	*T* [°C]	*t* [h]	Conversion[b] (yield)	*ee*[b]
1	5%	20	72	25 (–)	90(*S*)
2	5%	65	48	81 (74)	84(*S*)
3	10%	20	24	32 (–)	86(*S*)
4	10%	65	44	100 (90)	57(*S*)
5	5%[c]	65	48	– (37)	17(*S*)

[a] All reactions carried out in THF, with 1.7 equiv $NaCH(CO_2Me)_2$ as nucleophile. [b] Determined by HPLC using Daicel Chiralcel® OD column (Hexane/*i*PrOH 99:1) Abs. Configuration by comparison with known Pd-catalysed products.[16] [c] Prior to reaction, $AgBF_4$ was added to solution of $[(C_3H_5)PtCl]_4$ and **1** (AgCl was filtered off).

The palladium-catalysed reaction gives products of 97% *ee* under identical conditions (Pd:**1** = 1:2). If $AgBF_4$ is added to the mixture of $[(\eta^3\text{-}C_3H_5)PtCl]_4$ and (*S*)-P^N prior to the reaction, the *ee* is diminished considerably. This effect has also been observed by other workers using Pd catalysts.[23]

Given that we had observed differing selectivity to palladium in these reactions, we investigated if any nonlinear effects were present in either reaction. The plot of ligand *ee* against product *ee* in Figure 3 shows these results. The

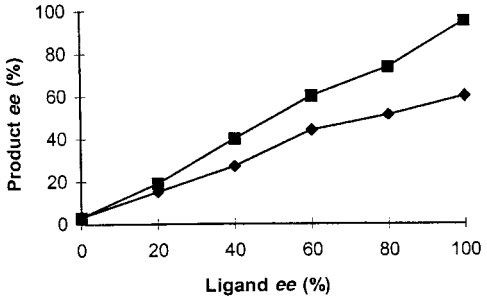
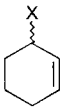


Figure 3. A plot of ligand *ee* against product *ee* for both palladium (■) and platinum (◆). Ligand to metal ratio is 2:1.

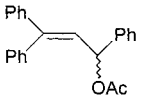
reactions were run with ligands of known *ee* (prepared by mixing accurately weighed samples of both enantiomers of ligand). The *ee* of the final product is shown against ligand *ee*. Both reactions were run with metal:ligand ratios of 1:2 (the platinum-catalysed reaction shows a marked decrease in *ee* under these conditions). There do not appear to be any significant nonlinear effects in either reaction.

We have also tested a number of other substrates. Whereas cyclohexenyl acetate (**8**) reacts at room temperature to give the desired product **9** with no problems, the more hindered 1,1,3-triphenylprop-2-enyl acetate (**10**) does not react even after several days at 65 °C.



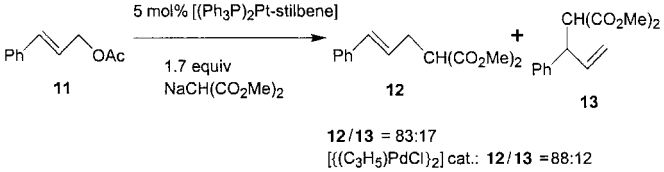
8: X = OAc

9: X = $CH(CO_2Me)_2$

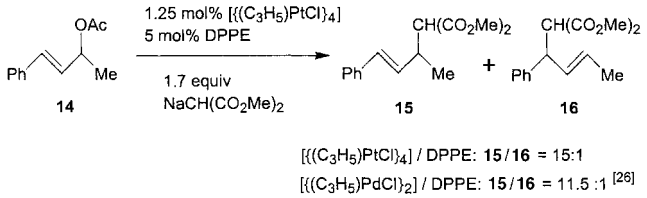


10

Cinnamyl acetate (**11**) gave a high yield of the two regioisomers **12** and **13** with a similar branched:linear preference to palladium (Scheme 6). When the unsymmetrically substituted acetate **14** is alkylated using $[(C_3H_5)PtCl]_4$ as the catalyst, the two regioisomers **15** and **16** are formed in a ratio of 15:1. The corresponding palladium catalyst system gives similar regioselectivities (Scheme 7).[26]

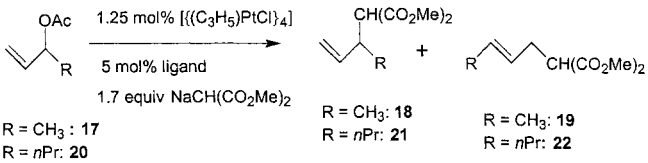


Scheme 6. Pt-catalysed allylic alkylation of cinnamyl acetate.



Scheme 7. Pt-catalysed allylic alkylation of acetate **14**.

We have also studied the butenyl acetates **17** as substrates (Scheme 8). Kurosawa[11] and Brown et al.[12] both observed better regioselectivities towards branched products when Pt is used as the catalyst for this reaction (when using "DIOP" as ligand: Pd catalyst, B/L = 1.3:1; Pt catalyst, B/L = 5:1). Generally Pd catalysts give poor regioselectivities in this reaction, although exceptions have been described.[27]



Scheme 8. Allylic alkylation of mono(alkyl)-substituted allylic acetates.

We tested the platinum catalysts shown in Table 8. When the platinum catalysts contain either PPh_3 or (*S*)-P^N as ligand, regioselectivity is poor, although there is a greater proportion of branched products when compared with palladium. Of particular interest is Entry 5: the use of bulky,

Table 8. Regioselectivity in the alkylation of but-2-enyl acetate (**17**) using Pt and Pd catalysts.

	Catalyst[a]	**18**/**19**[b]
1	$[(Ph_3P)_2Pt\text{-stilbene}]$	2.1:1
2	$[Pd(\eta^3C_4H_7)Cl(PPh_3)_2]$[c]	1:2.0
3	$[(S)\text{-P^N}]/[\{(C_3H_5)PtCl\}_4]$	1.0:1
4	$[(S)\text{-P^N}]/[\{(C_3H_5)PdCl\}_2]$	1:1.9
5	$Cy_3P/[\{(C_3H_5)PtCl\}_4]$	15:1
6	$Cy_3P/[\{(C_3H_5)PdCl\}_2]$	11:1

[a] Reactions were run at 20 °C in THF with 1.5 equiv $NaCH(CO_2Me)_2$ as nucleophile except Entry 3 (THF, 65 °C). In all cases conversion was 100%. The *E*/*Z* ratio was not accurately determined, but in all cases the linear products were almost predominantly of *E* configuration. [b] Determined by GC and confirmed by ^1H NMR spectroscopy [c] Ref. [11].

electron-rich tricyclohexylphosphine as ligand gives almost exclusive formation of branched products (**18**/**19** = 15:1).

The same trends are observed when using hexenyl acetate (**20**) (Table 9). In this case, however, there is a greater tendency to form linear products and only the platinum/tricyclohexylphosphine catalyst gives good regioselectivity (ca. 10:1) towards branched product **21**. The use of (*S*)-P^N as ligand gives excellent regioselectivity towards the linear product.

Kurosawa proposed that Pt gives more branched products

Table 9. Regioselectivity in the alkylation of hex-2-enyl acetate (**20**) using Pt and Pd catalysts.

	Catalyst[a]	**21**/**22**[b]	*E*/*Z* for **22**[b]
1	$[(Ph_3P)_2Pt\text{-stilbene}]$	1:1.8	10:1
2	$Ph_3P/[(C_3H_5)PdCl]_2$	1:4.1	10:1
3	$[(S)\text{-P^N}]/[\{(C_3H_5)PtCl\}_4]$	1:7.2	6:1
4	$[(S)\text{-P^N}]/[\{(C_3H_5)PdCl\}_2]$	1:13.1	9:1
5	$Cy_3P/[\{(C_3H_5)PtCl\}_4]$	9.8:1	10:1
6	$Cy_3P/[\{(C_3H_5)PdCl\}_2]$	3.1:1	6:1

[a] Reactions were run in THF at 20 °C with 1.5 equiv. of $NaCH(CO_2Me)_2$ as nucleophile (except Entry 3: THF, 65 °C). In all cases conversion was 100 %. [b] Determined by GC and confirmed by ^{1}H NMR spectroscopy.

than Pd as a result of the increased stability of the initial zero-valent platinum alkene product (Pt is a stronger π-donor than Pd). The branched products contain a more electron-poor double bond and are therefore favoured for platinum. Our results fit this hypothesis as the $(Cy_3P)_2Pt$ fragment is likely to be a very strong π-donor. When palladium is used in conjuction with this ligand, we also observed a high proportion of branched products. It may, therefore, be possible to control regioselectivity (towards formation of the most electron-poor double bond) by using highly basic phosphine ligands. Alternatively, the structure of Cy_3P may also play a part in determining regioselectivity. These particularly striking ligand effects will be studied in more detail in due course.

Conclusions

We have shown that a number of sources of zero-valent platinum will catalyse allylic alkylation reactions and we have utilised these to develop an asymmetric reaction using phosphino-oxazoline ligand **1** to control enantioselectivity. A selection of other substrates have also been studied and it has been found that platinum catalysts generally give somewhat better regioselectivity than palladium towards products that contain a more electron-poor double bond. When Cy_3P is used as ligand, highly regioselective alkylation of mono-(alkyl)-substituted allylic acetates is possible.

Experimental section

General: Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere, while all work up and purification procedures were carried out in air. Solvents were of HPLC grade and were used as received unless stated otherwise. Where a solvent is described as dry, it was freshly distilled from an appropriate drying agent. Elemental analyses were conducted on a Carbo Erba Stametazione EA1506 Analyser. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a Jeol GX400 instrument. Crystal structures were obtained with a CAD 4 automatic four circle diffractometer. $[(Ph_3P)_2Pt\text{-ethylene}]$, K_2PtCl_4, $PdCl_2$, $[\{(C_3H_5)PdCl\}_2]$, PPh_3, $(PhO)_3P$, Cy_3P, dimethyl malonate, and $[(cod)PdCl_2]$ were purchased from Aldrich Chemical Company and used without any purification. $[(Ph_3P)_4Pt]$,[28] $[(Ph_3P)_2Pt\text{-}trans\text{-stilbene}]$,[29] $[\{(PhO)_3P\}_4Pt]$,[28] $[(dppe)_2Pt]$,[30] $[\{(C_3H_5)PtCl\}_4]$,[31] (4*S*)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline,[16] $[Pt(dba)_2]$[15] and all allylic acetates[32] were prepared as described in the literature.

$[\{(S)\text{-P^N}\}PtCl_2]$ (4): A 50 mL round-bottom flask, charged with potassium tetrachloroplatinate (0.300 g, 0.723 mmol), (4*S*)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline (0.268 g, 0.716 mmol) and a magnetic stirring bead, was fitted with a reflux condensor with a rubber septum, evacuated and flushed with nitrogen. Dry acetonitrile (15 ml) was then added through a syringe and the suspension was refluxed for 6 h, by which time the potassium tetrachloroplatinate has disappeared. The reaction was stirred overnight. The solvent was then reduced to 1 mL in vacuo and diethyl ether added to yield a pale yellow air-stable precipitate containing compounds **4** and **5**. ^{31}P NMR (400 MHz, $CDCl_3$): $\delta = 5.8$ ($^1J_{P,Pt} = 3410$ Hz), 0.51 ($^1J_{P,Pt} = 3722$ Hz); ^{195}Pt NMR (400 MHz, $CDCl_3$): $\delta = -4200$ (br t, $^1J_{Pt,P} = 3410 - 3425$ Hz), -3550 (br dm, $^1J_{Pt,P} = 3660 - 3700$ Hz). These two compounds were separated by flash chromatography (CH_2Cl_2/MeOH 99:1). The desired product was eluted first in 81 % yield. Recrystallisation from chloroform/toluene gave yellow prisms suitable for X-ray diffraction. ^{31}P NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 0.51$ ($^1J_{P,Pt} = 3722$ Hz); ^{195}Pt NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = -3550$ (br dm, $^1J_{Pt,P} \approx 3660$ Hz); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.13$ (d, $^3J_{H,H} = 7$ Hz, 3H; C*H*$_3$), 0.83 (d, $^3J_{H,H} = 7$ Hz, 3H; C*H*$_3$), 2.72 – 2.78 (m, 1H; C*H*$(CH_3)_2$), 4.46 – 4.51 (m, 2H; C*H*$_2$O), 5.78 (m, 1H; C*H*N), 7.00 (dd, $^3J_{H,H} = 10.1$, 7.9 Hz, 1H; ArH), 7.38 – 7.71 (m, 12H; ArH), 8.12 (m, 1H; ArH); IR (Nujol): $\tilde{\nu} = 1622$, 1103, 954, 929, 752 cm^{-1}; $C_{24}Cl_2H_{24}NOPPt$ (639.42): calcd C 45.05, H 3.75, N 2.19; found C 44.7, H 3.69, N 2.13.

$[\{(S)\text{-P^N}\}PdCl_2]$ (7): CH_2Cl_2 was added to an evacuated one-necked round-bottom flask containing $PdCl_2$ (0.057 g, 0.318 mmol) and ligand **1** (0.113 g, 0.303 mmol). After being flushed with nitrogen, the reaction mixture was refluxed for 40 h. The brown reaction mixture was then filtered, and the resultant yellow precipitate was washed with Et_2O and collected on filter paper. It was then suspended in CH_2Cl_2, filtered and dried to yield the pure product. The compound could also be conveniently prepared from $[(cod)PdCl_2]$ by stirring with the ligand in CH_2Cl_2 at room temperature. Crystals of the CH_2Cl_2 solvate complex suitable for X-ray diffraction experiments were grown from CH_2Cl_2. Yield: approximately 70 %; ^{31}P NMR (161.7 MHz, $CDCl_3$, 20 °C): $\delta = 26.49$; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 0.01$ (d, $^3J_{H,H} = 6.78$ Hz, 3H; C*H*$_3$), 0.83 (d, $^3J_{H,H} = 7.15$ Hz, 3H; C*H*$_3$), 2.66, (m, 1H; C*H*$(CH_3)_2$), 4.37 (q, 1H; C*H*$_2$O), 4.49 (t, 1H; C*H*$_2$O), 5.58 (m, 1H; C*H*N), 6.93 – 8.14 (m, 14H; ArH); IR (Nujol): $\tilde{\nu} = 1626$, 1570, 1247, 1101 cm^{-1}; FAB MS (negative ion mode): *m*/*z*: 548.9 $[M]^+$; $C_{25}Cl_4H_{26}NOPPd$ (635.69): calcd C 47.2, H 4.09, N 2.20; found C 47.2, H 4.08, N 2.16.

Attempted preparation of $[\{(S)\text{-P^N}\}Pt\text{-stilbene}]$ (6): All procedures for this synthesis were carried out in the absence of air. A solution of $NaBH(OMe)_3$ (0.156 g, 1.219 mmol) in THF (4 mL) was added to a stirred solution of $[(S)\text{-P^N}]PtCl_2$ (0.300 g, 0.469 mmol) and stilbene (0.085 g, 0.469 mmol) in dry THF (9 mL) and stirred for 1 hour. The THF was then removed in vacuo, and the resultant black residue redissolved in toluene and filtered through a pad of Celite. The Celite was washed with toluene. The solvent was removed and the residue recrystallised by cooling a CH_2Cl_2/hexane solution to −70 °C to give an orange-brown powder in low to moderate yield. This impure material catalysed allylic alkylation enantioselectively. ^{31}P NMR (161.7 MHz, $CDCl_3$, 20 °C): $\delta = 9.76$ ($^3J = 4453$ Hz), peaks also at 29.56 and 0.62; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 0.13$ (d, $^3J_{H,H} = 7.02$ Hz), 0.81 (d, $^3J_{H,H} = 7.02$ Hz), 2.55 (m), 3.8 (m), 4.3 – 4.4 (m with satellites $^2J = 104$ Hz), 5.35 (m), 6.93 – 8.14 (m, ArH); IR (Nujol): $\tilde{\nu} = 1732$, 1597, 1300, 1154 cm^{-1}; FAB MS (positive ion mode): *m*/*z* (%): 659 (70), 568 (55) $[M - \text{stilbene}]^+$, 180 (100) [stilbene].

General procedure for allylic substitution reactions that use zero-valent platinum catalysts: A solution of the allylic acetate in dry solvent was added to an evacuated round-bottom flask containing 5 mol % catalyst and a

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stirring bead (and the chiral ligand, if appropriate). The flask was then flushed with nitrogen. A solution of $NaCH(CO_2Me)_2$ (1.7 equiv.) was added and the reaction mixture was stirred at the desired temperature for the given time. The reaction mixture was then diluted with CH_2Cl_2 and washed with NH_4Cl. The aqueous layer was washed with more CH_2Cl_2, and the organic extracts were combined and washed with water and brine. Column chromatography using 20% diethyl ether/petroleum ether as eluent gave the desired product.

Typical procedure for allylic alkylation using [{(*S*)-P^N}MCl_2]/NaB-H(OMe)$_3$: [{(*S*)-P^N}$PtCl_2$] (10 mg, 1.56×10^{-5} mol), (*S*)-P^N, if applicable, and dry THF (1.2 mL) were added to an evacuated round-bottom flask that contained a stirring bead. The flask was then flushed with nitrogen. After the reaction mixture was stirred for a few minutes, a solution of $NaBH(OMe)_3$ (4.5 mg, 3.2×10^{-5} mol) in THF (1.2 mL) was added. After 1–2 minutes of stirring, a THF solution of *rac*-(*E*)-1,3-diphenyl-prop-2-enyl acetate (80 mg, 3.18×10^{-4} mol) was added. A THF solution of sodium dimethyl malonate (83 mg, 5.39×10^{-4} mol) was then added, and the reaction was heated to the desired temperature for the appropriate time. The reaction was monitored by removing 0.1 mL of reaction mixture, filtering through a pipette containing cotton wool and a pad of silica (diethyl ether as eluent), removing solvent and analysing a solution of the resultant oil by HPLC (Chiracel OD® hexanes/*i*PrOH:99/1). It was possible to determine conversion and *ee* of products and starting material by using this method. When the reaction was finished, it was diluted with CH_2Cl_2 (30 mL) and washed with ammonium chloride. The aqueous layer was washed with CH_2Cl_2 and the combined organic extracts were washed with water (50 mL) and brine (40 mL), and dried ($MgSO_4$), and the solvent was removed. Pure **3** was obtained after column chromatography (20% diethyl ether/petroleum ether). It was identified by comparison of its ^{1}H and ^{13}C NMR spectroscopic, TLC and HPLC data with that of an authentic sample.[16]

Typical procedure for allylic alkylation using [{(C_3H_5)PtCl}$_4$] as catalyst: [(C_3H_5)PtCl]$_4$, (4.0 mg, 3.73×10^{-6} mol), (*S*)-P^N (5.3 mg, 1.43×10^{-5} mol) and dry THF (1.5 mL) were added to an evacuated round-bottom flask that contained a stirring bead. The flask was then flushed with nitrogen. After the reaction mixture was stirred for a few minutes, a THF solution of *rac*-(*E*)-1,3-diphenylprop-2-enyl acetate (80 mg, 3.18×10^{-4} mol in THF (1.0 mL) was added, followed by addition of the sodium dimethylmalonate solution (78 mg, 5.3×10^{-4} mol). The reaction was then stirred at the desired temperature and worked up and purified as before.

Dimethyl-1,3-diphenyl-prop-2-enyl malonate (3): ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C, $CDCl_3$): $\delta = 3.53$ (s, 3H; CO_2CH_3), 3.72 (s, 3H; CO_2CH_3), 3.97 (d, $^3J_{H,H} = 11$ Hz, 1H; $HC(CO_2Me)_2$), 4.29 (dd, $^3J_{H,H} = 11$, 8.4 Hz, 1H; C*H*CH), 6.34 (dd, $^3J_{H,H} = 15.8$, 8.3 Hz, 1H; =C*H*), 6.50 (d, $^3J_{H,H} = 15.9$ Hz, 1H; =C*H*), 7.20–7.35 (m, 10H; Ar*H*); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta =$ 49.06 (CH), 52.25 (CH_3), 52.43 (CH_3), 57.47 (CH), 126.22, 127.02, 127.42, 127.73, 128.57, 128.99 (ArC= and C=C), 131.67 (ArC), 136.68 (ArC), 167.61, (C=O), 168.03 (C=O); IR(thin film): $\tilde{\nu} = 1730$, 1598, 1493, 1248, 1218, 1156 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 324 (10), 205 (80), 193 (60), 149 (80), 101 (100); $C_{20}H_{20}O_4$: calcd 324.1361; found 324.1362.

Dimethyl-cyclohex-2-enyl malonate (9): ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): $\delta = 1.4–1.9$ (m, 4H; CH_2CH_2), 2.00 (m, 2H; CH_2), 2.92 (m, 1H; C*H*CH), 3.30 (d, $^3J_{H,H} = 9.5$ Hz, 1H; *H*C(CO$_2$Me)$_2$), 3.74 (s, 3H; CO_2Me), 3.75 (s, 3H; CO_2Me), 5.54 (m, 1H; =C*H*), 5.79, (m, 1H; C*H*=); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 20.77$ (CH_2), 24.83 (CH_2), 26.52 (CH_2), 35.29 (CH), 52.27 (CH), 127.23 (=CH), 129.55 (HC=), 168.74, (C=O), 168.79 (C=O); IR (thin film): $\tilde{\nu} = 2932$, 1736, 1649, 1435, 1332, 1267, 1195, 1160 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 212 (10) $[M]^+$, 152 (100), 93 (25), 81 (50); $C_{11}H_{16}O_4$: calcd 212.1048; found 212.1044.

Dimethyl-1-[(*E*)-styrl]ethyl malonate (15): ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): $\delta = 1.10$ (d, $^3J_{H,H} = 6.8$ Hz, 3H; CHCH_3), 3.0–3.1 (m, 1H; C*H*CH$_3$), 3.23 (d, $^3J_{H,H} = 7.9$ Hz, 1H; CHC*H*), 3.58 (s, 1H; CO_2Me), 3.61 (s, 1H; CO_2Me), 6.04, (dd, $^3J_{H,H} = 8.4$, 15.8 Hz, 1H; =C*H*), 6.36 (d, $^3J_{H,H} =$ 15.9 Hz, 1H; =C*H*), 7.1 (m, 5H; Ar*H*); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 18.37$ (CH_3), 37.62 (CH), 52.22 (CH_3), 52.30 (CH_3), 57.70 (CH), 126.16, 127.28, 127.65, 128.39, 130.71, 131.09 (ArCH, =CH), 137.0 (ArC–), 168.50 (C=O); IR (thin film): $\tilde{\nu} = 3026$, 2953, 1738, 1598, 1578, 1494, 1435, 1246, 1194, 1158, 1023, 969 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 262 (10) $[M]^+$, 202 (20), 143 (55), 131 (100); $C_{15}H_{18}O_4$: calcd 262.1205; found 262.1201.

(*E*)-Dimethyl-3-phenyl-prop-2-enyl malonate (12): ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C, $CDCl_3$): $\delta = 2.80$ (dt (app), $^3J_{H,H} =$ 7.3, 1.2 Hz, 2H; =CHCH_2), 3.55 (t, $^3J_{H,H} =$ 7.3 Hz, 1H; CH_2C*H*), 3.75 (s, 3H; CO_2Me), 3.76 (s, 3H; CO_2Me), 6.1 (dt, $^3J_{H,H} =$ 7.3, 15.6 Hz, 1H; =C*H*), 6.47 (d, $^3J_{H,H} = 15.6$ Hz, 1H; =C*H*), 7.2–74 (m, 5H; Ar*H*); IR (thin film): $\tilde{\nu} = 1745$, 1682, 1149, 1047, 1006, 964 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 248 (25), 188 (35), 129 (80), 117 (55); $C_{14}H_{16}O_4$: calcd 248.1049; found 248.1046.

Dimethyl(1-methylprop-2-enyl) malonate (18): ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): $\delta = 1.03$ (d, $^3J_{H,H} = 6.8$ Hz, 3H; CHCH_3), 2.89 (hex (app) 1H; C*H*Me), 3.24 (d, $^3J_{H,H} = 9$ Hz, 1H; C*H*CH), 3.66 (s, 3H; CO_2Me), 3.67 (s, 3H; CO_2Me), 4.99 (ddm, 2H; =CH_2), 5.70 (ddd, 1H; =C*H*); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 18.38$ (CH_3), 38.51 (CH), 52.69 (CH_3), 52.78 (CH_3), 57.89 (CH), 115.76 (CH_2), 139.80 (CH), 168.75 (CO_2Me), 168.81 (CO_2Me); IR (thin film): $\tilde{\nu} = 2956$, 1737, 1644, 1566, 1436, 1268, 1199, 1154 cm^{-1}.

(*E*)-Dimethylbut-2-enyl malonate (19): ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): $\delta = 1.56$ (dd, 3H; CH_3CH), 2.50 (dd, $^3J_{H,H} = 6.7$, 7.5 Hz, 2H; CHCH_2), 3.34 (t, $^3J_{H,H} = 7.7$ Hz, 1H; CH_2C*H*), 3.64 (s, 6H; CO_2Me), 5.30 (m, 1H; =C*H*), 5.49 (m, 1H; =C*H*); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 30.11$ (CH_3), 32.31 (CH), 38.51 (CH), 52.32 (CH_3), 126.47 (=CH), 128.76 (=CH), 169.57 (CO_2Me).

Dimethyl(1-propylprop-2-enyl) malonate (21): ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): $\delta = 0.80$ (t, $^3J_{H,H} = 7.1$ Hz, 3H; CH_3CH$_2$), 1.1–1.4 (m, 4H; CH_2CH_2), 2.70 (dq (app), 1H; CH_2C*H*), 3.31 (d, $^3J_{H,H} = 9$ Hz, 1H; CHC*H*), 3.62 (s, 3H; CO_2Me), 3.66 (s, 3H; CO_2Me), 4.98 (s (app), 1H; =C*H*H), 5.03 (dm, 1H; =CH*H*), 5.55 (dt (app), $^3J_{H,H} = 9.4$, 1H; 18 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 13.75$ (CH_3), 20.09 (CH_2), 34.41 (CH_2), 43.98 (CH), 52.17 (CH_3), 52.33 (CH_3), 56.89 (CH), 117.32 (=CH_2), 138.04 (=CH), 168.56 (CO_2Me), 168.76 (CO_2Me); IR (thin film): $\tilde{\nu} = 2956$, 1739, 1641, 1436, 1256, 1195, 1147 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 214 (15) $[M]^+$, 171 (35), 155 (100), 132 (95), 111 (60).

(*E*)-Dimethylhex-2-enyl malonate (22): ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): $\delta = 0.84$ (t, $^3J_{H,H} = 7.3$ Hz, 3H; CH_3CH$_2$), 1.33 (hex app, 2H; CH_3CH_2), 1.93 (q app, $^3J_{H,H} = 7.1$ Hz, 2H), 2.56 (t (app with fine splitting), 2H; CHCH_2), 3.40 (t, $^3J_{H,H} = 7.3$ Hz, 1H), 3.71 (s, 6H; CO_2Me), 5.32 (m, 1H; =C*H*), 5.50 (m, 1H; *H*C=); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 13.94$ (CH_3), 22.83 (CH_2), 32.34 (CH_2), 34.90 (CH_2), 52.36 (CH_3), 52.76 (CH), 125.40 (=CH), 134.14 (HC=), 169.53 (CO_2Me), 169.57 (CO_2Me); The *Z*-alkene, which was present only as a minor (inseparable) product, is distinguished by the following different signals in the ^{1}H NMR: $\delta = 2.01$ (q app, $^3J = 7.5$ Hz, 2H), 2.64 (tm, 2H), 3.45 (t, $^3J = 7.6$ Hz, 1H).

Crystal determination for [(*S*)-P^N]$PtCl_2$ (4): A crystal of approximate dimensions $0.25 \times 0.25 \times 0.15$ mm was used for data collection. For details see of data collectiona and refinement see Table 10. The structure was solved and refined with the SHELX 86[34] and SHELX 93[35] programs, respectively. In the final least-squares cycles in the refinement all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The asymmetric unit (shown in Figure 3), along with the labelling scheme used, was produced using ORTEX.[36]

Crystal determination for [(*S*)-P^N]$PdCl_2$ (7)

A crystal of approximate dimensions $0.3 \times 0.3 \times 0.3$ mm was used for data collection. For details see of data collectiona and refinement see Table 10. Data (2336 reflections) were corrected for Lorentz, polarization and 8% decay of the crystal in the X-ray beam, but not for absorption. The asymmetric unit consists of one molecule of the palladium complex and one molecule of dichloromethane. The structure was solved and refined with the SHELX 86[34] and SHELX 93[35] programs, respectively. In the final least-squares cycles of the refinement all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The asymmetric unit (shown in Figure 4), along with the labelling scheme used, was produced using ORTEX.[36]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-121672 (**4**) and CCDC-121673 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 10. Crystal data and structure refinement for **4** and **7**.

	4	**7**
formula	$C_{24}H_{24}Cl_2NOPPt$	$C_{25}H_{26}Cl_4NOPPd$
M_w	639.40	635.64
T [K]	293(2)	293(2)
λ [Å]	0.71069	0.71069
crystal system	monoclinic	monoclinic
space group	$P2_1$	$P2_1$
a [Å]	9.997(3)	10.218(4)
b [Å]	12.855(2)	12.815(2)
c [Å]	10.545(2)	10.729(3)
β [°]	112.10(2)	111.27(3)
V [Å^3]	1255.6(5)	1309.2(7)
Z	2	2
ρ_{calcd} [Mg m^{-3}]	1.691	1.612
μ [mm^{-1}]	5.879	1.197
F(000)	620	640
cystal size [mm]	0.25 × 0.25 × 0.15	0.3 × 0.3 × 0.3
θ range [°]	2.08 – 23.93	2.03 – 23.91
index ranges	$-11 \le h \le 10$	$-11 \le h \le 0$
	$0 \le k \le 14$	$-14 \le k \le 0$
	$0 \le l \le 12$	$-11 \le l \le 12$
reflections collected	2063	2336
independent reflections	2063 [R(int) = 0.0000]	2159 [R(int) = 0.0189]
absorption correction	DIFABS	–
transmission max/min	1.000/0.246	–
refinement method	Full-matrix least-squares on F^2	
data/restraints/parameters	2062/1/274	2151/1/300
goodness-of-fit on F^2	1.019	1.127
$R1$ [$I > 2\sigma(I)$]	0.0495	0.0484
$wR2$ [$I > 2\sigma(I)$]	0.1394	0.1173
$R1$ (all data)	0.0601	0.0623
$wR2$ (all data)	0.1602	0.1385
abs. structure parameter	-0.01(3)	0.00
largest diff. peak/hole [e Å^{-3}]	2.821/ – 2.385	1.301/ – 0.632
weighting scheme	[a]	[b]
extinction coefficient	0.0006(8)	–

[a] $w = 1/[\sigma^2(F_o^2) + (0.1220\,P)^2 + 5.7835\,P]$. [b] $w = 1/[\sigma^2(F_o^2) + (0.0834\,P)^2]$. $P = (F_o^2 + 2F_c^2)/3$ in both cases.

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