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Allyl, olefin, aryl and alkyl organometallic palladium complexes of 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholanyl]benzene

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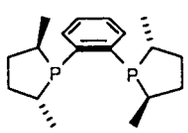
A series of organometallic chiral complexes of palladium containing the chelate Duphos, 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholanyl]benzene **1**, have been prepared. These include the 1,3-diphenylallyl cationic compound, [Pd(PhCHCHCHPh)(**1**)][CF_3SO_3] **2**, the palladium(0) fumaronitrile complex [Pd(NCCH=CHCN)(**1**)] **3**, and the pentafluorophenyl derivatives [Pd(R)(C_6F_5)(**1**)] (R = Me **4a**, Et **4b**, or Bu **4c**). The solid-state structures of **2** and **4a** have been determined by X-ray diffraction. The structure of complex **4a** deviates markedly from the expected square planar geometry. Duphos **1** affords a *ca.* 98% enantiomeric excess in the enantioselective allylic alkylation reaction of a 1,3-diphenylallyl precursor. Detailed ^{1}H and ^{13}C NMR results are reported.

One finds an ever-increasing number of chiral bidentate auxiliaries which show modest-to-excellent specificity in the general area of enantioselective homogeneous catalysis.[1–3] Primary amongst these are the bis-phosphine atropisomeric compounds 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (Binap)[4] and Biphep (see ref. 5) along with an increasing selection of oxazoline-based chelates containing either bis-oxazoline nitrogen donors or phosphinooxazoline, *i.e.* mixed co-ordination sphere chelates.[6] The cyclic bis-phosphine Duphos, **1**, represents



(*R*,*R*)-Duphos **1**

a relatively new addition which has been demonstrated to be successful in enantioselective hydrogenation reactions.[7] We report here on the synthesis and structures of several new organometallic Duphos complexes of palladium and suggest that these molecules demonstrate several interesting features.

Results and discussion

The organometallic Pd–Duphos complexes were prepared, in good yield, as shown in Scheme 1. The standard enantioselective allylic alkylation reaction[8] using a 1,3-diphenyl precursor and a malonate nucleophile is described in the Experimental section. The allyl complex [Pd(PhCHCHCHPh)(**1**)][CF_3SO_3] **2** and the methyl complex [Pd(Me)(C_6F_5)(**1**)] **4a** afforded suitable crystals and their structures were determined *via* X-ray diffraction. To the best of our knowledge these are the first reported solid-state structures of Pd–Duphos complexes.

X-Ray crystallography

The structure of the cationic complex **2** is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The immediate co-ordination sphere of **2** consists of the two P-donors of the chiral auxiliary and the 1,3-diphenylallyl anion. Sterically, the Duphos auxiliary creates a relatively small impression in that (i) the two Pd–P separations, *ca.* 2.28 Å, are almost identical suggesting little or no differentiation of the two sides of the cation and (ii) the two Pd–C(terminal) bond lengths, *ca.* 2.22–2.24 Å, are not significantly different. Moreover, all of these distances are rather standard.[10] Nevertheless, we note that the separations between C18 (a proximate Duphos methyl group) and (i) the allyl terminus C1L, 3.96 Å, and (ii) the proximate allyl-phenyl carbons C10L, *ca.* 3.9 Å, and C11L, *ca.* 3.6 Å, are both shorter than the corresponding separations between C6 (the second proximate Duphos methyl group) and

Table 1 Selected bond lengths [Å] and angles [°] with e.s.d.s in parentheses for complexes **4a** and **2**

Complex **4a**		Complex **2**	
Pd(1)–C(1L′)	2.091(7)	Pd(1)–C(2L)	2.190(6)
Pd(1)–C(1L)	2.189(5)	Pd(1)–C(3L)	2.221(6)
Pd(1)–P(1)	2.2502(19)	Pd(1)–C(1L)	2.238(5)
Pd(1)–P(2)	2.2863(18)	Pd(1)–P(2)	2.2794(14)
		Pd(1)–P(1)	2.2855(14)
		C(1L)–C(2L)	1.417(9)
		C(2L)–C(3L)	1.389(8)
C(1L′)–Pd(1)–C(1L)	87.0(2)	C(3L)–Pd(1)–C(1L)	66.3(2)
C(1L′)–Pd(1)–P(1)	167.4(2)	C(3L)–Pd(1)–P(2)	167.85(17)
C(1L)–Pd(1)–P(1)	91.65(16)	C(1L)–Pd(1)–P(2)	102.55(17)
C(1L′)–Pd(1)–P(2)	96.13(18)	C(3L)–Pd(1)–P(1)	103.71(17)
C(1L)–Pd(1)–P(2)	175.57(16)	C(1L)–Pd(1)–P(1)	167.60(18)
P(1)–Pd(1)–P(2)	85.93(6)	P(2)–Pd(1)–P(1)	86.66(5)

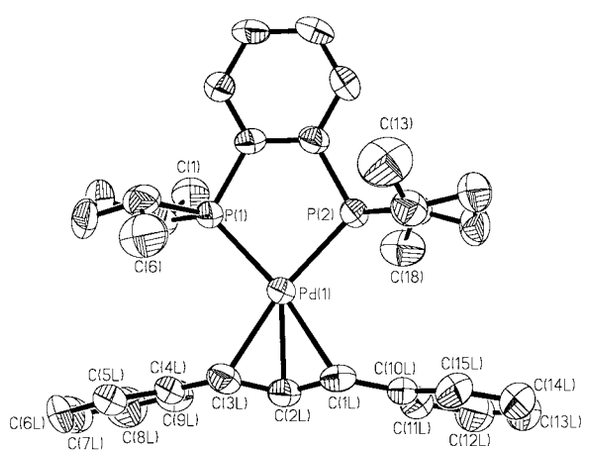
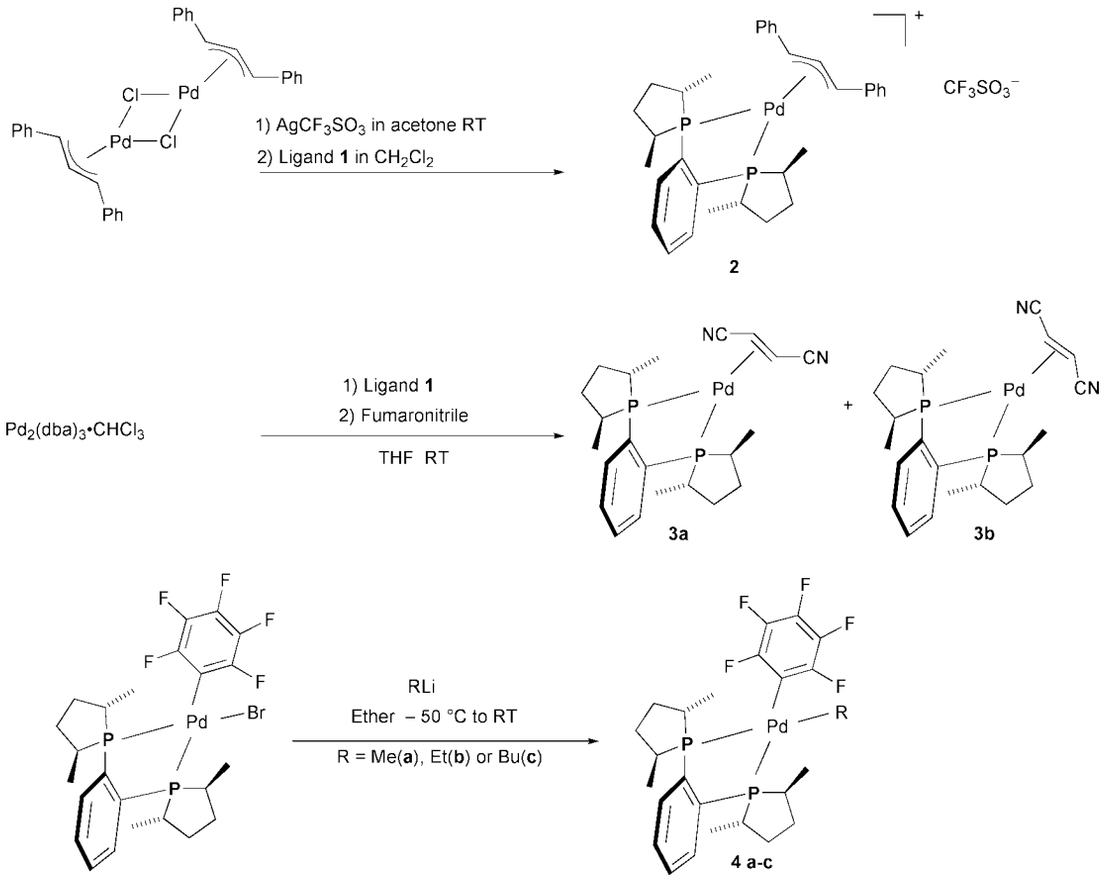
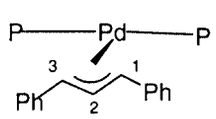


Fig. 1 An ORTEP[9] plot showing the allyl cation of complex **2**.



Scheme 1 Synthesis of the complexes.

(i) the allyl terminus, C3L, 4.27 Å, and (ii) the phenyl carbons C4L, 4.4 Å, and C5L, 4.1 Å, so that subtle distinctions exist between the two sides of the allyl ligand with respect to possible steric effects. Further, if one defines a plane containing the two P-donors and the metal, then the two terminal allyl carbons are found as shown in **5**. This type of modest rotation (in this case counter-clockwise) may arise in order to minimise the allyl phenyl/Duphos methyl group steric interaction.



5, fragment of **2**, C1L is *ca.* 0.32 Å and C3L *ca.* 0.254 Å above the P–Pd–P plane

The solid-state structure of the pentafluorophenyl complex [Pd(Me)(C_6F_5)(**1**)] **4a** is shown in Fig. 2. The immediate co-ordination sphere consists of the two Pd–P Duphos bonds and the Pd–C1L, methyl, and the Pd–C1L′, *ipso*-aryl interactions. Once again ligand **1** appears modest in size. The two Pd–P bond lengths, Pd–P1 2.250(2) and Pd–P2 2.286(2) Å, do not differ markedly although one might have expected the methyl ligand to exercise a strong *trans* influence. It is worth noting that the Pd–P separations in both the allyl compound **2** and the methyl-pentafluorophenyl complex, **4a**, are not very different.

Interestingly, the Pd–C1L bond length, 2.189(5) Å, for the methyl ligand represents the longest reported Pd–Me bond. For literature compounds with a Pd–Me bond *trans* to N-donors (TMEDA,[11a] bipy,[11b] P,N-chelate[12] or an S,N-chelate[13]), Pd–C lengths of *ca.* 2.02–2.09 Å are observed. Dekker *et al.*[14] report 2.068(2) Å in their [PdMeCl(PAN)], where PAN is the rigid dimethylamino-phosphino-naphthalene ligand 1-diphenylphosphino-8-dimethylaminonaphthalene. Alper and co-workers[15] find *ca.* 2.03 Å in a methylpalladium complex with a bridging formate. In two *cis*-dimethyl diphosphine derivatives, with the methyl ligand *trans* to the monodentate tertiary phosphine ligand,[16a] as well as in [Pd(Me)$_2$(dmpe)],[11a] the Pd–C methyl separations are *ca.* 2.09 Å. In cations [PdMe(dmpe)(amine)]$^+$ the values can be *ca.* 2.10–2.13 Å.[16b] Clearly, in all of these complexes the Pd–C distance is much shorter than that found for **4a**.

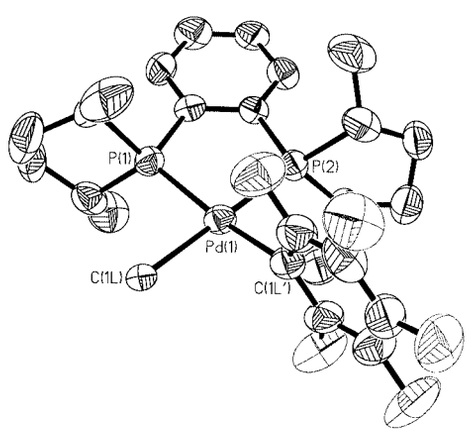
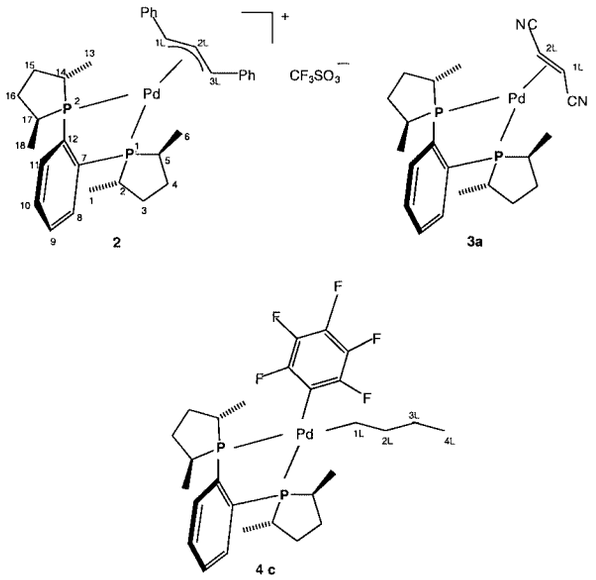


Fig. 2 An ORTEP plot showing complex **4a**.

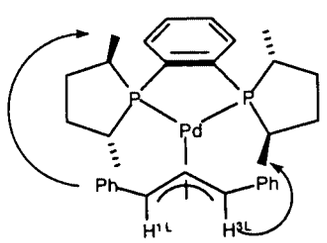
A closer look at the immediate co-ordination sphere of complex **4a** reveals that the methyl is −0.14 Å below, and the *ipso*-carbon C1L (of the C_6F_5 ligand) +0.44 Å above, the plane containing the two P-donors and the metal. This rather strong distortion from square planar geometry, which is reflected in the P(1)–Pd–C(1L′) angle, 167.4(2)°, may arise from the steric interaction between the C_6F_5 ligand and the proximate, *cis*, Duphos-methyl group. Consequently, although auxiliary **1** is small, its presence seems to have profound effects on the structure of this relatively simple molecule.

NMR Spectroscopy

Although the solid state structure of complex **2** is not especially informative, the solution ^{13}C NMR data clearly reveal asymmetry in the allyl bonding. The C1L resonance (see Scheme 2



Scheme 2 Numbering system.



6, 1,3-Diphenylallyl cation
indicating Me•••H3 NOE and short Me•••Ph interaction

for the numbering) appears at δ 93.1 whereas that for C3L, δ 82.8, appears at lower frequency suggesting that C1L is more "olefin-like" and thus more electrophilic. This electronic imbalance may result from the relatively short steric contact between the allyl-phenyl and a proximate Duphos-methyl group (left arrow in **6**) noted above. The ^{13}C assignment in **2** is based on (i) a detailed analysis of the Duphos-methyl groups using a ^{31}P–^{1}H correlation (see Fig. 3) plus COSY and NOESY methods to identify the protons and (ii) a ^{13}C–^{1}H correlation to connect the allyl protons to the appropriate carbons. A key aspect of the assignment involves the NOE from the H3L allyl proton to a proximate Duphos methyl (right arrow in **6**), as this allows a differentiation of the allyl termini. Similar differences in carbon chemical shift between allyl termini in 1,3-diphenylallyl palladium complexes have been reported,[17] and we show a selection of these values in Table 2. In the allylic alkylation reaction (shown in eqn. (1)) it is thought that the nucleophile will attack at the most electrophilic center.

In keeping with this idea we find the (*S*)-(1,3-diphenylallyl)-malonic acid dimethyl ester in *ca.* 98% enantiomeric excess (ee), which could arise from attack at the high frequency allyl carbon. There appears to be no correlation between observed ee and $\Delta\delta$, *i.e.* the difference in chemical shift between the allyl termini; $\Delta\delta$ for the Duphos analog is smaller than that observed for either Binap or MeO-Biphep,[17c] but the observed ee using ligand **1** is larger. In contrast to other NOE studies,[18] we find relatively few short contacts between the allyl substrate and the chiral auxiliary, suggesting that, generally speaking, Duphos **1** is not a very "intrusive" ligand.

Table 2 Allyl ^{13}C NMR data[a] for [Pd(η^3-PhCHCHCHPh)(phosphine)]$^+$

Phosphine chelate	δ ^{13}C terminal C[b]	central C
(*R*,*R*)-Duphos	93.1, 82.8	113.7
(*S*,*S*)-Diop	95.2, 92.9	112.1
(*S*)-Binap	104.6, 87.2	111.3
(*S*)-MeO-Biphep	103.3, 84.8	109
	98.2, 90.7	107.0
(*R*,*S*)-Josiphos	96.4, 82.0	110.9
	90.2, 89.6	112.6

Diop = 4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane; for definition of Josiphos see refs. 17(*c*) and 18(*a*). The two sets of terminal carbon chemical shifts are due to the presence of diastereomers. [b] The higher frequency of the two ^{13}C signals is assigned to that terminus which experiences the stronger steric interactions. Literature data from refs. 17(*c*) and 18(*a*).

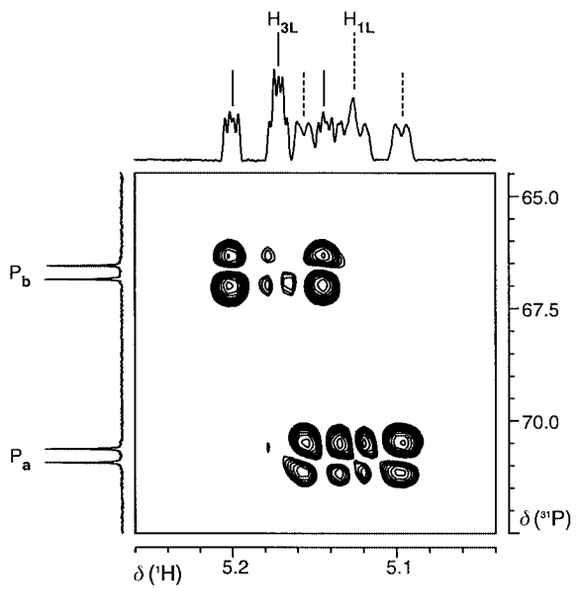
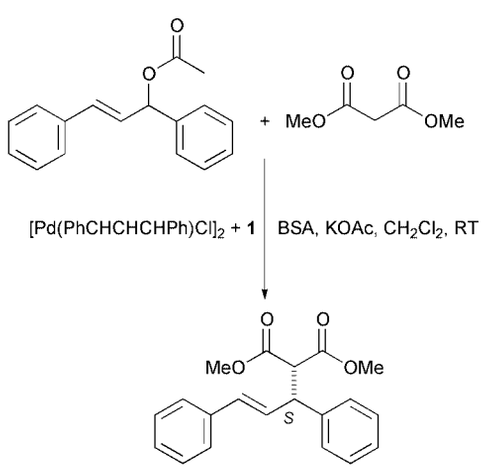


Fig. 3 ^{31}P–^{1}H Correlation showing the cross-peaks and spin–spin interactions which help to identify the terminal allyl protons of complex **2**. These terminal allyl protons, which correlate to their respective pseudo-*trans* P atoms, appear as triplets (similar ^{3}J(P,H) and ^{3}J(H,H) values) further split by long-range proton–proton and proton–phosphorus interactions. P_a and P_b correspond to P_1 and P_2, respectively.



(1)

The fumaronitrile palladium(0) complex, **3**, can be prepared from the moderately stable [Pd(dba)(**1**)] (dba = dibenzylidene acetone) and exists in two diastereomeric forms due to complexation of the two enantiotopic faces of the olefin. The ^{13}C NMR signals for CH-olefinic carbons are observed at relatively low

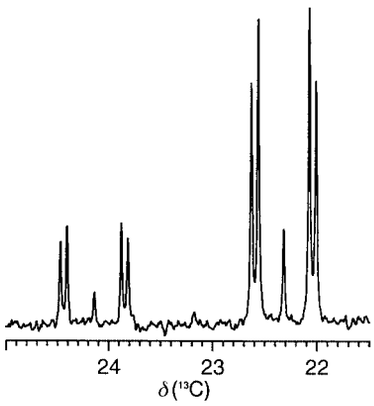


Fig. 4 Section of the ^{13}C NMR spectrum of both complexes **3a** and **3b** showing the second order AA′X character of the two olefinic ^{13}CH= resonances of the fumaronitrile ligands. The separation of the two most intense lines represents $^{2}J(P,C)_{cis} + {}^{2}J(P,C)_{trans}$. See ref. 24(*a*), p. 67 for related solutions.

frequency, at δ 24.1 and 22.3, consistent with previous observations for related complexes.[19,20] Interestingly, the fumaronitrile ^{13}CH resonances do not seem sensitive to the nature of the chelate, *i.e.* the values are very similar to those for N,N,[19] P,N [20] and P,P-chelates. These olefinic carbon resonances demonstrate strong second order character (see Fig. 4) as they represent the X part of an AA′X spin system.

The four-co-ordinate complexes **4** were prepared from the C_6F_5 bromo-analogs. These molecules were intended as models for the palladium catalysed enantioselective cross-coupling reaction in that they resemble possible intermediates shortly before reductive elimination. All of these C_6F_5 derivatives are stable in solution at ambient temperature over periods of hours.[21]

The NMR spectra for complexes **4a**–**4c** reveal several interesting features. They demonstrate restricted rotation about the Pd–*ipso*-C(aryl) bond, with the results that one observes five non-equivalent ^{19}F signals. Although this is not unusual in C_6F_5 complexes,[22,23] it is noteworthy as the Pd–Me ligand is modest in size. This is yet another hint that this Duphos auxiliary has more steric significance than the solid-state pictures indicate. The *o*-^{19}F spins couple to the *trans* ^{31}P selectively, *i.e.* the ^{31}P NMR spectra show a broadened doublet for the low frequency ^{31}P, *cis* to the pentafluorophenyl donor (resolved in **4b**), plus a complicated but symmetrical resonance for the high frequency ^{31}P spin, *trans* to the pentafluoroaryl donor. For **4a** this empiricism with respect to $^{4}J(P,F)_{trans}$ has been confirmed *via* an NOE from the methyl ligand to a proximate *cis*-Duphos methyl group, followed by a ^{31}P–^{1}H correlation to assign the Duphos methyl to its appropriate ^{31}P spin. For the directly bound σ carbon, one finds the usual[24] geometric dependence of $^{2}J(P,C)$, *e.g.* for **4a**, $^{2}J(P,C)_{trans} = ca.$ 101, $^{2}J(P,C)_{cis} = ca.$ 5 Hz. This methyl carbon resonance appears poorly resolved due to long-range interactions with the ^{19}F spins.

Conclusion

Despite its modest size, Duphos **1** is capable of inducing structural distortions in both complexes **2** and **4a**. Further, it would seem that these modifications are detectable in both the solid and solution states, *e.g.* distortions from square planarity and a long Pd–Me bond in **4a** plus selective differences in both ^{13}C chemical shifts and NOEs in **2**. As **1** is not very intrusive it will most likely efficiently transfer chirality where larger substrates and/or higher co-ordination numbers are involved.

Experimental

X-Ray crystallography

Yellow crystals of complex **2** were obtained by slow diffusion of hexane into a solution of the compound in dichloromethane. Diffraction data were collected on a Syntex P21 four-circle diffractometer at room temperature. The structure was solved by the Patterson method of SHELXS 86.[25] All non-hydrogen atomic positions were refined in the anisotropic mode by full-matrix least-squares calculations (SHELXL 93[26]) on F^2. Air stable, pale yellow crystals of **4a** were obtained by slow diffusion of pentane into a saturated CH_2Cl_2 solution. A prismatic single crystal was mounted on a glass capillary and a data set covering a hemisphere was collected on a Siemens SMART platform diffractometer equipped with a CCD detector. Data reduction plus corrections for Lorentz polarisation and absorption was performed using the programs SAINT[27] and SADABS.[28] The structure was solved by direct methods and refined by full-matrix least squares (*versus* F^2) with the SHELXTL program package.[29] Crystal data and structure refinements are summarised in Table 3.

CCDC reference number 186/2120.

See http://www.rsc.org/suppdata/dt/b0/b004148n/ for crystallographic files in .cif format.

Table 3 Summary of crystal data for [Pd(η^3-PhCHCHCHPh)(**1**)][CF_3SO_3] **2** and [Pd(Me)(C_6F_5)(**1**)] **4a**

	2	**4a**
Formula	$C_{34}H_{41}F_3O_3P_2PdS\cdot CH_2Cl_2$	$C_{25}H_{31}F_5P_2Pd$
M	833.99	594.84
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a/Å	13.0798(3)	10.635(2)
b/Å	11.4320(3)	14.242(2)
c/Å	13.2985(4)	17.120(3)
β/°	106.3940(10)	
V/Å^3	1907.66(9)	2593.1(7)
Z	2	4
T	RT	RT
μ/mm^{-1}	0.812	0.886
Reflections measured	19700	19409
Unique reflections	12152	5321
R(int)	0.0696	0.0885
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0554, 0.0967	0.0547, 0.1056

General

All manipulations were carried out under an argon atmosphere. THF and diethyl ether were distilled from sodium–benzophenone, CH_2Cl_2 from CaH_2 and hexane from sodium. (*E*)-3-Acetoxy-1,3-diphenyl-1-propene was prepared by standard procedures. All other chemicals were commercial products used as received. The chloro-bridged dimer [PdCl(η^3-PhCHCHCHPh)]$_2$ was prepared by standard methods. Routine ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker DPX-300 and 400 MHz spectrometers. Chemical shifts are given in ppm and coupling constants (J) in Hertz. The two-dimensional ^{1}H NOESY and ^{31}P–^{1}H correlation experiments were carried out at 400 MHz. Many of the ^{13}C resonances of complex **3** are somewhat complicated as they represent the X part of an AA′X spin system. For the olefinic carbons one can measure the sum [$^{2}J(P_A,C) + {}^{2}J(P_{A'},C)$] directly from the spectrum, however we have not undertaken a complete analysis and/or simulation. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

Syntheses

[Pd(η^3-PhCHCHCHPh)(1)][CF_3SO_3] 2. A solution of [PdCl(η^3-PhCHCHCHPh)]$_2$ (67 mg, 0.1 mmol) and $AgCF_3SO_3$ (51.4 mg, 0.2 mmol) in acetone (2 ml) was stirred for 1 h in the dark at room temperature. The AgCl formed was filtered through Celite and then washed with acetone. Ligand **1** (61.3 mg, 0.2 mmol) in 1 ml CH_2Cl_2 was added to the filtrate with stirring.

Stirring was continued for 30 min and the resulting yellow solution concentrated *in vacuo*. The crude yellow product was recrystallised from CH_2Cl_2 and hexane (1 mL CH_2Cl_2 condensed into the Schlenk tube and layered with hexane). Over a period of 24 h crystals were formed which were washed with hexane and dried in vacuum. Yield: 136 mg (90%). Calc. (found) for $C_{34}H_{41}F_3O_3P_2PdS{\cdot}CH_2Cl_2$: C, 50.04 (49.94); H, 5.16 (5.26%). MS (FAB^+, *m/z*): 606, $[M]^+$; and 307, $[\mathbf{1}]^+$. ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ 70.8 (d, J_{PP} = 49, P1) and 66.7 (d, J_{PP} = 49 Hz, P2). ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2): δ 13.9 (d, J_{PC} = 2, Me 1), 14.6 (d, J_{PC} = 3, Me 13), 16.8 (d, J_{PC} = 10, Me 18), 18.2 (d, J_{PC} = 11, Me 6), 34.5 (d, J_{PC} = 23, CH 2), 35.7 (d, J_{PC} = 5, CH_2 16) 37.1 (d, J_{PC} = 22, CH 14), 42.4 (d, J_{PC} = 23, CH 5), 44.2 (d, J_{PC} = 24, CH 17), 36.5 (2C, CH_2 3 and 4), 37.9 (CH_2 15), 82.8 (dd, J_{PC} = 28, 6, CH 3L), 93.1 (dd, J_{PC} = 25, 6, CH 1L), 113.7 (t, J_{PC} = 7.1, CH 2L), 127.5 (s, broad), 127.7 (t, J_{PC} = 3), 128.5 (t, J_{PC} = 3), 129.5 (t, J_{PC} = 3), 129.8 (t, J_{PC} = 2), 129.9 (t, J_{PC} = 2), 132.6 (m, 2C, CH 9 and 10), 134.2 (d, J_{PC} = 13, CH 8), 133.7 (d, J_{PC} = 3, CH 11), 137.0 (dd, J_{PC} = 6, 3), 138.4 (dd, J_{PC} = 6, 3), 140.9 (virtual t, $^1J_{PC} + {}^2J_{PC}$ = 66.4, C 7) and 140.5 (virtual t, $^1J_{PC} + {}^2J_{PC}$ = 66.4, C 12). ^1H NMR (400 MHz, CD_2Cl_2): δ −0.02 (m, 1 H, CH_2 16), 0.69 (m, 1 H, CH_2 4), 0.67 (dd, 3 H, CH_3 1, $J_{P1\text{-}H}$ = 16.1, $J_{H\text{-}H}$ = 7.0), 0.94 (dd, 3 H, CH_3 18, $J_{P2\text{-}H}$ = 20.4, $J_{H\text{-}H}$ = 7.0), 1.06 (dd, 3 H, CH_3 13, $J_{P2\text{-}H}$ = 15.81, $J_{H\text{-}H}$ = 7.2), 1.43 (dd, 3 H, CH_3 6, $J_{P1\text{-}H}$ = 20.7, $J_{H\text{-}H}$ = 7.0), 1.6–1.87 (m, 5 H, CH_2 3, 3′, 15,16′ and H 2), 2.0–2.20 (m, 2 H, CH_2 4′ and 15′), 2.45 (m, 1 H, H 17), 2.76–2.85 (m, 2 H, H5 and H14), 5.1–5.228 (m, 2 H, H1L and H3L), 6.84 (broad t, $J_{H\text{-}H}$ = 12.6 Hz, H2L), 7.31–7.43 (m, 2 H), 7.52–7.56 (m, 6 H) and 7.68–7.76 (m, 6 H).

[Pd(NCCHCHCN)(1)] 3a,3b. A mixture of $[Pd_2(dba)_3]{\cdot}CHCl_3$ (30 mg, 0.029 mmol) and ligand **1** (17.8 mg, 0.058 mmol) in THF (2 ml) was stirred at room temperature for 2 h. Fumaronitrile (4.5 mg, 0.058 mmol) was then added and stirring continued for 30 min. The resulting green-yellow solution was filtered through Celite, washed with THF and concentrated *in vacuo*. The crude yellow product was washed with ether (4 × 1 mL) and recrystallised from CH_2Cl_2 and hexane. Yield: 26 mg (91%). Calc. (found) for $C_{22}H_{30}N_2P_2Pd$: C, 53.83 (53.75); H, 6.16 (6.26); N, 5.71 (5.68%). MS (FAB^+, *m/z*): 490, $[M]^+$; 412.1, $[Pd(\mathbf{1})]^+$; and 307 $[\mathbf{1}]^+$. In the following "major" and "minor" refer to the more and less abundant components, respectively. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 67.4 (major) and 63.7 (minor). ^{13}C-{^1H} NMR (75.47 MHz, CD_2Cl_2): δ 15.0 (m, Me 1 and Me 13 major), 15.1 (m, Me 1 and Me 13 minor), 18.1 (m, Me 6 and Me 18 minor), 20.2 (m, Me 6 and Me 18 major), 22.3 (m, $^2J_{PC} + {}^2J_{PC}$ = 37, CH=, major), 24.1 (m, $^2J_{PC} + {}^2J_{PC}$ = 40, CH=, minor), 36.4 (m, CH_2 4 and CH_2 16 minor), 36.5 (m, CH_2 4 and CH_2 16 major), 36.9 (m, CH 2 and CH 14 major), 37.5 (broad s, CH_2 3 and CH_2 15 major), 37.6 (broad s, CH_2 3 and CH_2 15 minor), 38.7 (m, CH 5 and CH 17 major), 40.1 (m, CH 2 and CH 14 minor), 41.5 (m, CH 5 and CH 17 major), 123.1 (virtual t, $^3J_{PC} + {}^3J_{PC}$ = 6, CN major), 124.4 (virtual t, $^3J_{PC} + {}^3J_{PC}$ = 6, CN minor), 130.8 (s, CH 9 and CH 10 major and minor), 133.9 (m, CH 8 and CH 11 major and minor), 143.7 (dd, J_{PC} = 32, 30, C7 and C12 major) and 143.9 (dd, J_{PC} = 32, 30, C7 and C12 minor). ^1H NMR (300 MHz, CD_2Cl_2): δ 0.75 (dd, $J_{P\text{-}H}$ = 14.4, $J_{H\text{-}H}$ = 7.1, CH_3, 1 and 13 major), 0.84 (dd, $J_{P\text{-}H}$ = 14.4, $J_{H\text{-}H}$ = 7.1, CH_3, 1 and 13 minor), 1.34 (dd, $J_{P\text{-}H}$ = 20.6, $J_{H\text{-}H}$ = 7.0, CH_3, 6 and 18 major), 1.38 (dd, $J_{P\text{-}H}$ = 20.6, $J_{H\text{-}H}$ = *ca.* 7, CH_3, 6 and 18 minor), 1.55–2.35 (m, CH_2 3, 4, 15 and 16 major and minor), 2.6–2.75 (m, CH 2 and CH 14 major and minor), 2.75–2.9 (m, 4 H, CH 5 and CH 17 major and minor), 2.87 (m, CH=, minor), 3.07 (m, CH=, major), 7.55–7.68 (m, CH 9 and CH 10 major and minor), 7.74–7.80 (m,, CH 8 and CH 11 minor) and 7.80–7.88 (m, CH 8 and CH 11 major).

[Pd(alkyl)(C_6F_5)(1)] 4a–4c. To a solution of $[PdBr(C_6F_5)(\mathbf{1})]$ (30 mg, 0.45 mmol) in 2 mL of Et_2O at −50 °C was slowly added the corresponding alkyllithium (*ca.* 0.158 M solution in diethyl ether; 0.036 mmol, 0.8 equivalent). The white suspension was gently warmed to RT, filtered through Celite, and the solvent removed *in vacuo*. The residue was washed with pentane (5 × 2 mL) and the crude white product recrystallised from CH_2Cl_2 and pentane.

*Complex **4a**.* The crude product was recrystallised by slow diffusion of pentane into a CH_2Cl_2 solution. Over a period of 24 h crystals were formed which were washed with pentane. Yield: 19 mg (88%). Calc. (found) for $C_{25}H_{31}F_5P_2Pd{\cdot}H_2O$: C, 48.99 (48.61); H, 5.43 (5.13%). MS (FAB^+, *m/z*): 595, $[M]^+$; 580, $[Pd(C_6F_5)(\mathbf{1})]^+$; 412.1, $[Pd(\mathbf{1})]^+$; and 307, $[\mathbf{1}]^+$. ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ 66.1 (d, J_{PP} = 22.5, P2) and 71.3 (10 line multiplet, J_{PP} = 22.5 Hz, P1). ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2): δ −3.9 (broad dd, J_{PC} *ca.* 101 and *ca.* 5, Pd–Me), 14.46 (d, J_{PC} = 2.3), 14.53 (d, J_{PC} *ca.* 2), 17.3 (broad s), 17.4 (broad s), 36.27, 36.5, 36.62 (d, J_{PC} = 4.1), 36.9 (dd, J_{PC} = 19, 2), 37.12 (d, J_{PC} = 2.5), 37.55 (d, J_{PC} = 1.5), 37.87 (d, J_{PC} = 3.2), 40.88 (d, J_{PC} = 19), 42.46 (d, J_{PC} = 25), 131.07–132.22 (4 doublets, 4C), 133.38 (d, J_{PC} = 15.2), 133.57 (d, J_{PC} = 14.4 Hz) and 134–147 (multiplets, 6C). ^{19}F NMR (376 MHz, CD_2Cl_2): δ −112.75 (m, *o*, 1F), −115.56 (m, *o*, 1F), −164.28 (*p*, 1F), −164.8 (m, *m*, 1F) and −165.2 (m, *m*, 1F). (The ^{19}F resonances are complex multiplets which arise from ^2J(P,P) plus ^{19}F spin–spin coupling.) ^1H NMR (400 MHz, CD_2Cl_2): δ −0.25 (t, 3 H, CH_3, J_{PH} = 6.7), 0.85 (dd, 3 H, Me 13, $J_{P2\text{-}H}$ = 14.3, $J_{H\text{-}H}$ = 7.2), 0.98 (dd, 3 H, Me 1, $J_{P1\text{-}H}$ = 14.7, $J_{H\text{-}H}$ = 7.2), 1.22 (dd, 3 H, Me 18, $J_{P2\text{-}H}$ = 18.7, $J_{H\text{-}H}$ = 6.9), 1.39 (dd, 3 H, Me 6, $J_{P1\text{-}H}$ = 18.6, $J_{H\text{-}H}$ = 7.1 Hz), 1.56–1.89 (m, 4 H, H 3, 3′, 15 and 15′), 2.14–2.20 (m, 2 H, H 16 and 16′), 2.34–2.45 (m, 2 H, H 4 and 4′), 2.61–2.79 (m, 3 H, H 5, 14 and 17), 2.97 (m, 1 H, H 2), 7.62–7.65 (m, 2 H), 7.72 (m, 1 H) and 7.77–7.80 (m, 1 H).

*Complex **4b**.* ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ 63.79 (d, $J_{P\text{-}P}$ = 23.7 Hz with fine structure, P2) and 68.92 (14 line multiplet, P1). ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2): δ 10.0 (broad dd, J_{PC} *ca.* 101 and *ca.* 1.5, Pd–CH_2), 14.44 (d, J_{PC} = 1.3, Me 1), 14.69 (d, J_{PC} *ca.* 2, Me 13), 15.9 (d, J_{PC} = 5.5, CH_3), 17.12 (d, J_{PC} = 11.3, Me 6 or 18), 17.21 (dd, J_{PC} = 14, 3.5, Me 6 or 18), 35.58 (dd, J_{PC} = 23.3, 1, CH 5), 36.64 (broad s, CH_2 15), 36.8 (dd, J_{PC} *ca.* 16, 2, CH 14 or 17), 37.12 (d, J_{PC} = 2.8, CH_2 4), 37.50 (d, J_{PC} = 1.7, CH_2 16), 38.13 (d, J_{PC} = 2.8, CH_2 3), 40.76 (dd, J_{PC} = 16.7, 1, CH 14 or 17), 42.86 (dd, J_{PC} = 25.3, 0.8, CH 2), 130.9–132.2 (4 doublets, 4C), 133.37 (d, J_{PC} = 15), 133.52 (d, J_{PC} = 14.3) and 134–147 (multiplets, 6C). ^{19}F NMR (376 MHz, CD_2Cl_2): δ −112.99 (m, *o*, 1F), −115.66 (m, *o*, 1F), −164.35 (*p*, 1F) and −164.86 to −165.06 (m, *m*, 2F). (The ^{19}F resonances are complex multiplets which arise from ^2J(P,P) plus ^{19}F spin–spin coupling.) ^1H NMR (400 MHz, CD_2Cl_2): δ 0.82 (dd, 3 H, Me 13, $J_{P2\text{-}H}$ = 14, $J_{H\text{-}H}$ = 7.2 Hz), 0.98 (dd, 3 H, Me 1, $J_{P1\text{-}H}$ = 14.6, $J_{H\text{-}H}$ = 7.2), 1.04 (m, 3 H, CH_3), 1.22 (dd, 3 H, Me 18, $J_{P2\text{-}H}$ = 18.5, $J_{H\text{-}H}$ = 7), 1.30 (m, 1 H, CH_2), 1.39 (dd, 3 H, Me 6, $J_{P1\text{-}H}$ = 18.5, $J_{H\text{-}H}$ = 7 Hz), 1.50 (m, 1 H, CH_2), 1.56–1.7 (m, 2 H, CH_2 15 and 15′), 1.75–1.89 (m, 2 H, CH_2 4 and 4′), 2.14–2.20 (m, 2 H, CH_2 16 and 16′), 2.34–2.50 (m, 2 H, CH_2 3 and 3′), 2.5–2.69 (m, 2 H, CH 14 and CH 17), 2.79 (m,1 H, CH 5), 2.92 (m,1 H, CH 2), 7.57–7.66 (m, 2 H, CH 9 and 10), 7.71 (m, 1 H, CH 11) and 7.78 (m, 1 H, CH 8).

*Complex **4c**.* ^{31}P NMR (121.49 MHz, CD_2Cl_2): δ 62.9 (d, J_{PP} = 24 Hz, P2) and 68.4 (14 line multiplet, P1). ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2): δ14.18 (d, J_{PC} = 1, Me 1), 14.37 (d, J_{PC} = 1.4, Me 4L), 14.68 (d, J_{PC} *ca.* 2, Me 13), 17.0 (d, J_{PC} = 11, Me 6 or 18), 17.18 (dd, J_{PC} = 14, 3.5, Me 6 or 18), 17.85 (broad dd, J_{PC} *ca.* 99 and *ca.* 2, Pd–CH_2), 28.5 (d, J_{PC} = 12, CH_2 3L), 34.3 (d, J_{PC} = 4.8 Hz, CH_2 2L), 35.4 (dd, J_{PC} = 23.3, 1, CH 2), 36.6 (broad s, CH_2 15), 36.7 (dd, J_{PC} *ca.* 18, 2, CH 14 or 17), 37.13 (d, J_{PC} = 2.6, CH_2 16), 37.50 (d, J_{PC} = 1.8, CH_2 4), 38.13 (d, J_{PC} = 2.6, CH_2 3), 40.9 (dd, J_{PC} = 16, 0.8, CH 14 or 17), 42.86 (dd, J_{PC} = 25.1, 0.8, CH 5), 130.8–131.2 (4 doublets, 4C), 133.37 (d, J_{PC} = 15), 133.52 (d, J_{PC} = 14.3 Hz) and 134–147 (multiplets,

6C). ^{19}F NMR (376 MHz, CD_2Cl_2): δ −112.77 (m, *o*, 1F), −115.23 (m, *o*, 1F), −164.35 (*p*, 1F) and −164.9 to −165.1 (m, *m*, 2F). (The ^{19}F resonances are complex multiplets which arise from ^2J(P,P) plus ^{19}F spin–spin coupling.) ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.81 (t, 3 H, $J_{H\text{-}H}$ = 7.4, CH_3 4L), 0.83 (dd, 3 H, Me 13, $J_{P2\text{-}H}$ = 14, $J_{H\text{-}H}$ = 7), 0.98 (dd, 3 H, Me 1, $J_{P1\text{-}H}$ = 14.6, $J_{H\text{-}H}$ = 7.1), 1.87–1.9 (m, 2 H, CH_2 3L), 1.21 (dd, 3 H, Me 18, $J_{P2\text{-}H}$ = 18.5, $J_{H\text{-}H}$ = 7), 1.29–1.34 (m, 2 H, CH_2 1L), 1.39 (dd, 3 H, Me 6, $J_{P1\text{-}H}$ = 18.5, $J_{H\text{-}H}$ = 7 Hz), 1.46–1.55 (m, 2 H, CH_2 2L), 1.56–1.7 (m, 2 H, CH_2 15), 1.75–1.89 (m, 2 H, CH_2 4), 2.14–2.20 (m, 2 H, CH_2 16), 2.34–2.50 (m, 2 H, CH_2 3), 2.5–2.69 (m, 2 H, CH 14 and CH 17), 2.72–2.87 (m,1 H, CH 5), 2.92 (m,1 H, CH 2), 7.57–7.66 (m, 2 H, CH 9 and 10), 7.71 (m, 1 H, CH 11) and 7.78 (m, 1 H, CH 8).

Allylic alkylation

Dinuclear $[PdCl(PhCHCHCHPh)]_2$ (1.34 mg, 0.002 mmol) and the ligand **1** (1.5 mg, 0.005 mmol) in CH_2Cl_2 (2 ml) were stirred for 20 min at RT. 1,3-Diphenyl-2-propenyl acetate (50.4 mg, 0.2 mmol), dimethyl malonate (68 μL, 0.6 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (148 μL, 0.6 mmol), and KOAc (1 mg) were added and the mixture stirred at RT for 48 h. The resulting suspension was diluted with ether, washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated, and the oily residue purified by column chromatography (20% ethyl acetate in hexane) to give the product (64 mg, 99%; ee > 98%). The enantiomeric excess was determined by HPLC using OD-H as chiral column (hexane–isopropyl alcohol 98 : 2, 0.5 ml min^{-1}).

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