Diastereoisomeric Cationic π-Allylpalladium-(*P,C*)-MAP and MOP Complexes and Their Relationship to Stereochemical Memory Effects in Allylic Alkylation**

Guy C. Lloyd-Jones,*[a] Susanna C. Stephen,[a] Martin Murray,[a] Craig P. Butts,[a] Štěpán Vyskočil,*[b,+] and Pavel Kočovský*[b]

Abstract: The axially chiral ligands 2-(diphenylphosphanyl)-2′-methoxy-1,1′-binaphthalene (MOP; **6**) and 2′-dimethylamino-2-(diphenylphosphanyl)-1,1′-binaphthalene (MAP; **7**) coordinate to a cationic allylpalladium fragment in an unusual bidentate (*P,C*)-mode through the triarylphosphane and *ipso*-carbon atom (C1′). The readily prepared MAP and MOP complexes [Pd{(*P,C*)-(L)}(η^3-allyl)][OTf] (**9** (L = **7**) and **10** (L = **6**)) have been characterised in solution (NMR), in which two diastereoisomeric rotamers are observed. The stereochemical identity of the rotamers is established by one- and two-dimensional NMR spectroscopy experiments. In both the solid state and in solution, the allyl unit is shown to coordinate in a slightly distorted η^3-mode that results in a more alkene-like character at the allyl terminus *trans* to phosphane ligand. The opposite allyl terminus, which is *trans* to the *ipso*-carbon atom (C1′), is more strongly bound and the dominant allyl stereodynamic process involves C–C bond rotation in an η^1-allyl intermediate bound through this carbon. Palladium complexes of MAP and MOP are very efficient catalysts for allylic alkylation of racemic cyclopentenyl pivalate with [$NaCH(CO_2Me)_2$] in THF. Isotopic desymmetrisation revealed that the reaction occurs with powerful stereochemical memory effects and consequently with low global *ee* values. The memory effect is suggested to arise through selective generation of diastereoisomeric [Pd{(*P,C*)-L}(η^3-cyclopentenyl)]$^+$ ions (L = MAP or MOP) and subsequent capture by nucleophile before ion-pair collapse or equilibration occurs.

Keywords: isotopic labeling · memory effects · P,C coordination · palladium · π-allyl complexes

Introduction

A "memory effect" in Pd-catalysed allylic alkylation may be defined as the situation in which the reactions of isomeric allylic substrates do not obey the classical mechanism to give identical product ratios.[1] In the limiting regime, the stereochemical outcome of the reaction is governed not by the palladium–ligand assembly but solely by the stereochemical identity of the reacting substrate. Memory effects, first documented by Fiaud and Malleron in 1981,[2] have only recently enjoyed more widespread attention.[3] They may dramatically influence the *selectivity* of allylic alkylation reactions, in a manner that may be desirable[3b] or deleterious (Figure 1).[3a]

In 1998, Hayashi et al., described powerful *regiochemical* memory effects in the Pd-catalysed reactions of monosubstituted allylic acetates **1** (which gave **4**) and **2** (which gave **5**) with [$NaC(Me)C(CO_2Me)_2$] (**3**).[3b, 4] The high regiochemical retention (70–90%) was facilitated by use of the apparently monodentate monophosphine ligand "(*R*)-MOP"[5] ((*R*)-**6**, Figure 2). This result stood in stark contrast to all other Pd catalysts known at the time[6] which give products **4** and **5** (usually favouring **4**)[7] in ratios that are essentially independent of whether **1** or **2** is employed (i.e., no memory effect). In light of the results of Hayashi et al., we were thus puzzled by the observation that our recently introduced "MAP" ligand (**7**),[8] which is a close structural relative of MOP, did not behave analogously, and gave linear **4** as the major isomer (91–99%) from both **1** and **2** (R = Ph)[8a] (Figure 2).

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[**] MOP = 2-(diphenylphosphanyl)-2′-methoxy-1,1′-binaphthalene; MAP = 2′-dimethylamino-2-(diphenylphosphanyl)-1,1′-binaphthalene.

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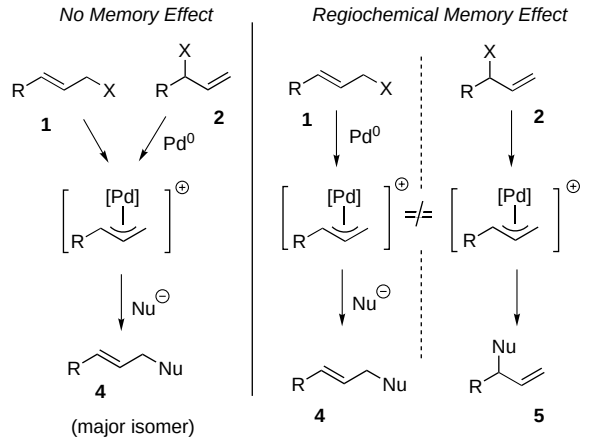


Figure 1. Left-hand reaction: a classical mechanism for allylic alkylation with a monosubstituted allylic electrophile (two regioisomers). Right-hand pair of reactions: a generic example of a memory effect in which the regiochemical identity of the substrate determines the outcome.

Two further differences between MOP and MAP were noted. The first was the lack of catalytic activity of Pd–MAP complexes in asymmetric alkene hydrosilylation[8a]—a reaction for which Pd–MOP complexes are outstandingly effective.[9] Secondly, Pd–MAP complexes display useful activity in Suzuki cross-coupling and Hartwig–Buchwald amination,[8a, b] whilst Pd–MOP complexes are not especially active. Based on X-ray crystallographic studies of MOP–Pd complexes[9d, 10] and reactivity/selectivity comparisons with analogous ligands in which the MeO is replaced by alkyl[9d] it has been demonstrated that the MeO group does not coordinate to Pd.[11] Thus a monodentate (*P,X*) coordination mode (*X* = e.g. OAc or Cl) is suggested for MOP in Pd-catalysed allylic alkylation.[3b, 4, 9, 10] Hence, we suspected that therein may lie the difference between MOP and MAP since in the latter, a *P,N* coordination mode (in which the Me_2N unit acts as a σ donor) is potentially available (see inset to Figure 2). A subsequent search for X-ray crystallographic evidence for this *P,N* coordination led instead to the surprising discovery of a novel (*P,C*)-coordination mode of *both* MAP and MOP ligands.[12] Herein, we describe the preparation of these stable and easily handled (*P,C*)-complexes (**9** and **10**; see Scheme 1) and the study of their stereodynamics in solution by two-dimensional NMR methods. We also demonstrate that palladium complexes of MOP and MAP are efficient catalysts for allylic alkylation of cyclopentenyl esters[13] with very high *stereochemical* memory and very low global *ee values*.

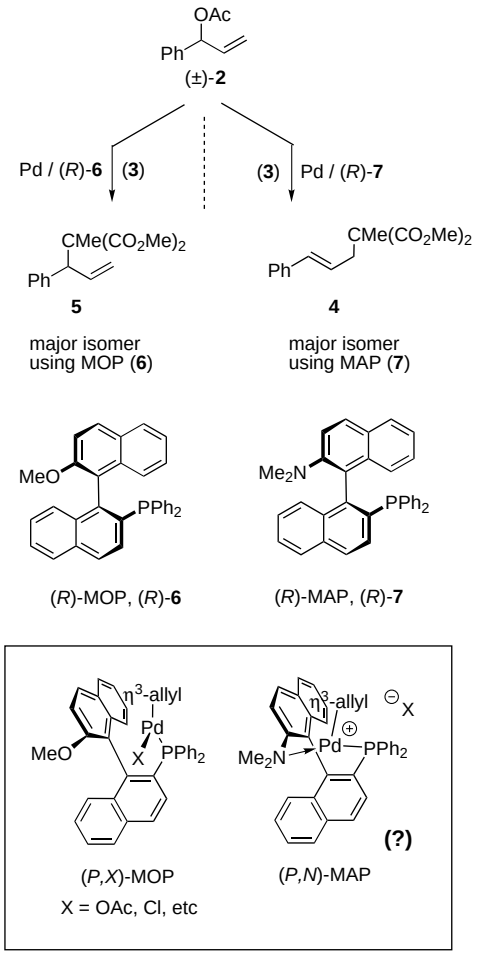


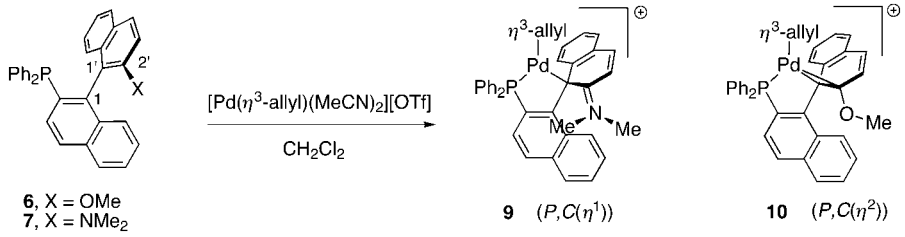
Figure 2. Differing results in allylic alkylation of isocinnamyl acetate catalysed by Pd complexes bearing MOP and MAP ligands. Inset: an earlier postulate (ref. [8a, b]) for the difference which arises by MAP bearing a better σ donor (Me_2N) being able to function as a bidentate ligand.

Abstract in Czech: *Axiálně chirální ligandy 2-(difenylfosfino)-2′-methoxy-1,1′-binaftalen "MOP" (**6**) a 2-(difenylfosfino)-2′-dimethylamino-1,1′-binaftalen "MAP" (**7**) koordinují kationoidní Pd-allylový fragment neobvyklým způsobem, při kterém se uplatňuje bidentátní (P,C)-ligace pomocí triarylfosfinové skupiny a ipso uhlíku (C1′). Snadno připravitelné komplexy těchto ligandů [Pd((P,C)-(L)(η³-allyl)][OTf] (**9** a **10**) byly charakterizovány v roztoku (NMR), kde byly pozorovány dva diastereoizomerní rotamery. Stereochemická identita těchto rotamerů byla určena pomocí 1 a 2D NMR experimentů. Bylo prokázáno, že v roztoku i pevném stavu je allylová jednotka koordinována jako η³-ligand a vykazuje mírnou distorzi, která vede ke zvýšení alkenového charakteru uhlíku orientovanému trans k fosfinu. Koncový uhlík na opačné straně allylové jednotky, který je orientován trans k ipso-uhlíku (C1′), je vázán pevněji. Převažující stereodynamický proces proto zahrnuje rotaci kolem C–C vazby v η¹-intermediátu, který je vázán přes tento koncový uhlík. Palladiové komplexy MAP a MOP ligandů jsou velmi účinnými katalyzátory allylové alkylace racemického cyklopentenylpivalátu s $NaCH(CO_2Me)_2$ v THF. Izotopická desymetrizace prokázala, že tato reakce probíhá s výrazným stereochemickým paměťovým efektem a tudíž s nízkým globálním ee. K paměťovému efektu patrně dochází z důvodu selektivního vzniku diastereoizomerních [Pd((P,C)-L)(η³-cyklopentenyl)]⁺ kationtů (L = MAP nebo MOP), které jsou atakovány nukleofilem dříve, než dojde k rozpadu iontového páru nebo stereochemické ekvilibraci.*

Results and Discussion

Preparation of (*P,C*)-(L)-Pd-π-allyl complexes 9 and 10: Reaction of (*S*)-MAP (*S*)-**7** with one equivalent of [Pd(η³-

allyl)(MeCN)$_2$][OTf] in CH_2Cl_2 at 25 °C occurred within seconds and afforded, after evaporation of the solvent, the cationic (*P,C*)-(**7**)-Pd-π-allyl complex (+)-**9** as an orange solid in >95% yield (Scheme 1). The pure complex was obtained as dark yellow crystals in 59% yield by slow diffusion of diethyl ether into its bright yellow solution in CH_2Cl_2. The (*S*)-MOP complex (+)-**10** was prepared analogously and isolated as pale yellow crystals (43%) by diffusion of diethyl ether into its solution in EtOAc. Single-crystal X-ray diffraction analysis[12a] revealed that MOP enters into a more η^2-type coordination (π) of the C1′–C2′ C=C bond with the Pd cation, whilst MAP, presumably because of its more electron-rich enamine character, enters into a more η^1-type coordination (σ) of C1′.[14]



6, X = OMe
7, X = NMe_2

9 (*P,C*(η^1))

10 (*P,C*(η^2))

Scheme 1. Preparation of cationic MAP and MOP allylpalladium complexes (+)-**9** and (+)-**10.**

Complex (+)-**9** exists, in the solid state, as a pair of diastereoisomeric allyl rotamers: aS_LaR_{Pd}-**9** (66%) and aS_LaS_{Pd}-**9** (34%), where the stereochemical descriptors refer to the axial chirality of the ligand (L) and the Pd–allyl axis (Pd).[15] On the basis of NMR spectroscopy, complex **9** maintains its (*P,C*)-ligated structure in solution (CD_2Cl_2) and aS_LaS_{Pd}-**9** is the major diastereoisomer (ca. 52%). Key evidence for the (*P,C*)-coordination mode in solution comes from the ^{13}C chemical shifts of C1′ and C2′.[16] Some selected NMR data of **9** are presented in Figure 3. Extensive one- and two-dimensional NMR spectroscopy experiments[17] were required in the full assignment of the ^{1}H, ^{13}C and ^{31}P NMR spectra of **9** and **10**. In contrast to the solid state,[12a] both diastereoisomers of **10** are observed in solution and aS_LaR_{Pd}-**10** is the major diastereoisomer (ca. 66%).

The deduction of the stereochemical identity of aS_LaS_{Pd}-**9** (52%) and aS_LaR_{Pd}-**9** (48%) allyl rotamers relied heavily on NOE contacts and anisotropic shifts induced by proximity to the ring current of a naphthalene ring (see circled protons in Figure 3). Particularly informative was the NOE between one of the *syn*-allyl-CH and the NMe_2 group in the minor isomer and the very different chemical shift of the *anti* protons on the allyl terminus *trans* to P between major ($\delta = 2.62$) and minor ($\delta = 4.24$) diastereoisomers. Such NOE and anisotropic shifts allowed the identification of key protons in the MAP ligand **7** within the complex: C3′-H, C8′-H, C7-H and C8-H (see lower part of Figure 3). These then provided definitive starting points in analysis of two-dimensional spectra. For complex **10**, the same process of analysis of NOE connectivities and anisotropic shifts of naphthyl[18] and allyl signals was employed in assignment of the ^{1}H NMR spectrum. These, together with the ^{13}C NMR shifts of C2′ ($\delta = 157$) and C(1′) ($\delta = 105$) indicate that MOP, like MAP, maintains (*P,C*)-ligation to the allylpalladium cation in solution.

Stereodynamics of cationic (*P,C*)-(L)-Pd-π-allyl complexes 9 and 10 in solution: Positive phase intermolecular correlations are observed in the PNOSY spectrum[19] of **9** at +24.8 °C, but not at −25 °C. Having assigned all allyl ^{1}H NMR signals of aS_LaR_{Pd}-**9** and aS_LaS_{Pd}-**9**, careful analysis of the cross-peaks at +24.8 °C indicates that they correspond to two different mechanisms of exchange as shown in Figure 4. In the major

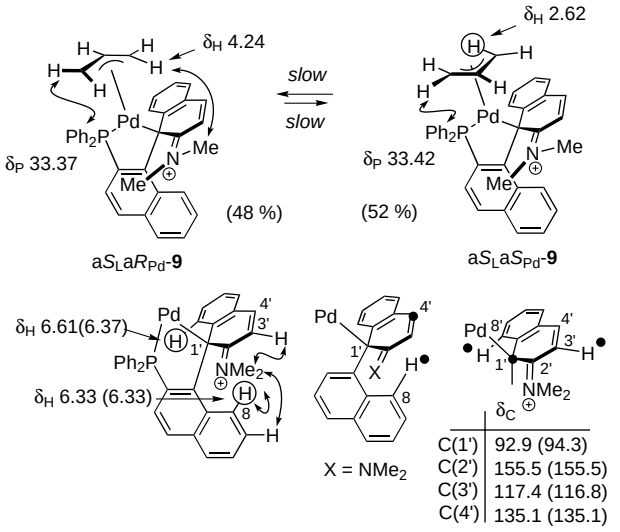


Figure 3. Selected one- and two-dimensional NMR data (CD_2Cl_2, −25 °C) for the two diastereoisomers of cationic complex **9** [(π-allyl)Pd-(*P,C*)-**7**][OTf]. In the lower part of the figure, chemical shifts of aS_LaR_{Pd}-**9** are in parentheses and follow those of aS_LaS_{Pd}-**9**. Selected NOE connectivities are indicated by double-headed arrows, selected FGHMBC correlations by small filled circles and selected anisotropic shifts by large open circles.

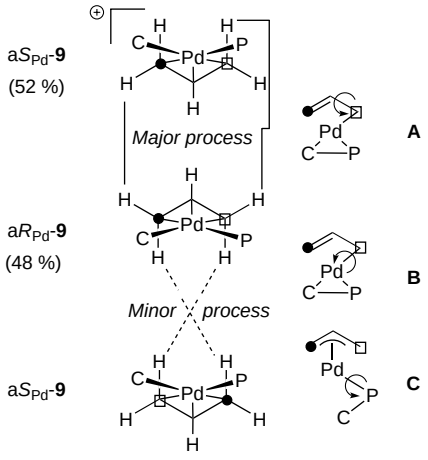


Figure 4. Intermolecular connectivities observed by PNOSY (500 MHz, CD_2Cl_2, 24.8 °C) between aS_LaR_{Pd}-**9** and aS_LaS_{Pd}-**9**. There are two modes of interconversion: **A** (solid lines) and **B**/**C** (dashed lines) with a relative rate ratio of about 0.7/0.3. Analogous connectivities are observed between aS_LaR_{Pd}-**10** and aS_LaS_{Pd}-**10**, with greater overall exchange rate and relative ratio of about 0.6/0.4.

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process (solid lines in Figure 4) there is *syn–anti* proton exchange at the terminal allyl carbon that is *trans* to C; neither *syn–anti* exchange at the terminal allyl carbon *trans* to P nor interchange of allyl termini were detected. These features are consistent with a switch from η^3-allyl to an η^1 intermediate (σ-bound through the carbon *trans* to C1′ of **7**), which allows a C–C rotation (in which the faces of the alkene moiety are exchanged) and then a regioselective return to η^3-mode of binding (**A** in Figure 4) in which the alkene re-coordinates *trans* to P.

The second and minor mode of interconversion of diastereoisomers occurs with interchange of allyl termini with no accompanying *syn–anti* exchange. Interchange of allyl termini requires apparent 180° π-allyl rotation about the Pd-(*C,P*)-ligand fragment. In the absence of an external ligand (e.g. Cl) to facilitate Berry pseudorotation, this must occur through rotation of a fragment which is monocoordinated to Pd and *cis* to a vacant coordination site. Two mechanisms would account for this process: either C–Pd rotation in an η^1-allyl (**B** in Figure 4) or P–Pd rotation when MAP is monocoordinate (a Bäckvall type mechanism,[20] **C** in Figure 4). There are a number of features in the NMR spectra that suggest the latter is dominant.[21] In addition to the intermolecular correlations, there were weak intramolecular exchange cross-peaks whose connectivities correspond to two-fold exchange (e.g., [**A** + **B**/**C**]) during the spin-mixing time ($\tau_m = 300$ ms). The PNOSY spectrum of complex **10** (24.7 °C) displayed the same set of connectivities as those observed with **9**, but with substantially increased line-broadening (one-dimensional) and cross-peak intensities (two-dimensional). This is presumably a reflection of the weaker bidentate ligation of MOP (η^2-type coordination (π) of C1′, C2′) in **10** relative to MAP (η^1-type coordination (σ) of C1′) in **9** (vide supra).

The stereodynamics observed with both **9** and **10** suggest a more σ-like (alkyl) character at the allyl carbon atoms *trans* to C and a more π-like (alkene) character between the central CH and the allyl termini *trans* to P. These conclusions are supported by the differences in ^{13}C NMR spectroscopic chemical shifts and Pd–C bond lengths (X-ray) between the two allyl termini in the two complexes (Figure 5).

Memory effects in allylic alkylation reactions of cyclopentenyl pivalate: Cyclopentenyl esters (e.g. **11**) are reactive substrates for Pd-catalysed allylic alkylation. The cyclic (*anti,anti*) π-cyclopentenylpalladium fragments in the intermediates that they generate are much less manipulable, in terms of torquoselectivity,[22] than the predominantly linear (*syn,syn*) π-allyl fragments generated by the ubiquitous 1,3-diphenylpropenyl esters. Consequently, the achievement of high enantioselectivity in the allylic alkylation of small, symmetrical cycloalkenyl substrates is a challenging and increasingly popular testing ground for asymmetric ligand design. Only a handful of catalyst systems are known to effect the alkylation of such substrates with high enantioselectivity.[23] A prerequisite to achieving high enantioselectivity with **11** is that both enantiomers converge on a single set of π-allylpalladium intermediates (**12** and **13** in Figure 6) which attain full dynamic equilibrium before nucleophilic attack.

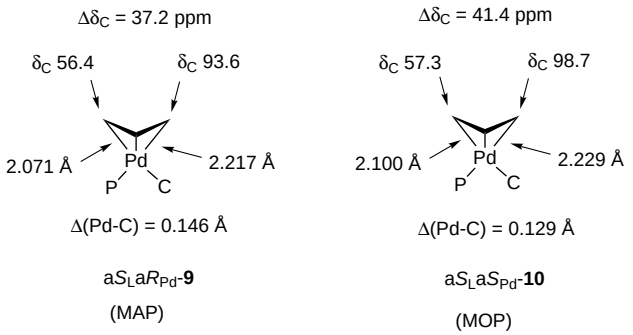


Figure 5. Selected solution (^{13}C NMR) and solid state (X-ray) data for aS_LaS_{Pd}-**9** and aS_LaS_{Pd}-**10** that suggest a more π-like (alkene) binding mode at the allyl termini *trans* to P. Similar data are observed in the other diastereoisomers of **9** and **10** in solution and also in **9** in the solid state (**10** exists as predominantly a single diastereoisomer in the solid state).

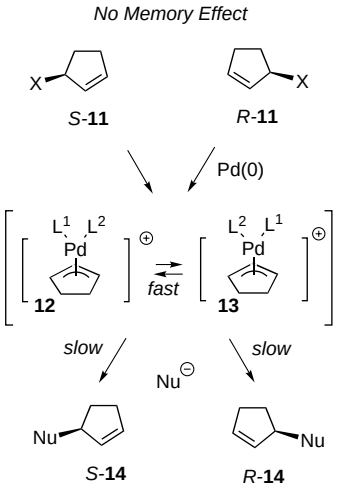
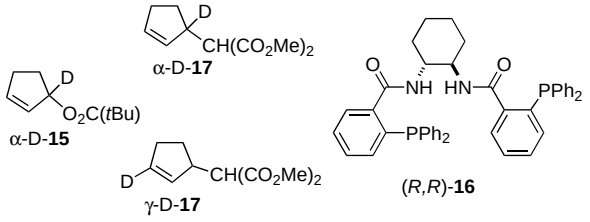


Figure 6. Pd-catalysed allylic alkylation of racemic cyclopentenyl substrate by a single reaction manifold. Under these conditions, the enantiomeric outcome in **14** is solely derived from ligand control and there is no memory effect.

Unlike the regiochemical memory effects outlined in Figure 1, in reactions of **11**, a stereochemical memory effect may be invisible[24] when *racemic* **11** is employed and **14** is produced in low *ee*. Use of enantiomerically pure substrate **11** is one method for the detection of memory effects in such systems. An alternative and more practical solution is to employ our recently developed isotopic desymmetrisation method which involves reaction of *racemic*-α-D-labelled cyclopentenyl ester (±)-**15** to give α-**17** and γ-**17**.[3c, 25] We have applied this approach in the study of *moderate* stereochemical memory effects observed in reactions catalysed by Pd complexes bearing the Trost modular ligand **16**.[3a, 26, 27]



We earlier reported that Pd complexes of MAP did not exhibit a *regiochemical* memory effect in the reaction of isocinnamyl acetate (**2**, R = Ph, X = OAc) with [NaCR-$(CO_2Me)_2$] (R = H or Me).[8a] Reactions of cyclopentenyl pivalate **11** (employed in its D-labelled form (±)-**15**)[28] proved very different (Table 1).

In THF with 5 mol% Pd catalyst bearing (*S*)-MAP and prepared in situ (entries 1 and 2) there is a high degree of regiochemical retention (*rr*) (81–86% α-**17**, 62–72% re (α))[29] and thus a powerful memory effect. Under halide-free conditions with complex (+)-**9** (i.e. Pd/L = 1:1), the effects are even more pronounced (90% α-**17**, 80% re, entry 3). In all three cases, isotopic desymmetrisation analysis reveals that the *R* enantiomer of **15** gives **17** with 64–84% *ee* (*R*),[30] whilst (*S*)-**15** gives **17** in slightly lower selectivity (48-68% *ee*) and of opposite configuration (*S*). Thus the global *ee* is very low (6–15% *ee* (*R*)) but does suggest that the latent selectivity of the catalyst favours production of (*R*)-**17**. When the reaction is performed in CH_2Cl_2 (in which the nucleophile is sparingly soluble), the memory effect disappears (0% re, entry 4) and both enantiomers of **15** give (*R*)-**17** with the same selectivity (52% *ee* (*R*)). Although the yield is much reduced in this latter reaction (42%), both enantiomers of **15** are completely consumed and are converted into **17** with equal efficiency.

Returning to reactions conducted in THF, the effects of a number of additives were tested (entries 5, 6 and 7). Firstly, addition of MAP ligand to pro-catalyst (+)-**9** (Pd/L = 1:1.5, entry 5) reduced the memory effect from 80% re to 76% re (α). Addition of 5 mol% Bu_4NCl (Pd/Cl = 1:1, entry 6) had a more pronounced effect giving **17** in 62% re (α)—identical to that observed when the catalyst was prepared in situ from $[Pd_2Cl_2(allyl)_2]$, entry 1).[31] However, addition of 5 mol% $[Bu_4N][Ph_3SiF_2]$ (Pd/F = 1:2, entry 7) had a lesser effect, only slightly decreasing the memory effect in the manifold involving (*S*)-**15** (giving **17** in 60% *ee* (*S*)).

Changing from Na^+ as nucleophile counter-ion to Cs^+ (entry 8) reduced the memory effect but also substantially reduced the yield of **17** (23%) and enantioselectivity in both manifolds. However, the base appears to act as reaction proceeds rather than prior to reaction and thus the concentration of "[$CsCH(CO_2Me)_2$]" is low (vide infra). Finally, use of racemic ligand (±)-**7** (entry 9) still gives high regiochemical retention and, obviously a racemic product (0% *ee* **17**). Although the high symmetry of the memory effect precludes the accurate extraction of relative rates of reaction of matched and mismatched substrates,[32] (*R*)-**15** may be described as chirality-matched with (*S*)-MAP and mismatched with (*R*)-MAP. Very similar results are observed with MOP (compare entries 10, 11 and 12 with entries 1, 2 and 9, respectively).

Mechanistic considerations: Under nearly all conditions studied, the memory effects with MAP and MOP ligands are far more powerful and more symmetrical than those observed with the Trost modular ligand **16**.[3a, 3c–e] The symmetry suggests that the π-allylpalladium(II) intermediates initially formed from opposite enantiomers of substrate are diastereoisomeric. The enantioselectivities arising in matched and mismatched manifolds under memory-effect conditions (in THF) are mostly a result of the influence of the *chirality* of the precursor **15**. By contrast, under nonmemory effect conditions (e.g. in CH_2Cl_2) the chirality of the precursor **15** has no influence on the enantiomeric outcome (52% *ee* *R*) which is a result solely of the influence of the chirality of the ligand (*S*)-**7** (see isotopically desymmetrised ^{13}C NMR spectroscopic analyses, Figure 7).

In order to better understand the origins of these memory effects, one would like to be able to isolate and characterise the intermediate π-cyclopentenylpalladium complexes. However, in our hands, this has not been successful. This is presumably a result of their instability through facile *syn*- or *anti*-β-hydride elimination[33] to give cyclopentadienyl hydridopalladium complexes which probably accounts for the poor yields of the catalysed reactions when the nucleophile concentration is low (see Table 1, entries 4 and 8). However,

Table 1. Allylic alkylation of cyclopentenyl pivaloate (±)-**15** ($\alpha/\gamma \geq 500$, 0.12 M) with 2.25 equivalents of $[NaCH(CO_2CH_3)_2]$ catalysed by 5 mol% Pd catalyst bearing MAP (**7**) and MOP (**6**) ligands.[a]

Entry	Ligand	Catalyst[b]	Additive [mol%]	*er*[c] (*R*/*S*)-**17** from: (*R*)-**15** (α/γ)	(*S*)-**15**(γ/α)	*rr* (α)[d] [%]	*ee*[e] **17** [%]	Yield **17**[f] [%]
1	(*S*)-**7**	**A**	–[g]	42/8	13/37	81 (79)	15 (10) (*R*)	85.3
2	(*S*)-**7**	**B**	–[g]	43/7	11/39	86 (82)	6 (6) (*R*)	80.7
3	(*S*)-**7**	**C**	–[g]	46/4	8/42	90 (88)	9 (8) (*R*)	80.1
4[h]	(*S*)-**7**	**C**	CH_2Cl_2	38/12	38/12	–[i] (50)	51 (52) (*R*)	42.4
5	(*S*)-**7**	**C**	(*S*)-**7** (2.5)	44/3	13/37	88 (81)	6 (14) (*R*)	94.7
6	(*S*)-**7**	**C**	F^-[j](5)	47/3	10/40	92 (87)	18 (14) (*R*)	85.3
7	(*S*)-**7**	**C**	Cl^-[k](5)	(–)[i]	(–)[i]	81 (–)[i]	(–)[i]	91.6
8	(*S*)-**7**	**C**	Cs^+ [l]	36/14	26/24	–[i](60)	25 (24) (*R*)	22.7
9	(±)-**7**	**A**	–[g]	40/10	10/40	82 (79)	0 (0)	87.0
10	(*S*)-**6**	**A**	–[g]	45/5	16/34	82 (79)	19 (22) (*R*)	81.8
11	(*S*)-**6**	**B**	–[g]	44/6	16/34	84 (78)	20 (20) (*R*)	86.4
12	(±)-**6**	**A**	–[g]	38/12	10/40	89 (78)	0 (4) (*S*)	83.5

[a] All reactions conducted in THF (except entry 4) and at 25 °C. [b] Catalyst is either generated in situ by reaction of ligand with $[Pd_2(\eta^3\text{-}C_3H_5)_2Cl_2]$ (conditions **A**) or $[Pd_2(dba)_2]\cdot CHCl_3$ (conditions **B**), (Pd/L = 1:1.5) or from pre-formed complex (+)-**9** (conditions **C**). [c] *er* = enantiomeric ratio as determined by ^{13}C NMR analysis. [d] *rr* = regiochemical retention (global α) as a mol fraction of **17** [$rr = (\alpha/\alpha + \gamma)$] where α and γ ratios were determined by ^2H NMR (and ^{13}C NMR). [e] *ee* = global *ee* of overall sample of **17** as determined by ^{13}C NMR analysis of CO_2Me signals, *ee* in brackets is *ee* calculated from α/γ ratios. [f] Yield of analytically pure **17** obtained after chromatography on silica gel. [g] No additive. [h] Reaction conducted in CH_2Cl_2 instead of in THF. [i] Not determined. [j] 5 mol% tetrabutylammonium triphenyl silyl difluoride. [k] 5 mol% tetrabutylammonium chloride. [l] Nucleophile generated in situ from $Cs_2CO_3/CH_2(CO_2Me)_2$.

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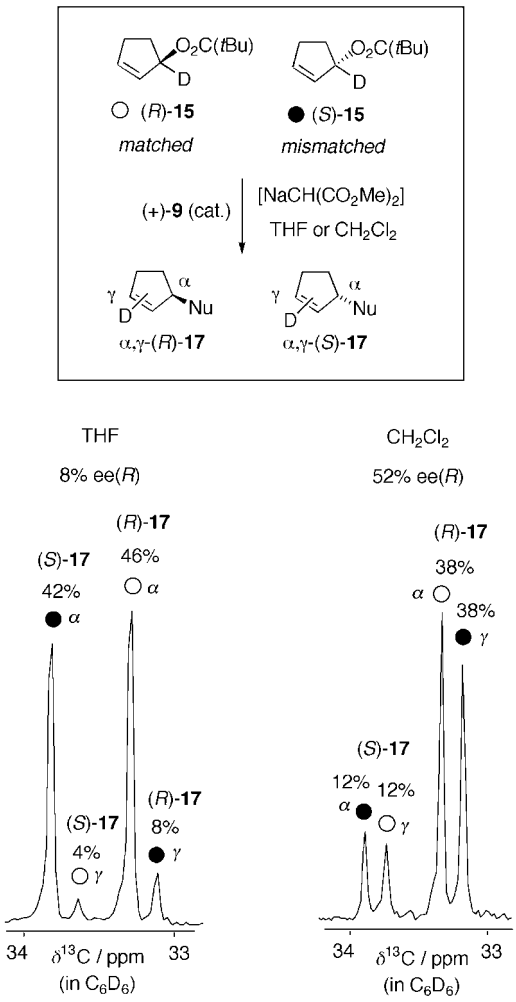
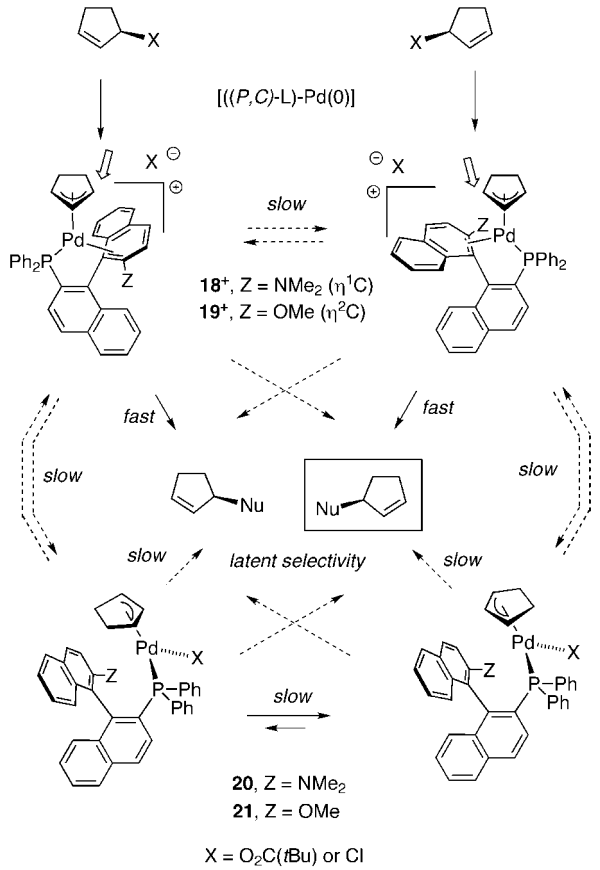


Figure 7. ^{13}C NMR analysis of allylic alkylation products (α,γ-D-**17**) arising from reaction of α-D-**15** with [NaCH(CO_2Me)$_2$] catalysed by pro-catalyst (+)-**9** in THF or CH_2Cl_2 (Table 1, entries 3 and 4). Products arising from matched and mismatched substrates are indicated with an open and closed circle respectively (only ^{13}C signals from C4 are shown). The analysis is based on a combination of two effects: the deuterium-label effects isotopic desymmetrisation (α and γ isomers cause different ^{13}C-isotope shifts at C(4) of **17**) and a chiral shift reagent [(+)-Eu(hfc)$_3$] allows distinction of (*R*)-**17** and (*S*)-**17**.



Scheme 2. A mechanistic rationale for the memory effects arising in allylic alkylation of cyclopentenyl pivalate (X = tBuCO$_2$ or Cl) by [NaCH(CO_2Me)$_2$] catalysed by Pd complexes bearing MAP or MOP ligands; see text for full discussion.

consideration of the π-allylpalladium complexes **9** and **10**, described earlier, may be instructive. In both complexes the allyl terminus *trans*-related to the π-accepting P donor has a longer Pd–C bond, has more π-character, higher ^{13}C chemical shift and is more readily dissociated from Pd. Consequently, this terminus might be expected to undergo nucleophilic attack by, for example, [NaCH(CO_2Me)$_2$] much more readily than that *trans* to *ipso*-C1′ (see Figures 4 and 5). This is consistent with the generally accepted concept of nucleophilic attack *trans* to the most π-accepting ligand[22a, b, 34] or at the weakest bound carbon atom.[34d] If one considers the formation of the π-allylpalladium(II) complex as the reverse process of nucleophilic attack, reaction Pd^0–MAP or Pd^0–MOP is expected to proceed through ionisation with the nucleofuge at the position *trans* to the P donor.[35] Therefore, enantiomeric cyclopentenyl pivalates should generate diastereoisomeric cations [(π-cyclopentenyl)Pd-(*P*,*C*)-L]$^+$ **18**$^+$ (L = MAP) or **19**$^+$ (L = MOP) (Scheme 2). These cations will afford *enantiomeric* allylic alkylation products on attack of the nucleophile at the allyl termini *trans* to P (see arrows indicating *trans* sites in Scheme 2). Based on the stereodynamics observed with **9** and **10**, one might anticipate that diastereoisomers of complexes **18**$^+$ and **19**$^+$, which cannot undergo C–C single bond rotation in η^1-allyl intermediates, should interconvert very slowly indeed.[36] Consequently, if nucleophilic attack is rapid and *trans* selectivity is high, then a powerful stereochemical memory effect will result.

In understanding the variability of the memory effect (see Table 1) we must further consider the diastereoisomeric cations **18**$^+$ and **19**$^+$. These are expected to exist as ion pairs in THF,[37] that is {**18**$^+$, X$^-$} and {**19**$^+$, X$^-$} where the identity of the counter-ion X$^-$ will depend on the exact reaction conditions. Collapse of the ion pair (see Scheme 2) would give [(π-cyclopentenyl)(X)Pd-(*P*)-L] complexes **20** (L = MAP) and **21** (L = MOP) and is thermodynamically favourable if X$^-$ is a better ligand for Pd$^+$ than C1′/C2′ (e.g. X = Cl).[3b, 10] However, although diastereoisomer interconversion in the resultant complexes will be slow,[38] the neutrality of **20** and **21** is expected to make them significantly less reactive towards a carbanion nucleophile than the cations **18**$^+$ and **19**$^+$.[39] Thus, under conditions where palladophilic ions are present (e.g. Cl, entries 1 and 7, Table 1) or when nucleophile concentration is low (e.g. entries 4 and 8, Table 1), or when there is poor solvation of the ion pair (e.g. CH_2Cl_2, entry 4,

Table 1), ion pair collapse (to **20** or **21**) and diastereoisomer equilibration will become a contributing factor. If complete diastereoisomer equilibration occurs prior to capture by nucleophile, the memory effect is absent and the *latent selectivity*[40] of the ligand is revealed.

Conclusion

Allylic alkylation reactions of cyclopentenyl pivalate (**11**) with [$NaCH(CO_2Me)_2$] in THF catalysed by Pd complexes of MOP and MAP proceed with powerful *stereochemical* memory effects and very low enantiomeric excess (as revealed by isotopic desymmetrisation analysis,[3c] Figure 7). These results highlight the danger of drawing conclusions about catalyst selectivity without testing for memory effects.

In an earlier study by Hayashi et al.,[3b] the reaction of cyclohexenyl acetate catalysed by [$Pd_2(allyl)_2Cl_2$]/MOP was shown to proceed with a powerful *regiochemical* memory effect. The regiochemical retention with cyclohexenyl acetate (82 % α) may be compared with the results we have obtained with cyclopentenyl pivalate under identical conditions using either MOP (82 % α) or MAP (81 % α) (Table 1, entries 1 and 10, respectively). To account for the powerful regiochemical retention observed in reactions of cyclohexenyl acetate, Hayashi et al.[3b] suggested a mechanism in which the catalytic flux involved nucleophilic attack of neutral [Pd(L)(X)-(π-C_6H_9)] complexes, directly analogous to **21**. Neutral complexes were invoked since evidence for bidentate (*P,C*)-coordination was not observed in the ^{1}H NMR spectra of *isolated* Pd^{II}-π-allyl complexes of MOP generated by addition of allylic esters to Pd^0(*P,C*)-MOP,[41] or by addition of MOP to [$PdX(\pi$-allyl)$]_2$,[3b] or in the X-ray crystal structure of a [MOP – Pd(Cl)(π-prenyl)] complex.[10]

However, we recently found a (*P,C*)-coordination mode in the X-ray crystal structures of *cationic* allylpalladium complexes (**9** and **10**) of MAP and MOP.[12a] We have now studied these complexes in detail by NMR and confirmed that, a) bidentate (*P,C*)-mode of coordination is maintained in solution and b) slow diastereoisomer interconversion proceeds predominantly through C–C rotation in an η^1-coordinated allyl intermediate (**A** in Figure 4). Consequently, oxidative addition of cyclopentenyl-type substrates to [Pd^0-(*P,C*)-L] complexes[41] is expected to generate analogous (π-cyclopentenyl)Pd cations $\mathbf{18}^+$ and $\mathbf{19}^+$ (Scheme 2) as the *primary* products. These nonisolable complexes are anticipated to undergo slow diastereoisomer interconversion (only via **B** or **C** in Figure 4). We therefore suggest that, with cycloalkenyl esters, the memory effects observed with MOP and MAP arise predominantly through rapid capture of the initially formed and more reactive ion-paired[37] complex {[(π-cycloalkenyl)Pd((*P,C*)-L)]$^+$[X]$^-$} in which the bidentate (*P,C*)-coordination mode present in the Pd^0 precursor is maintained. Poor solvation, presence of chloride or low nucleophile concentration are conditions that engender equilibration of collapse of the cation-anion pair to give the less reactive neutral complex [(π-cycloalkenyl)Pd(X)(L)] before nucleophilic attack. Future work will aim to address the stark differences between MOP and MAP in the Pd-catalysed allylic alkylation reactions of isocinnamyl type substrates (**2**) and the role of (*P,C*)-coordinated Pd – MAP complexes in the catalytic cycles of Suzuki and Hartwig – Buchwald reactions.[12a,b]

Experimental Section

General: Solvents and reagents were purified by standard procedures. Anhydrous solvents were purchased from Fluka or Aldrich and used as received. When appropriate, reactions were carried out under nitrogen or argon using standard Schlenk techniques. NMR experiments were performed on JEOL Delta 270, GX400 and Alpha 500 instruments. Spectral simulation (^{1}H) of the allyl signals of Pd complexes was performed using *g*-NMR software. Electrospray mass spectra were obtained on a VG Quattro instrument (Cone voltage 50 V). Elemental analysis of the compounds were performed by the analytical service of the School of Chemistry, University of Bristol. IR spectra: Perkin-Elmer 1600 FT, samples were prepared as thin films on NaCl or as KBr discs, absorptions are reported in cm^{-1} as strong (s), medium (m) or weak (w). Flash column chromatography: Merck silica gel 60 eluting with a constant gravity head of about 15 cm solvent. Thin layer chromatography: 0.25 mm, Merck silica gel 60 F254 visualising at 254 nm or with acidic (H_2SO_4) aq. $KMnO_4$ solution (ca. 2 %).

Preparation of complex (+)-9: A bright yellow solution of (*S*)-(−)-MAP (**7**) (585.0 mg, 1.21 mmol) in anhydrous CH_2Cl_2 (6.5 mL) was added to a colourless solution of [Pd(η^3-C_3H_5)(MeCN)$_2$]OTf (459.96 mg, 1.21 mmol) in anhydrous CH_2Cl_2 (11 mL), under nitrogen, to give a dark orange solution. Evaporation of the solvent afforded **9** as an orange solid (898.9 mg, 95 %). Crystallisation by diffusion of diethyl ether (v/v 5:1) into a solution of **9** in CH_2Cl_2 afforded a mixture of larger dark orange and smaller yellow crystals, 559.4 mg (59.4 %). M.p. dark orange crystals: 179.5 – 180 °C, yellow crystals: 199 °C. Both crystal habits dissolve to give the same complex **9** (NMR). $[\alpha]_D^{21} = 1024$ (c = 0.717 in CH_2Cl_2); ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, $CHDCl_2$): Compound aS_LaS_{Pd}-**9** (major): δ = 8.09 (br d, ^3J(H,H) = 8 Hz, 1H; C4-H), 8.03 (d, ^3J(H,H) = 8 Hz, 1H; C4′-H), 7.95 (d, ^3J(H,H) = 8 Hz, 1H; C5-H), 7.76 (d, ^3J(H,H) = 8 Hz, 1H; C5′-H), 7.73 (d, ^3J(H,H) = 8 Hz, 1H; C3′-H), 7.73 (m, 1H; C3-H), 7.53 (dd, ^3J(H,H) = 8, 8 Hz, 1H; C6-H), 7.52 – 7.29 (br m, 10H; arom. H), 7.24 (dd, ^3J(H,H) = 8, 8 Hz, 1H; C7-H), 7.22 (br dd, ^3J(H,H) = 8, 8 Hz, 1H; C6′-H), 6.96 (dd, ^3J(H,H) = 8, 8 Hz, 1H; C7′-H), 6.60 (d, ^3J(H,H) = 8 Hz, 1H; C8′-H), 6.30 (d, ^3J(H,H) = 8 Hz, 1H; C8-H), 5.73 (simul. dddd, ^3J(H,H) = 6.0, 6.7, 14, 14 Hz, 1H; allyl C2-H), 3.86 (simul. ddd, ^2J(H,H) = 1.0 ^3J(H,H) = 6, ^3J(H,P) = 6.0 Hz, 1H; allyl CH*syn, trans* ^{31}P), 3.68 (simul. ddd, ^2J(H,H) = 1.0, ^3J(H,H) = 6.7, ^4J(H,H) = 1.0 Hz, 1H; allyl CH*syn, cis* ^{31}P), 2.80 (simul. dd, ^2J(H,H) = 1.0, ^3J(H,H) = 14.0 Hz, 1H; allyl CH*anti, cis* ^{31}P), 2.78 (s, 6H; $N(CH_3)_2$), 2.59 (simul. ddd, ^2J(H,H) = 1.0, ^3J(H,H) = 14.0, ^3J(H,P) = 9.0 Hz, 1H; allyl CH*anti, trans* ^{31}P). Compound aS_LaR_{Pd}-**9** (minor): δ = 8.07 (br d, ^3J(H,H) = 8 Hz, 1H; C4-H), 7.98 (d, ^3J(H,H) = 8 Hz, 1H; C4′-H), 7.95 (d, ^3J(H,H) = 8 Hz, 1H; C5-H), 7.79 (d, ^3J(H,H) = 8 Hz, 1H; C3′-H), 7.73 (m, 1H; C3-H), 7.71 (d, ^3J(H,H) = 8 Hz, 1H; C5′-H), 7.53 (t, ^3J(H,H) = 8 Hz, 1H; C6-H), 7.52 – 7.29 (br m, 10H; arom. H), 7.24 (t, ^3J(H,H) = 8 Hz, 1H; C7-H), 7.17 (br t, ^3J(H,H) = 8 Hz, 1H; C6′-H), 6.88 (dd, ^3J(H,H) = 8 Hz, 1H; C7′-H), 6.36 (d, ^3J(H,H) = 8 Hz, 1H; C8′-H), 6.32 (d, ^3J(H,H) = 8 Hz, 1H; C8-H), 5.27 (simul. dddd, ^3J(H,H) = 14.0, 14.0, 6.7, 5.2, 1H; allyl C2-H), 4.21 (simul., ddd, ^2J(H,H) = 1.0, ^3J(H,H) = 14, ^3J(H,P) = 9 Hz, 1H; allyl CH*anti, trans* ^{31}P), 3.71 (simul., ddd, ^2J(H,H) = 1.0, ^3J(H,H) = 6.7, ^4J(H,H) = 1.0 Hz, 1H; allyl CH*syn, cis* ^{31}P), 3.18 (simul., dddd, ^2J(H,H) = 1.0, ^3J(H,H) = 5.2, ^3J(H,P) = 5.2, ^4J(H,H) = 1.0 Hz, 1H; allyl CH*syn, trans* ^{31}P), 2.96 (s, 6H; $N(CH_3)_2$), 2.58 (simul., dd, ^2J(H,H) = 1.0, ^3J(H,H) = 14.0, 1H; allyl CH*anti, cis* ^{31}P). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 26 °C, CD_2Cl_2), Compound aS_LaS_{Pd}-**9**: δ = 155.47 (C2′ = N), 147.18 (d, ^2J(C,P) = 27 Hz, C1), 135.08 (C4′), 134.20 (C9′), 130.15 (C4-H), 128.77 (C5′-H), 128.48 (C7′-H), 128.08 (C7-H), 127.97 (C3), 126.86 (C10′), 124.49 (C8′-H), 124.46 (C6′-H), 120.83 (d, ^2J(C,P) = 6 Hz; allyl C2), 117.41 (C3′-H), 92.94 (br s, C1′-Pd), 89.92 (d, ^3J(C,P) = 30 Hz; allyl C*trans* ^{31}P), 59.29 (d, ^2J(C,P) = 3 Hz, allyl C*cis* ^{31}P), 46.30 ($N(CH_3)_2$). Compound aS_LaR_{Pd}-**9**: δ = 155.47 (C2′ = N), 146.97 (d, ^2J(C,P) = 26 Hz, C1), 135.08 (C4′-H), 133.64 (C9′), 130.15 (C4-H) 128.82, (C5′-H), 128.37 (C7′-H), 128.09 (C7-H), 127.95 (C3-H), 126.64 (C10′), 124.60 (C8′-H), 124.22 (C6′-H), 120.04 (d, ^2J(C,P) = 6 Hz; allyl C2), 116.81 (C3′-H), 94.32 (br s, C1′-Pd), 93.56 (d, ^3J(C,P) = 30 Hz; allyl C*trans* ^{31}P), 56.43 (d, ^2J(C,P) = 3 Hz, allyl C*cis* ^{31}P), 47.11 ($N(CH_3)_2$).

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The following carbon signals could not be distinguished between compounds aS_LaR_{Pd}-**9** and aS_LaS_{Pd}-**9**: δ)134.01 and 133.70 (2 × d ^3J(C,P) = 14 Hz, arom.C-H*ortho*), 133.19 (C(10)), 132.74 and 132.43 (2 × d, ^3J(C,P) = 13 Hz, arom.C-H*ortho*), 132.38 and 132.26 (C9), 131.49, 131.43, 131.31, and 131.12 (4 × d, ^4J(C,P) = 2 Hz, arom.C-H*para*), 129.83, 129.68, 129.68 (3 × C_{ipso}); 129.25 and 129.16 (2 × d, ^4J(C,P) = 8 Hz, arom.C-H*meta*), 128.96 and 128.81 (2 × d, ^4J(C,P) = 11 Hz, arom.C-H*meta*), 128.60 (C6-H), 128.53 (C5-H), 124.65 (C8-H): C2 was not located. ^{31}P NMR (202 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2): δ = 33.42 (s, aS_LaS_{Pd}-**9**), 33.37 (s, aS_LaR_{Pd}-**9**); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3054w, 1613w, 1435m, 1264s, 1151m, 1097w, 1030m, 815w, 750w, 697w, 638m, 529m; MS (electrospray): *m*/*z*: 629 [*M* − OTf]$^+$; elemental analysis calcd for $C_{38}H_{33}NO_3PSF_3Pd$ (778.13) (%): C 58.66, H 4.27, N 1.80; found: C 58.23, H 4.33, N 1.93.

Preparation of Complex (+)-10: A colourless solution of (*S*)-(−)-MOP (**6**) (85.00 mg, 0.18 mmol) in anhydrous CH_2Cl_2 (2.3 mL) was added to a colourless solution of [Pd(η^3-C_3H_5)(MeCN)$_2$]OTf (68.69 mg, 0.18 mmol) in anhydrous CH_2Cl_2 (1.2 mL), under nitrogen, to give a bright yellow solution. Evaporation of solvent afforded crude (+)-**10** as a bright yellow oil. Crystallisation by diffusion of diethyl ether (v/v, 5:1) into a solution of (+)-**10** in EtOAc (v/v, 5:1) afforded yellow crystals, 59.7 mg (43.4 %). M.p. 176 °C (darkens); $[\alpha]_D^{21}$ = 276 (c = 0.245 in CH_2Cl_2); ^{1}H NMR (500 MHz, CD_2Cl_2, −25 °C, $CHDCl_2$): Compounds aS_LaR_{Pd}-**10** (major) and aS_LaS_{Pd}-**10** (minor): δ = 8.09 (d, ^3J(H,H) = 8 Hz, 1H; C5′-H), 7.33–7.62 (m, 14H; C3-H, C6-H, C6′-H, C7′-H, Ph$_2$), 7.18 (ddd, ^3J(H,H) = 7, 7, ^4J(H,H) = 1 Hz, 1H; C7-H), Compound aS_LaR_{Pd}-**10**: δ = 8.17 (d, ^3J(H,H) = 8 Hz, 1H; C4′-H), 8.05 (d, ^3J(H,H) = 8 Hz, 1H; C4-H), 7.94 (d, ^3J(H,H) = 8 Hz, 1H; C5-H), 7.80 (d, ^3J(H,H) = 8 Hz, 1H; C3′-H), 7.14 (d, ^3J(H,H) = 8 Hz, 1H; C8′-H), 5.96 (d, ^3J(H,H) = 8 Hz, 1H; C8-H); 5.70 (simul. dddd, ^3J(H,H) = 6.0, 6.4, 13.1, 14.3 Hz, 1H; allyl C2-H), 3.66 (simul. ddd, ^2J(H,H) = 1.0, ^3J(H,H) = 6.4, ^4J(H,H) = 1.0 Hz, 1H; allyl CH*syn, cis* ^{31}P), 3.61 (s, 3H, OCH_3), 3.098 (simul. ddd, ^2J(H,H) = 1.0 ^3J(H,H) = 13.1, ^3J(H,P) = 9.7 Hz, 1H; allyl CH*anti, trans* ^{31}P), 3.085 (simul. dddd, ^2J(H,H) = 1.0, ^3J(H,H) = 6.0, ^3J(H,P) = 9.5, ^4J(H,H) = 1.0 Hz, 1H; allyl CH*syn, trans* ^{31}P), 2.48 (simul. dd, ^2J(H,H) = 1.0, ^3J(H,H) = 14.3 Hz, 1H; allyl CH*anti, cis* ^{31}P); compound aS_LaS_{Pd}-**10**: δ = 8.20 (d, ^3J(H,H) = 8 Hz, 1H; C4′-H), 8.04 (d, ^3J(H,H) = 8 Hz, 1H; C4-H), 7.93 (d, ^3J(H,H) = 8 Hz, 1H; C5-H), 7.89 (d, ^3J(H,H) = 8 Hz, 1H; C3′-H), 6.94 (d, ^3J(H,H) = 8 Hz, 1H; C8′-H), 5.94 (d, ^3J(H,H) = 8 Hz, 1H; C8-H), 5.22 (simul. dddd, ^3J(H,H) = 6.0, 6.0, 14.0, 14.3 Hz, 1H; allyl C2-H), 3.80 (simul. ddd, ^2J(H,H) = 1.0, ^3J(H,H) = 14.3, ^3J(H,P) = 9.0 Hz, 1H; allyl CH*anti, trans* ^{31}P), 3.73 (s, 3H, OCH_3), 3.43 (simul. ddd, ^2J(H,H) = 1.0, ^3J(H,H) = 6.7, ^4J(H,H) = 1.0 Hz, 1H; allyl CH*syn, cis* ^{31}P), 2.89 (simul. dd, ^2J(H,H) = 1.0, ^3J(H,H) = 14.0 Hz, 1H; allyl CH*anti, cis* ^{31}P), 2.80 (simul. dddd, ^2J(H,H) = 1.0, ^3J(H,H) = 6.0, ^3J(H,P) = 6.0, ^4J(H,H) = 1.0 Hz, 1H; allyl CH*syn, trans* ^{31}P); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2): aS_LaR_{Pd}-**10** and aS_LaS_{Pd}-**10**: δ = 143.1 (^2J(C,P) = 27 Hz; C1), 136.1 (d, ^1J(C,P) = 2 Hz; C2), 134.2 (C9′), 133.8 (d, ^2J(C,P) = 13 Hz; C*ortho*), 133.4 (C5′-H), 133.0 (C10′), 132.8 (C9), 132.7 (C10), 132.3 (br d, ^2J(C,P) = 19 Hz; C*ortho*), 131.4 (d, ^3J(C,P) = 7 Hz; C4-H), 130.5 (C*para*), 130.1 (d, ^3J(C,P) = 11 Hz; C*meta*), 131.0 (d, ^3J(C,P) = 11 Hz; C*meta*), 129.2 (C6), 129.1 (C5), 128.7 (C7), 128.6 (C*para*), 127.9 (C3), 126.3 (C6′, C8′), 125.5 (C8-H), 121.7 (C2 allyl), 116.5 (C3′), 105.4 (C1′), 57.30 (OCH_3); aS_LaR_{Pd}-**10** 155.8 (C2′)134.8 (C4′), 129.5 (C7′), 100.6 (allyl C*trans* ^{31}P),59.1 (allyl C*cis* ^{31}P); aS_LaS_{Pd}-**10**: δ = 156.7 (C2′), 134.6 (C4′-H), 129.7 (C7′-H), 98.8 (allyl C*trans* ^{31}P),59.3 (allyl C*cis* ^{31}P); ^{31}P NMR (CD_2Cl_2, 202 MHz, 21 °C): 33.7 (s, aS_LaR_{Pd}-**10**), 32.7 (s, aS_LaS_{Pd}-**10**); MS (electrospray): *m*/*z*: 615.54 [*M* − OTf]$^+$; elemental analysis calcd for $C_{37}H_{30}O_4PSF_3Pd$ (765.09) (%): C 58.11, H 3.96; found: C 58.31, H 3.93.

1-[$^2H_1$]-cyclopentenyl pivalate 15: Cyclopent-2-enone (12.89 mL, 154 mmol) in Et_2O (125 mL) was added dropwise to a suspension of Li$Al[^2H_4]$ (2.21g, 52.6 mmol) in Et_2O (50 mL). After complete addition, water (12 mL) was added dropwise (CAUTION!) followed by $MgSO_4$ (ca. 10 g). The resulting suspension was stirred overnight and then filtered through Celite, the filtrate concentrated in vacuo (250 mmHg, 40 °C) to about 15 mL, distilled and the fraction boiling at 59 °C at about 20 mmHg collected to afford (±)-1-[$^2H_1$]-cyclopent-2-en-1-ol, (10.5g, 83 %) as a colourless liquid. To a stirred solution of (±)-1-[$^2H_1$]-cyclopent-2-en-1-ol (2.0 g, 23.5 mmol) in CH_2Cl_2 (100 mL) was added Et_3N (3.52 mL, 25.3 mmol), DMAP (60 mg, 0.54 mmol) and, finally, Me_3CCOCl (2.90 mL, 23.6 mmol). After 19 h, the reaction mixture was poured into water (100 mL), extracted with CH_2Cl_2 (150 mL), dried ($MgSO_4$) and concentrated in vacuo to afford a pale yellow oil. This was purified by chromatography on silica gel (hexanes/EtOAc, 12:1) and then by kugelrohr distillation (oven T = 160 °C, ca. 20 mmHg) to give (±)-**15** (3.37 g, 85 %) as a colourless oil, tlc, hexane/EtOAc, 12:1, R_f = 0.5. ^{1}H NMR ($CDCl_3$, 270 MHz, 21 °C, TMS): δ = 6.1 (m, 1H; C3-H), 5.8 (m, 1H; C2-H), 2.5 (m, 1H; C4-H*syn*), 2.3 (m, 2H; C4-H*anti*, C5-H*anti*), 1.75 (m, 1H; C5-H*syn*), 1.2 (s, 1H; C(CH_3)$_3$); ^{2}H NMR ($CHCl_3$,46 MHz, 21 °C, $CDCl_3$): δ = 5.6 (br s, C1-^{2}H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 21 °C, TMS): δ = 178.6 (C=O), 137.2 (C3), 129.4 (C2), 89.9 (t, ^1J(C,D) = 24 Hz, C1), 38.6 (*C*(CH$_3$)$_3$), 31.1 (C4), 29.7 (C5), 27.2 (C(*C*H$_3$)$_3$).

Palladium-catalysed allylic alkylation with memory effect: The following procedure (Table 1, entry 3) is typical: In a Schlenk tube, [Pd(η^3-C_3H_5)[(*S*)-**7**)]][O_3SCF_3] (+)-(**9**) (23.02 mg, 0.030 mmol) was stirred, under N_2, in THF (1.0 mL) at 25 °C for 20 min to afford an orange solution/brown dispersion. In a separate Schlenk tube, (±)-**15** (100 mg, 0.59 mmol) was added through microsyringe to a solution of [NaCH(CO_2CH_3)$_2$] (**13**) (205.0 mg, 1.33 mmol) in THF (4.1 mL). The solution of complex **9** was added resulting in rapid formation of a bright orange, slightly viscous solution. TLC (hexane/EtOAc, 12:1) after 5 min indicated the presence of **17** (R_f = 0.34) and absence of (±)-**15** (R_f = 0.50). The reaction mixture was immediately quenched by addition of aqueous NH_4Cl (10 mL, 2.65 M) and extracted with CH_2Cl_2 (4 × 25 mL). The combined extracts were dried ($MgSO_4$) and evaporated to afford a pale brown oil and solid. This was applied to a pre-solvated silica gel column (2.5 × 9 cm) and eluted with hexane/EtOAc, 12:1, collecting 14 mL fractions (gravity column). Fractions 4–7 (containing material of R_f = 0.34) were evaporated to afford a mixture of (1′)[$^2H_1$]- and (3′)[$^2H_1$]-dimethyl (2′-cyclopentenyl)methanedicarboxylate α-**17** and γ-**17**, respectively, as a colourless oil (94.1 mg, 80.1 %). ^{2}H NMR ($CHCl_3$, 46 MHz, 21 °C, $CDCl_3$): δ = 5.85 (br s, C3′-^{2}H; γ-**17**), 3.34 (br s, C1′-^{2}H; α-**17**); ratio α/γ = 0.90:0.10.

Analysis of regioisotopomeric enantiomers of ***17*** *by ^{13}C NMR spectroscopy*: α/γ-**17** (40 mg, 0.20 mmol) was dissolved in C_6D_6 (0.70 mL) and then (+)-[Eu(hfc)$_3$] (132.0 mg, 0.11 mmol; hfc = 3-(heptafluoropropylhydroxymethylene)-D-camphorate) was added to give a clear bright yellow solution. The enantiomer ratios of the isotopomers were estimated by integration of the ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C) spectrum and then applying correction factors determined by reference to a 1.02:1.00 sample of racemic α-**17**/γ-**17**. The following relative integrals (%) were obtained: (*S*)-α/γ-**17** (45.5 %) 54.06, 53.57 ((CO_2CH_3)$_2$); (*R*)-α/γ-**17** (54.5 %) 53.86, 53.72 ((CO_2CH_3)$_2$); (*S*)-α-**17** (42 %) 33.63 (C4′), 30.79 (C5′); (*R*)-α-**17** (46 %) 33.33 (C4′), 30.37 (C5′), (*S*)-γ-**17** (4 %) 33.51 (C4′), 30.91 (C5′), (*R*)-γ-**17** (8 %) 33.21 (C4′), 30.49 (C5′).

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[1] a) J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, **1995**; for reviews of *asymmetric* allylic alkylation see: b) G. Consiglio, R. M. Waymouth, *Chem. Rev.* **1989**, *89*, 257–276; c) C. G. Frost, J. Howarth, J. M. J. Williams, *Tetrahedron: Asymmetry* **1992**, *3*, 1089–1122; d) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96,* 395–422.

[2] J. C. Fiaud, J. L. Malleron, *Tetrahedron Lett.* **1981**, *22*, 1399–1402, see also: B. M. Trost, N. R.Schmuff, *Tetrahedron Lett.* **1981**, *22*, 2999–3000.

[3] a) B. M. Trost, R. C. Bunt, *J. Am. Chem. Soc.* **1996**, *118,* 235–236; b) T. Hayashi, M. Kawatsura, Y. Uozumi, *J. Am. Chem. Soc.* **1998**, *120*, 1681–1687; c) G. C. Lloyd-Jones, S. C. Stephen, *Chem. Eur. J.* **1998**, *4*, 2539–2549; d) G. C. Lloyd-Jones, S. C. Stephen, *Chem. Commun.* **1998**, 2321–2322; e) C. P. Butts, J. Crosby, G. C. Lloyd-Jones, S. C. Stephen, *Chem. Commun.* **1999**, 1707–1708; f) A. J. Blacker, M. L. Clarke, M. S. Loft, J. M. J. Williams, *Org. Lett.* **1999**, *1*, 1969–1971; g) U. Burckhardt, M. Baumann, A. Togni, *Tetrahedron: Asymmetry* **1997**, *8*, 155–159.

[4] T. Hayashi, M. Kawatsura, Y. Uozumi, *Chem. Commun.* **1997**, 561 – 562.
[5] "MOP" (or "MeO-MOP") is 2-(diphenylphosphanyl)-2′-methoxy-1,1′-binaphthalene, see: T. Hayashi, *Acta. Chem. Scand.* **1996**, *50*, 259 – 266, and references therein.
[6] However, more recently, PCy_3 has been shown to exert a powerful memory effect—see ref. [3f].
[7] For a designed exception see: a) R. Prétôt, A. Pfaltz, *Angew. Chem.* **1998**, *110*, 337 – 339; *Angew. Chem. Int. Ed.* **1998**, *37*, 323 – 325; b) R. Prétôt, G. C. Lloyd-Jones, A. Pfaltz, *Pure Appl. Chem.* **1998**, *70*, 1035 – 1040.
[8] "MAP" (**7**), is 2′-(dimethylamino)-2-(diphenylphosphanyl)-1,1′-binaphthalene, see: a) Š. Vyskočil, M. Smrčina, V. Hanuš, M. Polášek, P. Kočovský, *J. Org. Chem.* **1998**, *63*, 7738 – 7748; b) Š. Vyskočil, M. Smrčina, P. Kočovský, *Tetrahedron Lett.* **1998**, *39*, 9289 – 9292; for an independent, practically identical synthesis of MAP, see: c) K. Ding, Y. Wang, H. Yun, J. Liu, Y. Wu, M. Terada, Y. Okubo, K. Mikami, *Chem. Eur. J.* **1999**, *5*, 1734 – 1737.
[9] a) Y. Uozumi, T. Hayashi, *Tetrahedron Lett.* **1993**, *34*, 2335 – 2338; b) Y. Uozumi, T. Hayashi, *J. Synth. Org. Chem. Jap.*, **1993**, *51*, 1087 – 1096; c) Y. Uozumi, K. Kitayama, T. Hayashi, *Tetrahedron: Asymmetry* **1993**, *4*, 2419 – 2422; d) Y. Uozumi, K. Kitayama, T. Hayashi, K. Yanagi, E. Fukuyo, *Bull. Chem. Soc. Jap.* **1995**, *68*, 713 – 722; e) see also ref. [4].
[10] T. Hayashi, H. Iwamura, M. Naito, Y. Matsumoto, Y. Uozumi, M. Miki, K. Yanaga, *J. Am. Chem. Soc.* **1994**, *116*, 775 – 776.
[11] See however: a) M. Nandi, J. Jin, T. V. RajanBabu, *J. Am. Chem. Soc.* **1999**, *121*, 9899 – 9900; b) N. Nomura, J. Jin, H. Park, T. V. RajanBabu, *J. Am. Chem. Soc.* **1998** *120*, 459 – 460.
[12] a) P. Kočovský, Š. Vyskočil, I. Císařová, J. Sejbal, I. Tišlerová, M. Smrčina, G. C. Lloyd-Jones, S. C. Stephen, C. P. Butts, M. Murray, V. Langer, *J. Am. Chem. Soc.* **1999**, *121*, 7714 – 7715; b) P. Kočovský, Š. Vyskočil, A. V. Malkov, G. C. Lloyd-Jones, *Pure Appl. Chem.* **1999**, *71*, 1425 – 1433; for other examples of this coordination mode see: c) S. H. Bergens, P. Leung, B, Bosnich, A. L. Rheingold, *Organometallics* **1990**, *9*, 2406 – 2408; d) N. M. Brunkan, P. S. White, M. R. Gagné, *J. Am. Chem. Soc.* **1998**, *120*, 11 002 – 11 003.
[13] Hayashi et al. have reported that the allylic alkylation of *racemic* D-labelled cyclohexenyl acetate using a Pd-(*R*)-MOP based complex, occurs with high *regiochemical* retention. However, the differing outcomes from the enantiomeric manifolds of the reaction were not explored, despite enantiomerically pure catalyst being employed; see reference [3b].
[14] These differences are reflected in the degree of pyramidalisation at *ipso*-C1′ (cf. valence angle Pd-C1′-C(1): 109.2° (**10**) and 110.5° (**9**)), the Pd−C1′/Pd−C2′ bond lengths: 2.34/2.47 Å (**10**) and 2.26/2.75 Å (**9**) and the Pd-C1′-C2′ angles (78° (**10**)/94° (**9**)). Only one diastereoisomer of **10** is present (albeit disordered) in the solid state. However, differences in diastereoisomer preferences between **9** and **10** in the solid state are likely to be dictated by crystal packing forces rather than by any interpretable intramolecular bias.
[15] This nomenclature for the absolute configuration for square-planar π-allyl metal complexes containing *meso*-type π-allyl and two different ligands was suggested by Hayashi, see ref. [3b]. For the axis perpendicular to the square plane, we assign highest priority to the central allyl CH (which lies above or below the square plane) and thus, for complexes **9** and **10**, when this axis is aligned vertically behind the horizontal P−C1′ axis, if P is on the left and C1′ on the right, then the aS_{Pd} (or *P*-helicity) diastereoisomer has the allyl central CH above the square plane.
[16] Location of the C1′ signals, which were broad and weak, was rather difficult. The assignment was confirmed by correlation with C8′-*H* and C3′-*H* (FGHMBC). A strong cross-peak between C8-*H* and *C4′-H*, unlikely to arise from scalar coupling ($^3J_{C,H}$), was observed (FGHMBC). For leading references on through-space coupling see: H. Schröder, E. Haslinger, *Magn. Reson. Chem.* **1994**, *32*, 12 – 15. Van der Waals radii contact is a likely mechanism for through-space coupling and this result, together with the high field anisotropic shift of C(8)-*H* ($\delta = 6.30$), supports there being a quite similar geometry in solution to that observed in the X-ray structure (see ref. [12a]).
[17] PECSY, TOCSY, NOE-difference, PNOSY, $^1H\{^{31}P\}$-difference, direct C – H correlation, FGHMBC and FGHSQC experiments were run at 500 MHz (^1H) in nitrogen-saturated CD_2Cl_2. In assignment of structure, some experiments were run at −25 °C to avoid complications of diastereoisomer interconversion.
[18] It should be noted that there are no strong anisotropic shifts of aromatic protons (all $\delta > 6.9$) in the ^1H NMR spectrum of the *monodentate* complex [(π-cyclohexenyl)(Cl)Pd-(*P*)-MOP], see supporting information in ref. [3b], nor in the *monodentate* complex [(π-prenyl)(Cl)Pd-(*P*)-MOP] ($\delta = 6.96 – 8.04$) see ref. [10]. Both of these complexes were prepared by addition of MOP to dimeric (Cl)Pd-allylic precursors.
[19] Two-dimensional phase-sensitive NOE spectra (PNOSY, 500 MHz, CD_2Cl_2, N_2-sat, $\tau_m = 300$ ms) allow distinction of chemical exchange (positive phase) cross peaks from intramolecular NOE and exchange-NOE (negative phase) and scalar coupling (dispersive phase). Quantitative rate data may be extracted from the cross-peak three-dimensional integrals by analysis (usually computerised) of the exchange matrix, see for example: E. W. Abel, I. Moss, K. G. Orrell, V. Sik, D. Stephenson, *J. Chem. Soc. Dalton Trans.* **1987**, 2695 – 2701.
[20] A. Gogoll, J. Örnebro, H. Grennberg, J.-E. Bäckvall, *J. Am. Chem. Soc.* **1994**, *116*, 3631 – 3632.
[21] a) Pd−C rotation in an η^1-allyl intermediate would be expected to be accompanied by C−C rotation and thus *syn* – *anti* exchange, but this was not detected at either allyl terminus. b) The ^1H and ^{13}C NMR chemical shifts of the *syn* and *anti* methyl groups in the NMe_2 groups are isochronous in each diastereoisomer (this was confirmed by observation of one $^3J_{C,H}$ and two $^1J_{C,H}$ cross peaks from the ^1H dimension to a single signal in the ^{13}C dimension in the FGHMBC spectra). Thus, although the C1′−Pd bond should cause restricted rotation about what is formally an N=C2′ double bond, there must in fact be rotation to allow interconversion of the *syn* and *anti* methyl groups faster than the NMR time scale. c) The ^{13}C chemical shifts of C1′ are broad in both diastereoisomers, suggesting a C1′−Pd bond oscillation close to the NMR time-scale. These last two points are indicative of equilibrium between bidentate (*P,C*)- and monodentate (*P*)-coordination mode of the ligand **7** and this was observed in the analogous [MAP(**7**)-$PdCl_2$] complex, see ref. [12a].
[22] Torquoselectivity refers to the rotational selectivity in the displacement of the η^3-Pd-π-[C1−C2−C3] allyl unit about the Pd – allyl axis as the nucleophile attacks C1 or C3 to generate an η^2-Pd-π-[C3=C2]-C1 or η^2-Pd-π-[C1=C2]−C3 alkene complex, respectively. For discussions see: a) A. Pfaltz, *Acta Chem. Scand.* **1996**, *50*, 189 – 194 and references therein; b) J. M. Brown, D. I. Hulmes, P. J. Guiry, *Tetrahedron* **1994**, *50*, 4493 – 4506; c) S. Ramdeehul, P. Dierkes, R. Aguado, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. A. Osborn, *Angew. Chem.* **1998**, *110*, 3302 – 3304; *Angew. Chem. Int. Ed.* **1998**, *37*, 3118 – 3121.
[23] a) B. M. Trost, R. C. Bunt, *J. Am. Chem. Soc.* **1994**, *116*, 4089 – 4090; b) E. J. Bergner, G. Helmchen, *Eur. J. Org. Chem.* **2000**, 419 – 423, and references therein; c) P. Dierkes, S. Ramdeehul, L. Barloy, A. De Cian, J. Fischer, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. A. Osborn, *Angew. Chem.* **1998**, *110*, 3299 – 3301; *Angew. Chem. Int. Ed.* **1998**, *37*, 3116 – 3118; d) A. Saitoh, M. Misawa, T. Morimoto, *Tetrahedron: Asymmetry*, **1999**, *10*, 1025 – 1028.
[24] That is to say it is not evident whether there is a single reaction manifold and the ligand (L*) induces low selectivity or there is a multiple manifold (i.e. a memory effect).
[25] The ratios of the *four* enantiomeric regioisotopomers, (*R*)-*α*-**17**, (*R*)-*γ*-**17**, (*S*)-*α*-**17** and (*S*)-*γ*-**17**, may be analysed by ^{13}C NMR spectroscopy in the presence of a chiral shift reagent. Based on an inversion-inversion sequence, the enantiomeric outcome of the reaction of *both* enantiomers of substrate can be studied simultaneously. Overall retention has been confirmed in the Pd-catalysed reaction of (*R*)-**15** with 2.25 equivalents of $NaCHE_2$ (5 mol% [(dppf)Pd(allyl)][OTf], THF, 25 °C, 60 sec.) which gave (*R*)-*α*-**17** and (*S*)-*γ*-**17** exclusively (> 96%). For some examples of reactions that do not proceed thorough inversion-inversion, see: a) I. Starý, P. Kočovský, *J. Am. Chem. Soc.* **1989**, *111*, 4981 – 4982; b) H. Kurosawa, S. Ogoshi, Y. Kawasaki, S. Murai, M. Miyoshi, I. Ikeda, *J. Am. Chem. Soc.* **1990**, *112*, 2813 – 2814; c) I. Starý, J. Zajíček, P. Kočovský, *Tetrahedron* **1992**, *48*, 7229 – 7250; d) H. Kurosawa, H. Kajimaru, S. Ogoshi, H. Yoneda, K. Miki, N. Kasai, S. Murai, I. Ikeda, *J. Am. Chem. Soc.* **1992**, *114*, 8417 – 8424; e) C. N. Farthing, P. Kočovský, *J. Am. Chem. Soc.* **1998**,

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120, 6661–6672; f) M. E. Krafft, A. M. Wilson, Z. Fu, M. J. Proctor, O. A. Dasse, *J. Org. Chem.* **1998**, *63*, 1748–1749.

[26] These effects were first reported in 1996 by Trost and Bunt (see ref. [3a]), and linked to the poor performance of the ligand **16** under more conventional conditions, compared to the outstanding selectivity under optimised conditions (see ref. [23a]).

[27] The origin of the memory effect, which manifests a dual and asymmetric manifold, is still a matter of debate. Asymmetric ion-pairing between nucleofuge and a Pd-allyl cation in which ligand **16** is bonded through both P donors was originally suggested by Trost et al. (see ref. [3a]); see also: a) B. M. Trost, R. C. Bunt, *J. Am. Chem. Soc.* **1998**, *120*, 70–79; b) B. M. Trost, X. Ariza, *J. Am. Chem. Soc.* **1999**, *121*, 10727–10737. We have suggested an alternative process in which the ionisation of the mismatched enantiomer of substrate is accompanied by (or prefaced by) a dissociation of one of the P donors (see ref. [3c, e].

[28] Negligible secondary kinetic isotope effects are observed in these reactions, see for example Table 1, entry 4.

[29] "re" is global regiochemical excess (%); re $(\alpha) = 100[(\alpha\text{-}\gamma)/(\alpha+\gamma)]$.

[30] These *ee* values are quoted in ignorance of the isotopic label, that is that which would be observed if unlabelled substrate **11** were employed. For the details of the *ee* determination, see the Experimental Section.

[31] $[Pd_2dba_3]\cdot CHCl_3$ can sometimes act as a source of chloride, see: O. Loiseleur, P. Meier, A. Pfaltz, *Angew. Chem.* **1996**, *108*, 218–220; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 200–202, and the results in Table 1, entry 2 could be due to the dba or the chloride.

[32] The equation $(k_m/k_{mm}) = [x_m/(1-x_m)]$; where $x_m = [(\alpha_{obs}-\alpha_{mm})/(\alpha_m-\alpha_{mm})]$ {where α_{obs}, α_{mm} and α_m are the mole fractions α-**17** observed with (±)-L, and from matched/mismatched manifolds with enantiomerically pure L, and x_m the mole fraction of substrate fractionated through matched manifold} can be applied providing that $\alpha_m \neq \alpha_{mm}$.

[33] G. R. Cook, P. S. Shanker, *Tetrahedron Lett*. **1998**, *39*, 4991–4994.

[34] a) P. E. Blöchl, A. Togni, *Organometallics* **1996**, *15*, 4125–4132; b) T. R. Ward, *Organometallics* **1996**, *15*, 2836–2838; c) H. Steinhagen, M. Reggelin, G. Helmchen, *Angew. Chem.* **1997**, *109*, 2199–2202; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2108–2110; for recent discussion of the relationship between Pd–C allyl bond lengths and regioselectivity of nucleophilic attack see: d) C. Jonasson, M. Kritikos, J.-E. Bäckvall, K. J. Szabó, *Chem. Eur. J.* **2000**, *6*, 432–436.

[35] H.-J. Gais, H. Eichelmann, N. Spalthoff, F. Gerhards, M. Raabe, *Tetrahedron: Asymmetry* **1998**, *9*, 235–248.

[36] Unlike **9** and **10**, which were studied under strictly "Pd^{II} conditions", $\mathbf{18}^+$ and $\mathbf{19}^+$ will be generated in the presence of Pd^0-MAP or Pd^0-MOP respectively. A mechanism involving π-allyl transfer from Pd^{II} to Pd^0 by S_N2 transfer can be ruled out on the grounds that a) MOP and MAP are bulky and bidentate and b) such a process would erode the strict inversion-inversion sequence used for ^{13}C NMR analysis and thereby alter the 50:50 product distribution (which is not observed). For discussion of π-allyl transfer from Pd^{II} to Pd^0 see K. L. Granberg, J.-E. Bäckvall, *J. Am. Chem. Soc.* 1992, **114**, 6858.

[37] C. Amatore, A. Jutand, G. Meyer, L. Mottier, *Chem. Eur. J.* **1999**, *5*, 466–473.

[38] This is based on the cyclohexenyl analogues of **21** (where L = PPh_3 or MOP and X = Cl) which have been studied by Hayashi et al., see ref. [3b]. The interconversion of enantiomers (L = PPh_3) and diastereoisomers (L = MOP) occurs very slowly, the key difference being the effect of excess L on the rate (10 mol% PPh_3, ca. 40-fold rate increase at −15 °C; 100 mol% MOP, ca. 1.2-fold at 20 °C). This difference was ascribed to the steric bulk of MOP inhibiting generation of $[(\pi\text{-cyclohexenyl})Pd(L)_2]^+[Cl]^-$.

[39] For a discussion see: B. Åkermark, S. Hasson, B, Krakenberger, A. Vitagliano, K. Zetterberg, *Organometallics.* **1984**, *3*, 679–682, and references therein.

[40] Although a latent selectivity of 52% *ee* is obtained in CH_2Cl_2, the latent selectivity in THF need not be of similar magnitude: I. J. S. Fairlamb, G. C. Lloyd-Jones, S. C. Stephen, unpublished results. Note that $[aR_La R_{Pd}]$ is the major diastereoisomer of [(π-cyclohexenyl)(Cl)Pd-(*P*)-**6**] (see ref. [3b]) and that this corresponds to that which would be expected in analogous complex **21**, if the major diastereoisomer in solution reflects the major enantiomer of product (**17**) generated.

[41] A long-lived palladium(**0**) complex of MOP (Pd/**6** = 1) has been reported by Hayashi et al. (see ref. [3b]); this behaviour contrasts the analogous but unstable PPh_3 complex (P/Pd = 1) which rapidly disproportionates. The stability of the MOP complex was ascribed to bidentate (*P,C*)-coordination. Based on the high-field ^1H NMR chemical shifts of C7′-H ($\delta = 6.00$) and C8′-H ($\delta = 6.22$), the C7′=C8′ unit of the naphthyl ring was assigned as the site of (η^2-Pd) coordination. Low chemical shifts of both C8-H and C8′-H are observed in complex **10** (C8-H, $\delta = 5.86$; C8′-H, $\delta = 6.88/7.15$), **9** (C8-H, $\delta = 6.30/6.32$; C8′-H, $\delta = 6.60/6.36$) and MAP-$PdCl_2$ (C8-H, $\delta = 6.33$; C8′-H, $\delta = 6.58$, see ref. [12a]). We ascribe these high-field shifts to anisotropic effects of the naphthyl rings (see complex **9**, Figure 3). Oxidative addition of cyclopentenyl pivalate **11** to Pd^0 complexes of MOP or MAP could thus occur from either a bidentate (*P,C*)-[C7′=C8′] or (*P,C*)-[C1′=C2′] type complex (with a 1,3-Pd shift from the former) to give cations $\mathbf{18}^+$ and $\mathbf{19}^+$.

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