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Cyclometallated Palladium Diphosphane Compounds Derived from the Chiral Ligand (*S*)-PhCH(Me)NMe_2. Michael Addition Reactions to the Vinylidene Double Bond

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Treatment of (*S*)-PhCH(Me)NMe_2 (**1**) with palladium(II) acetate in toluene gave the dinuclear cyclometallated complex [Pd{(*S*)-C_6H_4CH(Me)NMe_2-*C2,N*}(μ-OAc)]$_2$ (**2**), inwhich the ligand is bonded to the palladium atom through the nitrogen phenyl carbon atoms. The reaction of **2** with aqueous sodium chloride gave the chloro-bridged complex **3**. The reaction of **3** with (*R*,*R*)-DIOP [(4*R*,5*R*)-4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane], in a complex/phosphane 1:1 molar ratio, gave [{Pd[(*S*)-C_6H_4CH(Me)NMe_2-*C2,N*]Cl}$_2$(μ-(*R*,*R*)-DIOP)] (**4**). The reaction of **3** with $(Ph_2P)_2$C=CH_2 (vdpp) in a 1:2 molar ratio in the presence of NH_4PF_6 or$NaClO_4$afforded[Pd{(*S*)-C_6H_4CH(Me)NMe_2-*C2,N*}{$(Ph_2P)_2$C=CH_2-*P,P′*}][Y] [Y = PF_6^- (**5**); Y = ClO_4^- (**6**), respectively]. The treatment of **5** with acetylacetone in the presence of anhydrous sodium carbonate or with methanol afforded the addition products, [Pd{(*S*)-C_6H_4CH(Me)NMe_2-*C2,N*}{$(Ph_2P)_2$-$CHCH_2$R-*P,P′*}][PF_6] [R = CH(COMe)$_2$ (**7**); R = OMe (**8**), respectively], in good yield. The treatment of **6** with methyl acetoacetate and anhydrous sodium carbonate afforded the addition derivative [Pd{(*S*)C_6H_4CH(Me)NMe_2*C2,N*}{$(Ph_2P)_2$-$CHCH_2$CH-(COMe)(COOMe)-*P,P′*}][ClO_4] (**9**). The NMR spectra of the addition products showed that some of the resonances were duplicated due to the existence of optical isomers. The X-ray crystal structure of complexes **2**, **5**, and **7** were determined by single-crystal X-ray diffraction analysis.

Introduction

The chemistry of cyclometallated transition metal complexes has attracted much attention in the past as they exhibit a number of applications that range from their use as building blocks for molecular architectures of higher complexity[1] to compounds with interesting mesogenic,[2] luminescent and electronic properties,[3] as well as their potential use in the medicinal and biological fields.[4] In particular, optically-active cyclometallated complexes, especially those derived from tertiary amines, have proven to be useful reagents as catalysts,[5] as agents for the determination of enantiomeric excess,[6] as resolving agents,[7] or as stoichiomeric reagents in the asymmetric synthesis of phosphanes.[8]

These types of ligands, especially those that bear two or more phosphorus donors, play a substantial and increasing role in coordination and organometallic chemistry. Their wide-range of steric and electronic specifications, which are suitable for a variety of applications in catalytic processes, in stabilizing different metal oxidation states, and in forming homo- and heteropolymetallic complexes, enable these ligands to fulfil this role.[9]

Furthermore, over the past few years we have become interested in the synthesis of novel cyclometallated complexes and in their reactivity with tertiary diphosphanes, such as $(Ph_2P)_2$C=CH_2, 1,1-bis(diphenylphosphanyl)ethene (vdpp). It has been shown that free vdpp is scarcely susceptible to nucleophilic attack and reacts directly only in the presence of a strong base (for instance KO*t*Bu) or with molecules such as phosphanes and arsines.[10] However, coordination to different metal centres strongly activates the C=C bond towards nucleophilic attack, which is probably due to an additional induced polarization of the double bond in the starting complex and a relief of the angle strain at the P–C–P carbon after addition.[11] We have recently reported that a cyclometallated moiety is capable of polarizing the C=CH_2 double bond of vdpp to afford addition products with different primary and secondary amines or 1,3-dicarbonyl compounds, to give functionalized diphosphane ligands.[12,13] Herein we further research the application of addition reactions to vdpp as a method to prepare new diphosphanes by using a chiral cyclometallated fragment as the activating agent of the vinylic double bond in order to explore the possibility of a steroespecific synthesis. We also report a new route to a complex commonly used as a template in asymmetric synthesis, namely compound **3**.

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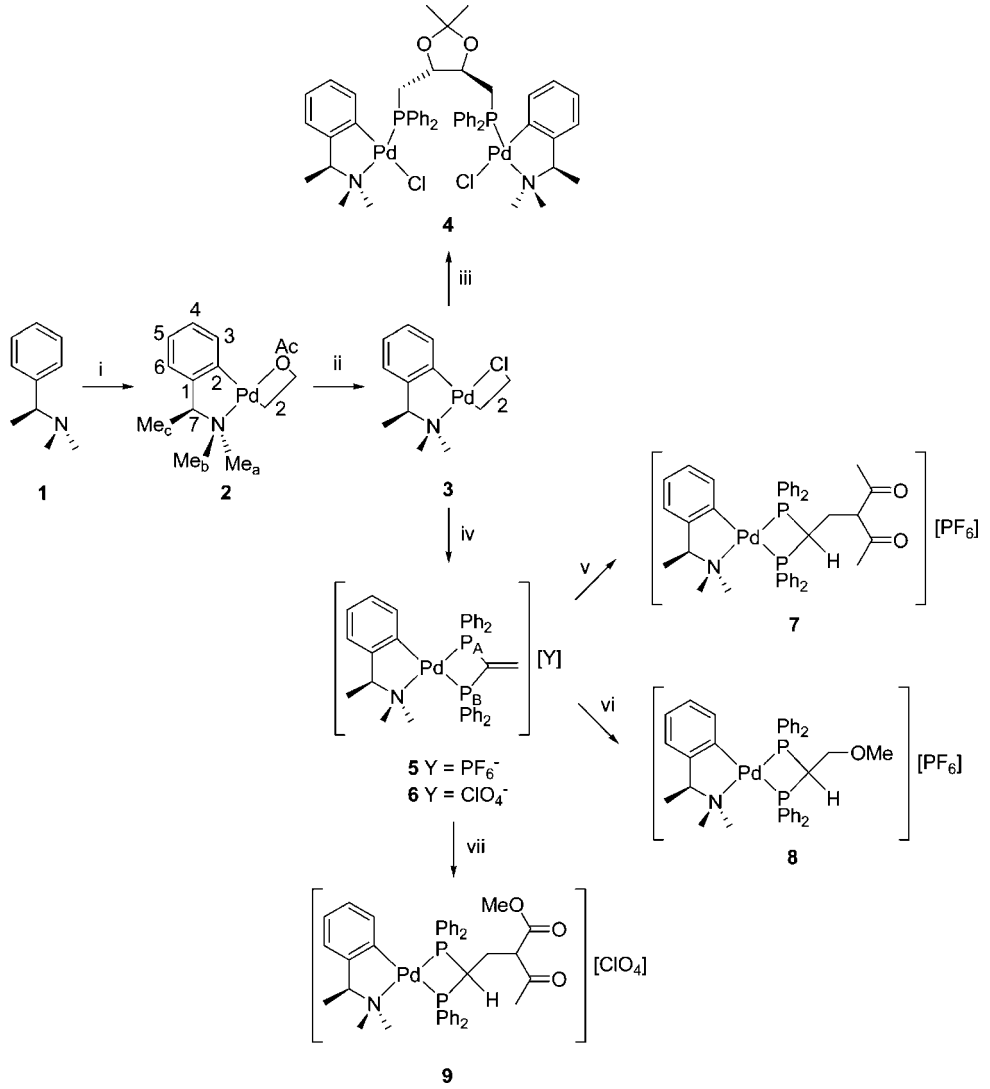
Results and Discussion

For the convenience of the reader the compounds and the reactions are shown in Scheme 1.

The reaction of **1** with palladium(II) acetate in anhydrous toluene gave the dinuclear cyclometallated complex [Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}(μ-OAc)]$_2$ (**2**) in 90% yield. Complex **2** was fully characterized. The mass FAB spectrum of **2** showed a cluster of peaks centered at 628 amu, which correspond to the molecular ion. The isotopic pattern was in good agreement with the proposed dinuclear structure. The quadruplet at δ = 3.65 ppm [^3J(H7Me$_c$) = 6.8 Hz] was assigned to H7 and was a coupled to the adjacent methyl protons, whose resonance signal was a doublet at δ = 1.06 ppm. The signals assigned to the Me$_a$ and Me$_b$ groups were two singlets, δ = 2.61 and 2.15 ppm, which confirmed their diastereotopic nature.

If one considers the folded structure of the complex and the asymmetric nature of the C7 carbon atom, three isomers are possible for complex **2**. There are the *syn* and *anti* isomers, which depend on the relative orientation of the cyclometallated moieties in the dinuclear molecule. However, the presence of only one singlet at δ = 2.06 ppm for the CH_3COO protons in the ^{1}H NMR spectrum and two singlets at δ = 180.6 and 24.6 ppm for the *C*OO and *C*H_3COO carbons, respectively, in the $^{13}C\{^1H\}$ NMR spectrum, are indicative of symmetrical bridging acetate ligands and are, thus, in agreement with the *anti* formulation. We have previously found that, when both isomers are present, steric factors may determine the relative *anti*/*syn* ratio due to the folded structure of the complex, which sets the two neighbouring cyclometallated moieties in a mutual nearly parallel arrangement.[14] Accordingly, since the *syn* conformation brings the NMe_2 and Me$_c$ methyl groups close to one an-



Scheme 1. (i) Pd(AcO)$_2$, toluene; (ii) NaCl, acetone/water; (iii) (*R*,*R*)-DIOP, acetone; (iv) vdpp (1:2 molar ratio), acetone, NH_4PF_6(**5**); $NaClO_4$(**6**); (v) $MeCOCH_2COMe/Na_2CO_3$ (1:2 molar ratio), chloroform; (vi) MeOH; (vii) $MeCOCH_2COOMe/Na_2CO_3$ (1:2 molar ratio), chloroform; (vii) $MeCOCH_2COOMe/Na_2CO_3$ (1:2 molar ratio), chloroform.

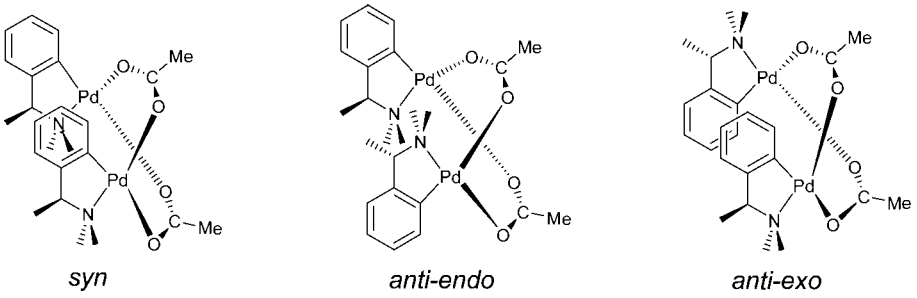


Figure 1. The *syn*, *anti-exo*, and *anti-endo* isomers for compound **2**.

other, the *anti* disposition is favoured in order to relieve the steric hindrance. We have previously found that when the *syn* isomer is obtained, conversion to the *anti* derivative occurs smoothly at room temperature.[14]

In addition, due to the asymmetric nature of C7, *anti-endo* and *anti-exo* stereoisomers may be present in the solution, depending on the relative disposition of the Me_c at C7 (Figure 1). The *anti-endo* disposition situates the Me_c methyl close to the phenyl ring of a neighbouring cyclometallated ligand in the dinuclear structure thereby causing a considerable repulsion and, therefore, the preferred disposition in the solid state (vide infra) is the most thermodynamically stable *anti-exo* isomer. In order to further clarify these assumptions a ^{1}H NOESY experiment was carried out for **2**. The spectrum showed contacts between Me_c and H7, H6 and both NMe_2 groups, as well as a very weak contact with H5. The contact between H7, H6, and H5 could also be distinguished. One of the NMe_2 groups (Me_b at δ = 2.15 ppm) showed a strong correlation with H7 as a result of the relative disposition of this group in the molecule (Me_b is oriented towards the internal face in the dimeric form and is closer to the H7 proton than to Me_a, which is on the external side).

The Crystal Structure of 2

Single crystals of **2** were obtained from a chloroform/*n*-hexane solution. The crystal consists of dinuclear molecules separated by van der Waals distances. The molecular structure is illustrated in Figure 2 and corresponds to the *anti* isomer with the cyclometallated moieties in an open book disposition linked by two acetate bridging ligands.

The Pd(1)–Pd(2) bond length of 2.966(1) Å is similar to the values reported for related complexes[14] and may be regarded as non-bonding. Each palladium atom shows a slightly distorted square-planar geometry and is bonded to a nitrogen and a carbon atom from the organic ligand, and to two oxygen atoms from the two bridging acetate groups. The most noticeable distortion of the ideal coordination sphere corresponds to the C–Pd–N bite angle of 81.9(1)° (see Tables 1 and 2).

The Pd(1)–C(2) and Pd(2)–C(11) bond lengths of 1.947(3) and 1.955(3) Å, respectively, are somewhat shorter than the values predicted from their covalent radii,[15] but are similar to the values found earlier.[14] However, the

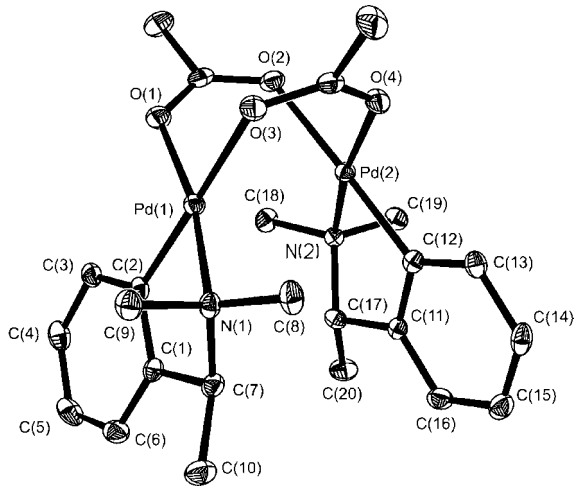


Figure 2. The molecular structure of [Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}(μ-OAc)]$_2$ (**2**). The hydrogen atoms have been omitted for clarity.

Pd(1)–N(1) and Pd(2)–N(2) bond lengths of 2.080(2) and 2.075(2) Å, respectively, are in agreement with the values based on the sum of the covalent radii for nitrogen and palladium.[14,15] The differing Pd–O bond lengths reflect the greater *trans* influence of the phenyl ring compared to the dimethylamine group [Pd–$O_{(trans\text{-}C)}$, 2.146(2) Å; Pd–$O_{(trans\text{-}N)}$, 2.053(2) Å].

As a result of the palladium atoms being bridged by two mutually *cis* μ-acetate ligands, the metallated Schiff bases are forced to lie above one another in the dinuclear molecules. This leads to interligand repulsions and results in the coordination planes of the palladium atoms (planes 1 and 2) being tilted at an angle of 36.4°.

The cyclometallated rings are not planar due to sp^3 hybridization in the C(7) and C(17) carbon atoms and can adopt a δ or a λ conformation. Both conformations have been reported for related compounds[16] but it has been postulated that the λ conformation minimizes the steric hindrance between the methyl groups. However, the structure of complex **2** shows that both rings adopt the δ conformation (Figure 3), in which the repulsion between the methyl groups of the adjacent cyclometallated ligands in the molecule is minimized [two of the methyl groups, C(10)–Me and C(20)–Me, are situated on opposite faces of the molecule and the rest are almost coplanar with the corresponding cyclometallated moieties, see Figure 4].

Table 1. The crystallographic data for complexes **2**, **5**, and **7**.

	2	**5**	**7**
Empirical formula	$C_{24}H_{34}N_2O_4Pd_2{\cdot}2CHCl_3$	$C_{36}H_{36}F_6NP_3Pd$	$C_{41}H_{44}F_6NO_2P_3Pd$
Formula mass	866.07	795.97	893.08
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1$	$P2_1$
a [Å]	9.271(1)	12.535(1)	9.874(1)
b [Å]	15.013(1)	18.500(1)	11.208(1)
c [Å]	24.166(2)	25.680(1)	19.065(1)
β [°]		94.956(1)	96.431(1)
V [Å^3]	3363.5(5)	3622.6(4)	2096(6)
Z	4	4	2
μ [mm^{-1}]	1.579	0.702	0.618
Max., min. transmissions	0.626, 0.531	0.943, 0.728	0.94, 0.85
$\rho_{calcd.}$ [g cm^{-3}]	1.710	1.459	1.419
θ range [°]	1.60 to 28.29	1.30 to 28.29	2.08 to 28.28
Reflections collected	23975	23341	14997
Independent reflections	8362 (R_{int} = 0.038)	16178 (R_{int} = 0.032)	9112 (R_{int} = 0.057)
Absolute structure parameter		0.17(3)	0.04(3)
R_1 [a]	0.0256	0.0539	0.0472
wR_2 [b]	0.0446	0.1555	0.1203

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $[F > 4\sigma(F)]$. [b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, all data.

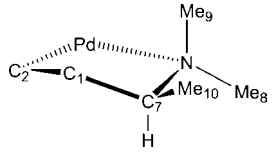


Figure 3. The conformation of the cyclometallated ring in compound **2**.

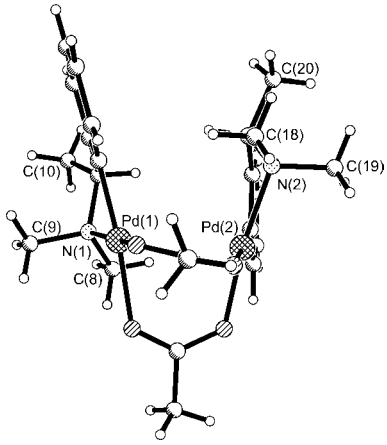


Figure 4. The reduced interligand repulsions in **2** are due to the δ conformation of the cyclometallated rings.

The treatment of **2** with sodium chloride in a mixture of acetone and water yielded the chloride-bridged complex [Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}(μ-Cl)]$_2$ (**3**) as a mixture of the *syn* and *anti* isomers, in ca. 90% yield. The synthesis of **3** from the reaction between **1** and $Na_2[PdCl_4]$ has been previously reported,[17] but the two-step method reported herein represents an overall yield of >85%, which is a significant improvement on that of the one reported earlier (65%).

The reaction of **3** with the tertiary diphosphane (4*R*,5*R*)-4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane [(*R*,*R*)-DIOP] in a 1:1 molar ratio gave the dinuclear complex [{Pd[(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*]Cl}$_2$(μ-(*R*,*R*)-DIOP)] (**4**). The singlet at δ = 34.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum, which is for the two equivalent phosphorus nuclei of the bridging ligand, is shifted to a higher frequency than the signals in the spectrum of the free phosphane. This is in agreement with the coordination of the phosphorus atoms to the metal center.[18] The ^1H NMR spectrum for **4** showed that the NMe_2 resonances are coupled to the ^{31}P nuclei [δ = 2.74 ppm, ^4J(MeP) = 1.96 Hz; δ = 2.70 ppm, ^4J(MeP) = 2.92 Hz]. The FAB-MS spectrum was in agreement with the fragmentation sequence shown in Scheme 2.[19]

The treatment of **3** with 1,1-bis(diphenylphosphane)ethene (vdpp) in a 1:2 molar ratio, and ammonium hexafluorophosphate or sodium perchlorate as appropriate, in acetone at room temperature gave the mononuclear cyclometallated palladium(II) complexes [Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}{$(Ph_2P)_2C{=}CH_2$-*P*,*P*′}](X) [X = PF_6^- (**5**) and X = ClO_4^- (**6**), respectively] in good yield. The IR spectra showed bands at 850 and 1090 cm^{-1}, which arose from the corresponding counterions PF_6^- and ClO_4^-, respectively. The FAB-MS spectra showed peaks at m/z = 650 that was assigned to $[M]^+$ (with loss of the PF_6^- or ClO_4^- ion), after consideration of the palladium isotopes. In the $^{31}P\{^1H\}$ NMR spectra two doublets [$^2J(P_AP_B) \approx 25$ Hz] were assigned to the non-equivalent phosphorus atoms. The assignment was made in accordance with the assumption that a ligand with a greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to a lower frequency.[18] In the ^1H NMR spectra the C=CH_2 resonance appeared as a multiplet due to coupling to both of the phosphorus nuclei. Also, the NMe_2 signals showed coupling to the phos-

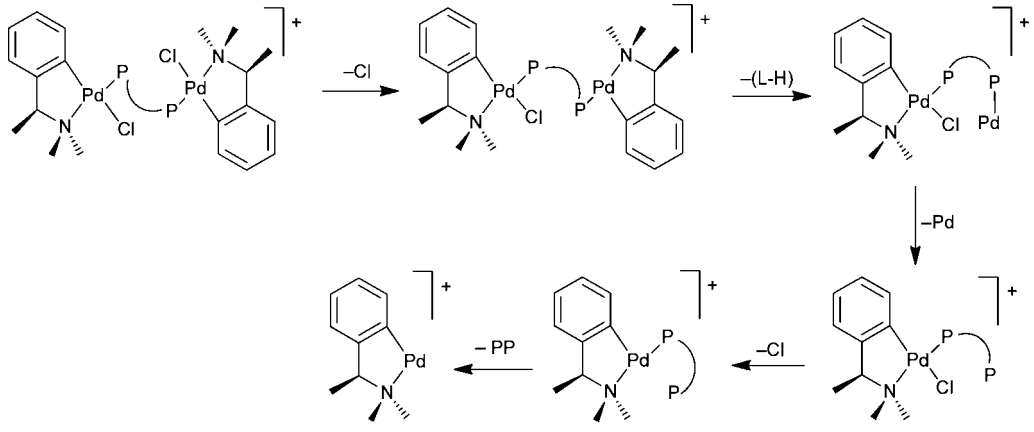
Table 2. Selected bond lengths [Å] and angles [°] for complexes **2**, **5**, and **7**.

	2	**5**	**7**
Pd(1)–C(2)	1.943(3)	1.975(12)	2.024(6)
Pd(1)–N(1)	2.078(2)	2.123(9)	2.141(6)
Pd(1)–O(1)	2.064(2)		
Pd(1)–O(3)	2.150(2)		
Pd(2)–C(12)	1.955(3)		
Pd(2)–C(38)		2.062(9)	
Pd(2)–N(2)	2.075(2)	2.139(9)	
Pd(2)–O(2)	2.146(2)		
Pd(2)–O(4)	2.053(2)		
Pd(1)–P(1)		2.240(3)	2.230(2)
Pd(1)–P(2)		2.395(3)	2.384(2)
Pd(2)–P(3)		2.410(3)	
Pd(2)–P(4)		2.253(3)	
Pd(1)–Pd(2)	2.9663(4)		
C(11)–C(12)		1.33(1)	1.524(8)
C(46)–C(47)		1.29(1)	
C(13)–C(14)			1.519(10)
C(13)–C(15)			1.551(10)
C(14)–O(1)			1.212(9)
C(15)–O(2)			1.217(9)
C(2)–Pd(1)–N(1)	81.95(11)	81.4(4)	80.2(2)
C(2)–Pd(1)–O(1)	92.73(10)		
O(1)–Pd(1)–O(3)	91.17(8)		
O(3)–Pd(1)–N(1)	93.45(8)		
C(12)–Pd(2)–N(2)	81.88(9)		
C(12)–Pd(2)–O(4)	92.52(10)		
O(4)–Pd(2)–O(2)	90.45(7)		
O(2)–Pd(2)–N(2)	95.15(8)		
N(1)–Pd(1)–P(2)		107.6(3)	108.10(17)
P(2)–Pd(1)–P(1)		72.95(9)	73.75(5)
P(1)–Pd(1)–C(2)		98.1(3)	97.89(17)
C(38)–Pd(2)–N(2)		81.4(4)	
N(2)–Pd(2)–P(3)		105.2(3)	
P(3)–Pd(2)–P(4)		72.34(10)	
P(4)–Pd(2)–C(38)		100.7(3)	
P(1)–C(11)–P(2)		98.3(4)	95.4(2)
P(3)–C(46)–P(4)		98.4(4)	
C(8)–N(1)–C(7)–C(10)	71.1(3)	168.8(10)	170.4(6)
C(9)–N(1)–C(7)–C(10)	–49.3(3)	48.7(12)	52.5(8)
C(18)–N(2)–C(17)–C(20)	68.8(3)		
C(19)–N(2)–C(17)–C(20)	–52.0(3)		
C(44)–N(2)–C(65)–C(45)		47.0(12)	
C(43)–N(2)–C(65)–C(45)		167.8(9)	

phorus nuclei $\delta \approx 3.0$ ppm [$^4J(MeP_A) = 1.9$ Hz] and $\delta = 2.81$ ppm [$^4J(MeP_A) = 3.4$ Hz, $^4J(MeP_B) = 3.4$ Hz]. The ^{1}H NOESY spectrum for **5** showed close contact between Me_c, H7, and H6, as well as contact between H7 and H6. A strong correlation between Me_c and one of the amine methyl groups (Me_b at $\delta = 2.81$ ppm), and a weaker one with the other methyl group (Me_a at $\delta = 2.99$ ppm), were observed. This was in agreement with the distances in the crystal structure for **5**, for example, d(Me_c–Me_b) = 2.83 Å and d(C7–Me_b) = 2.54 Å as opposed to (Me_c–Me_a) = 4.00 Å and d(C7–Me_a) = 2.42 Å.

The reaction of **5** with acetylacetone, a symmetrical 2,4-dicarbonylic nucleophile, under nitrogen in dry chloroform for 16 h at 45 °C, and in the presence of anhydrous sodium carbonate, yielded the addition product [Pd{(*S*)-C_6H_4CH(Me)NMe_2-*C2*,*N*}{$(Ph_2P)_2CHCH_2CH(COMe)_2$-*P*,*P*′}][$PF_6$] (**7**). Similarly, treatment of **5** with the β-keto ester methyl acetoacetate gave a mixture of the desired addition compound and the starting material. Nevertheless, reaction of **6** with methyl acetoacetate for 3 d under similar reaction conditions afforded pure [Pd{(*S*)-C_6H_4CH(Me)NMe_2-*C2*,*N*}{$(Ph_2P)_2CHCH_2CH(COMe)(COOMe)$-*P*,*P*′}][$ClO_4$] (**9**). The FAB-MS spectra for the complexes showed the peaks corresponding to the molecular ions after loss of the corresponding counterion (750 and 766 amu for **7** and **9**, respectively). The IR spectra of the complexes showed strong bands due to the C=O groups [1702 cm^{-1} (**7**); 1718 and 1736 cm^{-1} (**9**)].

The ^{1}H NMR spectra exhibited substantial differences with respect to the starting materials. Thus, the resonance of the vinylidene protons was absent and a multiplet at $\delta \approx 4.6$ ppm was assigned to the P_2CH resonance. The 1,3-dicarbonyl moiety proton resonances were clearly distinguishable and the multiplets at $\delta = 3.71$ ppm and $\delta = 3.30$ ppm for **7** and **9**, respectively, were assigned to the α-proton. The NMR spectra, however, were of considerable complexity, which indicated that some of the resonances were duplicated. The $^{31}P\{^1H\}$ NMR spectra for **7** and **9** showed four and eight doublets, respectively. This observa-



Scheme 2. The FAB-MS fragmentation scheme for complex **4**.

tion may be explained by the new stereogenic carbon centers generated by the nucleophilic addition to the vinyl group. Thus, the reaction with acetylacetone generated a new stereogenic carbon (*R* or *S*) situated in the α position with respect to the phosphorus atoms and two stereoisomers [(C7*S*,C11*S*) and (C7*S*,C11*R*)] were obtained. In the case of complex **9**, an additional stereocenter was produced at the α carbon to the C=O groups, thus, four different stereoisomers were synthesized [(*S*,*S*,*S*), (*S*,*R*,*S*), (*S*,*R*,*R*), and (*S*,*S*,*R*)] (Figure 5).

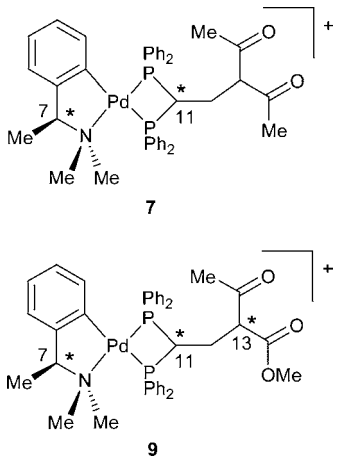


Figure 5. The stereogenic carbon centers for compounds **7** and **9**.

The diastereomeric ratio was 1:1 and 1:1:1:1 for **7** and **9**, respectively. These ratios were calculated from the signal integrations in the $^{31}P\{^{1}H\}$ spectra. In spite of the chiral nature of the parent complexes **5** and **6**, no stereoselectivity was observed for the addition products.

A stirred solution of **5** in methanol at 45 °C for 3 d afforded complex [Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}{$(Ph_2P)_2CHCH_2OMe$-*P*,*P′*}][PF_6] (**8**) in an acceptable yield after the addition of MeO^- to the $(Ph_2P)_2C{=}CH_2$ vinylic bond. The FAB-MS showed a peak at 682 amu for the $[M]^+$. The strong bands observed in the IR spectrum were assigned to the PF_6^- counterion. The ^1H NMR spectrum was in accordance with the proposed structure. Two sets of signals were present due to the diastereoisomers produced by the presence of the two chiral carbons atoms and were assigned to the methyl and the methoxy groups. The $^{31}P\{^{1}H\}$ NMR spectrum showed four doublets, which is in agreement with the existence of equimolar amounts of the (C7*S*,C11*S*) and (C7*S*,C11*R*) stereoisomers.

The Crystal Structures of 5 and 7

Suitable crystals of **5** and **7** were grown by the diffusion of diethyl ether into chloroform solutions of these complexes. They consisted of discrete molecules, separated by normal van der Waals distances. The labelling schemes for the complexes are shown in Figures 6 and 7, respectively (see Exp. Section). The crystal structure of **5** comprises two molecules per asymmetric unit, both of which have very similar bond lengths and angles. The discussion of **5** will be limited to only one of the molecules. The crystal structure of **7** comprises only the (C7*S*, C11*S*) stereosisomer, which crystallizes selectively from the equimolar solution of the (*S*,*S*) and the (*S*,*R*) diasteromers (vide supra and Tables 1 and 2).

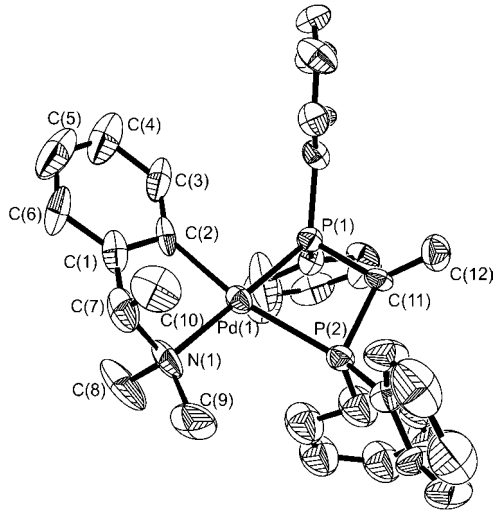


Figure 6. The molecular structure of the cation for [Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}{$(Ph_2P)_2C{=}CH_2$-*P*,*P′*}][PF_6] (**5**). The hydrogen atoms have been omitted for clarity.

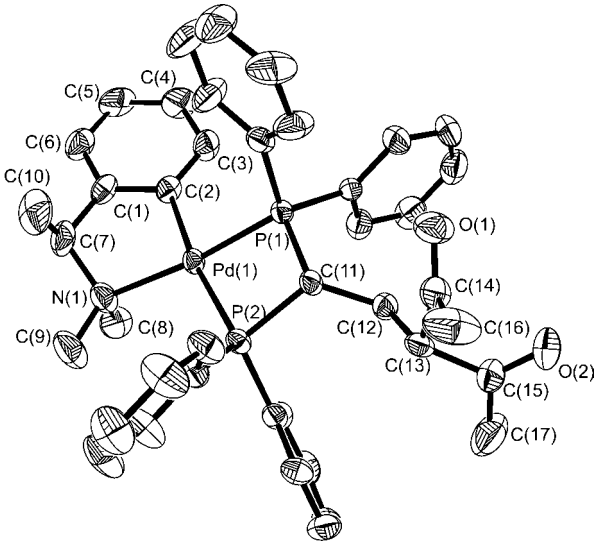


Figure 7. The molecular structure of the cation for [Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}{$(Ph_2P)_2CHCH_2CH(COMe)_2$-*P*,*P′*}][$PF_6$] (**7**). The hydrogen atoms have been omitted for clarity.

The coordination sphere around each palladium atom consists of a nitrogen atom from the amine group, a carbon atom from the phenyl ring, and two phosphorus atoms from a chelating diphosphane ligand in a slightly distorted square-planar coordination environment. The sum of the angles around each palladium is approximately 360°, with the most noticeable distortions corresponding to the chelate angles C(2)–Pd(1)–N(1) and, especially, P(1)–Pd(1)–P(2). The requirements of the four-membered chelate ring is also shown in the P(1)–C(11)–P(2) angle of 98.3(4)° and 95.4(2)°

for **5** and **7**, respectively, in agreement with the sp^3 hybridization of C(11). The values are smaller than those reported for the uncoordinated vdpp (118.4°).[20] Similar bond angles have been found in other four-membered chelates involving coordinated phosphanes.[21] The bond lengths for the palladium atom are in accordance with those found for similar complexes.[12,13]

For **5**, the C(11)–C(12) bond length is 1.335(10) Å, which is within the range expected for a carbon–carbon double bond and is similar to the value of 1.34 Å in the free vdpp. The corresponding bond length in **7** is 1.524(8) Å, which is in accordance with a carbon–carbon single bond (ca. 1.50 Å). The carbon–oxygen bond lengths for **7** are C(14)–O(1) 1.212(9) Å and C(15)–O(2) 1.217(9) Å, which are within the expected range for a C=O double bond (ca. 1.21 Å), whereas the C(13)–C(14) and C(13)–C(15) bond lengths of 1.519(10) and 1.551(10) Å, respectively, are in agreement with a C–C single bonds. This thereby confirmed the presence of the 1,3-dicarbonyl moiety in its keto form.

The C(10) carbon in both **5** and **7** occupies an axial position and consequently the cyclometallated ring adopts the λ conformation in contrast to the δ conformation found in the structure of **2** (vide supra). The λ disposition minimizes the steric repulsion between C(10), C(8), and C(9) and, in the absence of the interligand repulsions present in the acetate-bridged complex **2** due to its folded structure, is the more stable conformation.

Experimental Section

General Procedures: All of the manipulations to synthesize the addition compounds were performed under prepurified Ar by using the standard Schlenk technique. All of the solvents were distilled prior to use from the appropriate drying agents.[22] All of the chemicals were used as supplied from the commercial sources.

Safety Note: *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts should be prepared and handled with caution.*

The microanalyses were carried out with a Carlo–Erba Elemental Analyzer, Model 1108. The IR spectra were recorded as Nujol mulls or KBr discs with a Perkin–Elmer 1330 instrument and with a Mattson spectrophotometer. The NMR spectra were obtained from $CDCl_3$ solutions of the complexes, were referenced to $SiMe_4$ [^1H, $^{13}C\{^1H\}$] or 85% H_3PO_4 [$^{31}P\{^1H\}$], and were recorded with Bruker Avance 300 and 500 (for the NOESY experiments) spectrometers. All of the chemical shifts were reported downfield from the standards. The FAB mass spectra were recorded with a Quatro mass spectrometer equipped with a Cs ion gun and 3-nitrobenzyl alcohol (3-NBA) was used as the matrix.

[Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}(μ-OAc)]$_2$ (2): A pressure tube containing (*S*)-*N*,*N*-dimethyl-1-phenylethylamine (**1**) (0.149 g, 1.000 mmol), palladium(II) acetate (0.224 g, 1.000 mmol), and dry toluene (15 cm^3) was sealed under argon. The resulting mixture was heated at 50 °C for 15 h. After cooling to room temp., the solution was filtered through cellite to remove the small amount of black palladium that was formed. The solvent was removed under vacuum and the oil that formed was recrystallized from chloroform/hexane to yield the desired product as a yellow solid, which was filtered, washed with hexane, and dried under vacuum; yield 90%. $C_{24}H_{34}N_2O_4Pd_2$ (627.34): calcd. C 45.9, H 5.5, N 4.5; found C 46.2, H 5.8, N 4.6. IR: $\tilde{\nu}_{as}$(COO) = 1589 (s), 1571 (s) cm^{-1}; $\tilde{\nu}_s$(COO) = 1413 (s) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.02 [m, 1 H, H4], 6.98 [dd, ^3J(H3H4) = 7.0 Hz, ^4J(H3H5) = 1.0 Hz, 1 H, H3], 6.63 [d, ^3J(H5H6) = 7.3 Hz, 1 H, H6], 3.65 [q, 1 H, H7], 2.61 [s, 3 H, Me_a], 2.15 [s, 3 H, Me_b], 2.06 [s, 3 H, *Me*COO], 1.06 [d, $^3J(CH_3H7)$ = 6.8 Hz, 3 H, Me_c] ppm. $^{13}C\{^1H\}$ NMR (75.46 MHz, $CDCl_3$): δ = 180.6 (Me*C*OO), 150.8, 145.8 (C1, C2), 131.7, 125.1, 124.1, 121.9 (C3, C4, C5, C6), 72.4 (C7), 47.9, 45.1 (Me_a, Me_b), 24.6 (*Me*COO), 10.4 (Me_c) ppm. FAB-MS: *m*/*z* = 628 $[M]^+$, 569 $[M - OAc]^+$, 313 $[(L\text{-}H)Pd(OAc)]^+$, 254 $[(L\text{-}H)Pd]^+$.

[Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}(μ-Cl)]$_2$ (3): A solution of **1a** (0.200 g, 0.320 mmol) in acetone (10 cm^3) was treated with a saturated solution of NaCl in water (ca. 20 cm^3). The mixture was stirred for 2 h at room temp., after which the yellow precipitate that formed was filtered off, washed with water, and dried with anhydrous $CaCl_2$; yield 89%. $C_{20}H_{28}Cl_2N_2Pd_2$ (580.16): calcd. C 41.4, H 4.9, N 4.8; found C 41.5, H 4.6, N 4.8. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 6.90 [m, 3 H, H4, H5, H6], 7.21 [m, 1 H, H3], 3.88 [m, 1 H, H7], 2.94, 2.92, 2.68, 2.65 [s, 6 H, Me_a, Me_b], 1.59 [d, $^3J(CH_3H7)$ = 6.8 Hz, 3 H, Me_c] ppm. FAB-MS: *m*/*z* = 547 $[M - Cl]^+$, 254 $[(L\text{-}H)Pd]^+$.

[{Pd[(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*]Cl}$_2$(μ-(*R*,*R*)-DIOP)] (4): (*R*,*R*)-DIOP (0.021 g, 0.043 mmol) was added to a solution of **3** (0.025 g, 0.043 mmol) in acetone (15 cm^3). The resulting mixture was stirred for 30 min. The white precipitate that formed was stirred for a further 1.5 h, filtered off, washed with cold (4 °C) acetone, and dried under vacuum; yield 56%. $C_{51}H_{60}N_2O_2P_2Pd_2$ (1007.79): calcd. C 60.8, H 6.0, N 2.8; found C 60.6, H 5.9, N 2.7. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 4.54 [m, 1 H, OC*H*], 3.73 [m, 1 H, H7], 2.74 [d, ^4J(MeP) = 1.96 Hz, 3 H, Me_a or Me_b], 2.70 [d, ^4J(MeP) = 2.92 Hz, 3 H, Me_a or Me_b], 3.01, 2.40 [m, 2 H, CH_2P], 1.77 [d, $^3J(CH_3H7)$ = 6.3 Hz, 3 H, Me_c], 1.12 [s, 6 H, C(=O)Me] ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 34.3 (s) ppm. FAB-MS: *m*/*z* = 1043 $[M - Cl]^+$, 895 $[M - Cl\text{-}(L\text{-}H)]^+$, 788 $[(L\text{-}H)PdCl(PP)]^+$, 751 $[(L\text{-}H)Pd(PP)]^+$, 254 $[(L\text{-}H)Pd]^+$.

[Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,N}{$(Ph_2P)_2C{=}CH_2$-*P*,*P*′}][PF_6] (5): $(Ph_2P)_2C{=}CH_2$ (0.137 g, 0.345 mmol) was slowly added to a stirred suspension of **3** (0.100 g, 0.172 mmol) in acetone (10 cm^3). The resulting yellow solution was stirred for 30 min, after which an excess of ammonium hexaflurophosphate was added. Water (ca. 10 mL) was added dropwise until the added salt dissolved and the resulting mixture was stirred for 30 min. The white precipitate that formed was filtered off, washed with water, and dried with anhydrous $CaCl_2$; yield 95%. $C_{36}H_{36}F_6NP_3Pd$ (796.0): calcd. C 54.3, H 4.6, N 1.7; found C 54.0, H 4.6, N 1.5. IR: $\tilde{\nu}(PF_6)$ = 830–870 (br. s) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.15 [m, 2 H, H4, H5], 7.05 [m, 1 H, H6], 6.75 [m, 1 H, H3], 6.28 [m, 2 H, C=CH_2], 3.99 [m, 1 H, H7], 2.99 [d, $^4J(MeP_A)$ = 1.9 Hz, 3 H, Me_a], 2.81 [t, $^4J(MeP_B)$ = 3.4 Hz, 3 H, Me_b], 1.71 [d, $^3J(CH_3H7)$ = 6.4 Hz, 3 H, Me_c] ppm. $^{13}C\{^1H\}$ NMR (75.46 MHz, $CDCl_3$): δ = 139.6 [t, ^3J(PC) = 6.0 Hz], 137.4 br., 129.8 br., 126.4 br., 124.0 br. (C3, C4, C5, C6), 75.3 (C7), 52.6, 49.4 (NMe_2), 22.9 (Me_c) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 14.2 [d, ^2J(PP) = 24.6 Hz, P_A], –3.6 (d, P_B) ppm. FAB-MS: *m*/*z* = 650 $[M]^+$, 502 $[Pd(PP)]^+$.

[Pd{(*S*)-$C_6H_4CH(Me)NMe_2$-*C2*,*N*}{$(Ph_2P)_2C{=}CH_2$-*P*,*P*′}][ClO_4] (6): Compound **6** was obtained by following a similar procedure to the one described for **5**, but by using sodium perchlorate instead of ammonium hexafluorophosphate; yield 98%. $C_{36}H_{36}ClNO_4P_2Pd$ (750.5): calcd. C 57.6, H 4.8, N 1.9; found C 57.1, H 4.5, N 1.8. IR: $\tilde{\nu}(ClO_4)$ = 1060–1110 (br. s) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.10, 6.8 [m, 4 H, H3, H4, H5, H6],

6.30 [m, 2 H, C=CH_2], 3.99 [m, 1 H, H7], 3.00 [d, ^4J(MeP$_A$) = 1.9 Hz, 3 H, Me$_a$ or Me$_b$], 2.83 [t, ^4J(MeP$_A$) = 3.4 Hz, ^4J(MeP$_B$) = 3.4 Hz, 3 H, Me$_a$ or Me$_b$], 1.72 [d, ^3J(CH$_3$H7) = 6.4 Hz, 3 H, Me$_c$] ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 14.0 (d, ^2J(PP) = 25.4 Hz, P$_A$), –3.9 (d, P$_B$) ppm. FAB-MS: *m*/*z* = 650 [M]$^+$, 502 [Pd(PP)]$^+$.

[Pd{(*S*)-C$_6$H$_4$CH(Me)NMe$_2$-*C2*,*N*}{(Ph$_2$P)$_2$CHCH$_2$CH(COMe)$_2$-*P*,*P′*}][PF$_6$] (7): A solution of **5** (0.025 mg, 0.031 mmol) and MeCOCH$_2$COMe (7 μL, 0.062 mmol) in dry chloroform (10 cm^3) was heated at 45 °C for 16 h under Ar in the presence of anhydrous sodium carbonate (catalytic amount). The resulting suspension was cooled to room temp., filtered through Celite, and the solvent was removed under reduced pressure to give an oil. This residue was triturated with diethyl ether, filtered, washed with cold diethyl ether, and dried in vacuo to yield the desired product as a yellow solid; yield 79%. $C_{41}H_{44}F_6NO_2P_3Pd$ (896.11): calcd. C 54.9, H 4.9, N 1.6; found C 54.6, H 4.6, N 1.5. IR: $\tilde{\nu}$(C=O) = 1702 (s) cm^{-1}, $\tilde{\nu}$(PF$_6$) = 830–870 (br. s) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.05, 6.55 [m, 4 H, H3, H4, H5, H6], 4.61 [m, 1 H, PC*H*], 3.93 [m, 1 H, H7], 3.71 [m, 1 H, C*H*(COMe)$_2$], 2.99 s, 2.76 s, 2.73 m, 2.56m [6 H, Me$_a$ and Me$_b$], 1.94, 1.85 [s, 6 H, COCH_3], 1.73 [d, ^3J(CH_3H7) = 6.3 Hz], 1.61 [d, ^3J(CH_3H7) = 6.3 Hz, 3 H, Me$_c$] ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 15.5 [d, ^2J(PP) = 47.5 Hz, P$_A$], –5.7 [d, P$_B$], 14.4 [d, ^2J(PP) = 48.3 Hz, P$_A$], –7.8 [d, P$_B$] ppm. FAB-MS: *m*/*z* = 750 [M]$^+$.

[Pd{(*S*)-C$_6$H$_4$CH(Me)NMe$_2$-*C2*,*N*}{(Ph$_2$P)$_2$CHCH$_2$OMe-*P*,*P′*}][PF$_6$] (8): A suspension of **5** (0.025 mg, 0.031 mmol) in methanol (10 cm^3) was stirred at 45 °C for 3 h. After cooling to room temp., the solvent was removed under vacuum and the oily residue triturated with diethyl ether/hexane (1:1) to yield a white solid, which was filtered, washed with hexane, and dried in vacuo; yield 81%. $C_{37}H_{40}F_6NOP_3Pd$ (828.04): calcd. C 53.7, H 4.9, N 1.7; found C 53.9, H 5.0, N 1.7. IR: $\tilde{\nu}$(PF$_6$) = 830–870 (br. s) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.10, 6.60 [m, 4 H, H3, H4, H5, H6], 4.62 [m, 1 H, PC*H*], 3.90 [m, 1 H, H7], 3.25 [m, 2 H, CH_2O], 3.03 s, 2.82 s, 2.79m, 2.63m [6 H, Me$_a$ and Me$_b$], 2.94, 2.90 [s, 6 H, OCH_3], 1.76 [d, ^3J(H7H10) = 6.3 Hz,], 1.63 [d, ^3J(H7H10) = 6.3 Hz, 3 H, Me$_c$] ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 9.3 [d, ^2J(PP) = 47.5 Hz, P$_A$], –17.1 [d, P$_B$], 8.7 [d, ^2J(PP) = 48.3 Hz, P$_A$], –19.4 [d, P$_B$] ppm. FAB-MS: *m*/*z* = 682 [M]$^+$, 533 [Pd(PP)]$^+$.

[Pd{(*S*)-C$_6$H$_4$CH(Me)NMe$_2$-*C2*,*N*}{(Ph$_2$P)$_2$CHCH$_2$CH(COMe)-(COOMe)-*P*,*P′*}][ClO$_4$] (9): Compound **9** was synthesized by following a similar procedure to that described for **7**, but by using complex **6** and MeCOCH$_2$COOMe as the starting materials, and a reaction time of 3 days; yield 84%. $C_{41}H_{44}ClNO_7P_2Pd$ (866.60): calcd. C 56.8, H 5.1, N 1.6; found C 56.3, H 4.9, N 1.5. IR: $\tilde{\nu}$(C=O) = 1736 (s), 1718 (s) cm^{-1}, $\tilde{\nu}$(ClO$_4$) = 1060–1110 (br. s) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.04, 6.55 [m, 4 H, H3, H4, H5, H6], 4.66 [m, 1 H, PC*H*], 4.01 [m, 1 H, H7], 3.66, 3.64 [s, 3 H, COO*Me*], 3.30 [m, 1 H, C*H*(CO)$_2$], 3.02 s, 2.77 s, 2.74m, 2.58m [6 H, Me$_a$ and Me$_b$], 2.15 [m, 2 H, CH_2], 1.97, 1.85 [s, 3 H, CO*Me*], 1.73 [d, ^3J(H7H10) = 6.3 Hz], 1.62 [m, 3 H, Me$_c$] ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 15.0 [d, ^2J(PP) = 46.6 Hz, P$_A$], –5.3 [d, P$_B$], 14.6 [d, ^2J(PP) = 46.6 Hz, P$_A$], –5.8 [d, P$_B$], 14.3 [d, ^2J(PP) = 47.5 Hz, P$_A$], –6.9 [d, P$_B$], 14.2 [d, ^2J(PP) = 46.6 Hz, P$_A$], –7.9 [d, P$_B$] ppm. FAB-MS: *m*/*z* = 766 [M]$^+$.

X-ray Crystallographic Study: The three-dimensional, room temperature X-ray data were collected with a Bruker Smart 1k CCD by using graphite-monochromated Mo-K_α radiation. All of the measured reflections were corrected for Lorentz and polarization effects, and for absorption by semi-empirical methods based on the symmetry-equivalent and repeated reflections. The structures were solved by direct methods and were refined by full-matrix least-squares on F^2. The hydrogen atoms were included in the calculated positions and were refined in the riding mode. The refinement converged with the allowance for thermal anisotropy of all the non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97.[23]

CCDC-772658 (for **2**), -772659 (for **5**), and -772660 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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