Nucleophilic addition of 1,3-dicarbonyl compounds as a route to functionalized cyclopalladated complexes with chelated 1,1-bis(diphenylphosphino)ethene

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Received (in London, UK) 22nd April 2002, Accepted 17th July 2002
First published as an Advance Article on the web 20th August 2002

Treatment of the chloride-bridged complex [Pd{2,4-(OMe)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}(μ-Cl)]$_2$ (**1**) with 1,1-bis(diphenylphosphino)ethene (vdpp) and NH$_4$PF$_6$ or NaClO$_4$ in 1:2 molar ratio afforded the mononuclear cyclometallated palladium(II) complexes [Pd{2,4-(OMe$_2$)C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$C=CH$_2$-*P*,*P′*}](X) (**2**, X = PF$_6$; **3**, X = ClO$_4$). The structure of **2** has been determined by X-ray diffraction analysis. Reaction of **2** with acetylacetone in the presence of anhydrous sodium carbonate yielded in high yield the addition product [Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$CH(COMe)$_2$-*P*,*P′*}](PF$_6$) (**4**). The ^{31}P-{^{1}H} NMR spectrum showed a greater ^2J(PP) coupling constant than the one observed for the starting complex. Reaction of **2** with diethyl malonate afforded a 7:3 mixture of the addition product [Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$CH(COOEt)$_2$-*P*,*P′*}](PF$_6$) (**5**) and the starting complex. The desired addition compound could be isolated in pure form by treatment of **3** with diethyl malonate yielding [Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$CH(COOEt)$_2$-*P*,*P′*}](ClO$_4$) (**16**). The reaction of **2** with asymmetric nucleophiles such as methyl acetoacetate, ethyl propionylacetate, ethyl acetoacetate, methyl 4-chloroacetoacetate, 1,1,1-trifluoroacetylacetone and thenoyltrifluoroacetone afforded the corresponding addition derivatives, [Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(PH$_2$P)$_2$CHCH$_2$CH(COR$_1$)(COR$_2$)-*P*,*P′*}]-(PF$_6$) (R$_1$ = Me, R$_2$ = OMe, **6**; R$_1$ = Et, R$_2$ = OEt, **7**; R$_1$ = Me, R$_2$ = OEt, **8**; R$_1$ = CH$_2$Cl, R$_2$ = OMe, **9**; R$_1$ = Me, R$_2$ = CF$_3$, **10**; R$_1$ = CF$_3$, R$_2$ = 2-SC$_4$H$_3$, **11**). The NMR spectra showed some resonances were duplicated, suggesting the existence of optical isomers, as a consequence of the existence of two chiral carbon atoms in the diphosphine moiety, (Ph$_2$P)$_2$*C**HCH$_2$*C**H(COR$_1$)(COR$_2$). The molecular structure of compound **7** has been determined by X-ray crystallography confirming the spectroscopic data. The crystal structure of **7** comprises equimolar amounts of the (C16*R*, C18*S*) and (C16*S*, C18*R*) enantiomers. Reaction of **2** with 1-(2-furyl)-1,3-butanedione, ethyl 2-methylacetoacetate, 3-chloroacetylacetone and methyl 2-chloroacetoacetate gave compounds [Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$C(R$_1$)(COMe)(COR$_2$)-*P*,*P′*}](PF$_6$) (R$_1$ = H, R$_2$ = 2-OC$_4$H$_3$, **12**; R$_1$ = Me, R$_2$ = OEt, **13**; R$_1$ = Cl, R$_2$ = Me, **14**; R$_1$ = Cl, R$_2$ = OMe, **15**). The ^2J(PP) coupling constants for **14** and **15** were smaller than in the other addition compounds due to the presence of the neighbouring chlorine atom. Treatment of **2** with 3-ethylacetylacetone or 2,2,6,6-tetramethyl-3,5-heptanedione did not give any addition product. However, reaction of **3** with 3-ethylacetylacetone yielded a mixture of **3**/[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$C(Et)(COMe)$_2$-*P*,*P′*}](ClO$_4$) (**17**) in 1:1 molar ratio.

Introduction

Ligands having two or more phosphorus atoms play a substantial and still growing role in coordination and in organometallic chemistry, owing to their wide range of steric and electronic specifications suitable for a great variety of applications such as their use in catalytic processes or their ability to stabilize different oxidation states, as well as to form homo- and heteropolymetallic complexes.[1]

Nevertheless, little work has been reported relative to the design and availability of new types of phosphines: probably due to the often multistage synthetic methods required, which are not adaptable to the preparation of new functionalized phosphines. These ligands may either be prepared independently and then integrated into a metal coordination sphere or constructed *via* direct reaction on a phosphine ligand when already coordinated to the metal center. Typical examples are the C–H acidity of the methylene group in Ph$_2$PCH$_2$PPh$_2$ (bis(diphenylphosphino)methane, dppm)[2] or the activated vinylidene group of (Ph$_2$P)$_2$C=CH$_2$, 1,1-bis(diphenylphosphino)ethene (vdpp).

(Ph$_2$P)$_2$C=CH$_2$ is well known as a versatile ligand in coordination chemistry. It can act as mono- or bidentate towards one metal atom and it may also give polynuclear complexes with or without metal–metal bonds. The presence of a carbon–carbon double bond has aroused interest in the study of its addition reactions. On the one hand, it has been shown that vdpp is scarcely susceptible to nucleophilic attack and reacts directly

DOI: 10.1039/b203864a

only in the presence of a strong base (*i.e.*, K^{t}BuO) with molecules such as phosphines and arsines, [3] or when the quaternization of both phosphorus atoms by reaction with MeI or MeSO$_3$F promotes additional activation in the C=C bond.[4]

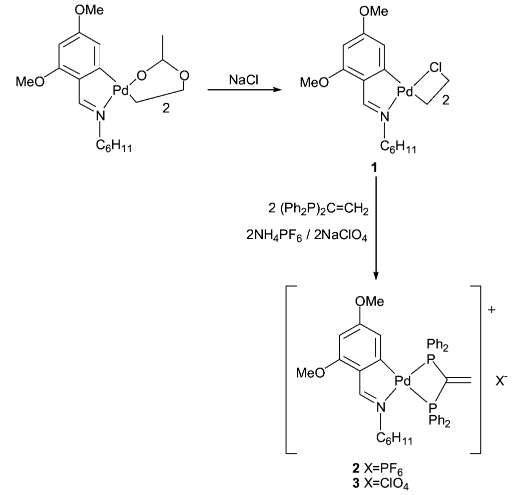
On the other hand, coordination to different metallic centres strongly activates the C=C bond towards the nucleophilic attack of species HNu, probably due to an additional induced polarization of the double bond in the starting complex and a relief of angle strain at the carbon adjacent to both phosphorus atoms after addition. Many different metal fragments promote these type of reactions when complexed to vdpp, which generally is acting as a chelating ligand, such as in the tetracarbonyl derivatives of group six metals,[5] Fe(0)[6] and Ru(II)[7] compounds, Pd(II), Pt(II) and Pt(IV) salts,[8] or Au(III) complexes;[9] even Au(I) compounds with an A-frame structure in which the phosphine is acting as a bridging ligand may undergo addition reactions.[10] Coupling reactions of vdpp can be achieved by treatment with lithium *via* coordination of the alkali metal to the phosphine.[11]

Cyclometallated complexes are well documented for a great variety of metal centres and ligands. These compounds are successfully used in organic synthesis,[12] catalysis,[13] photochemistry[14] and optical resolution processes,[15] and are rather promising as potential biologically active materials[16] and liquid crystals.[17] We have been interested in cyclopalladation reactions of differently substituted Schiff base ligands derived from [C,N,X] (X = O, S, N) terdentate ligands[18] or [C,N] Schiff bases,[19] as well as imidazoles[20] and ferrocenylimines.[21] 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[22] and we now present the synthesis of cyclometallated compounds derived from functionalized diphosphine ligands with pendant 1,3-dicarbonylic arms.

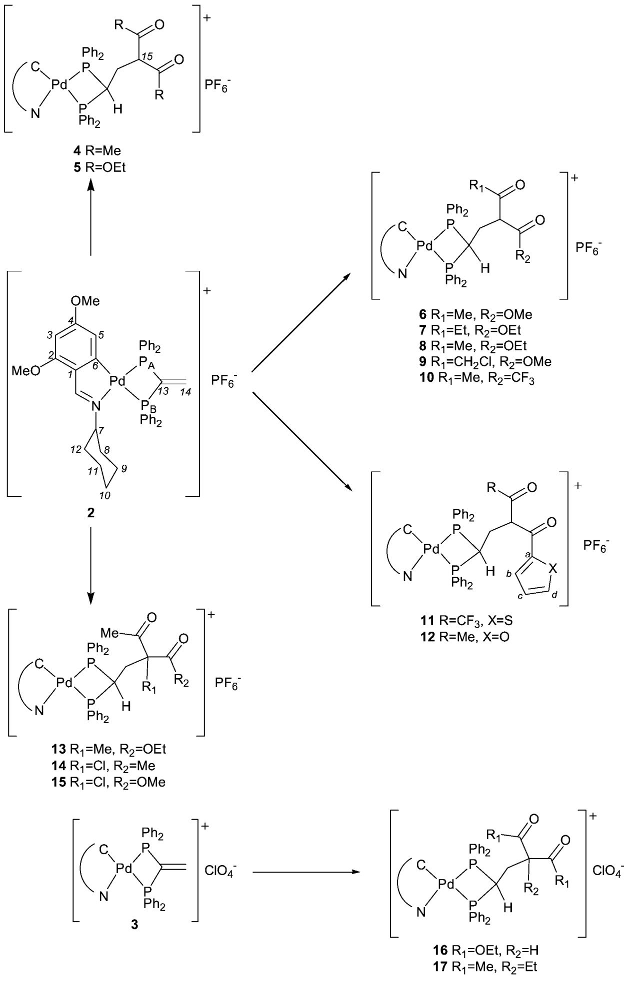
Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1 and 2. Treatment of [{Pd[2,4-(OMe)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*]}(μ-CH$_3$CO$_2$)]$_2$, a dinuclear cyclometallated complex with acetate-bridging ligands,[23] with aqueous sodium chloride, in a metathesis reaction, afforded the chloride-bridged complex [{Pd[2,4-(OMe)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*]}(μ-Cl)]$_2$, **1**. Nitrogen coordination to metal center was supported by the shift towards lower frequency in the IR spectrum of the ν(C=N) stretching vibration with respect to the corresponding one in the free imine (1579 and 1640 cm^{-1}, respectively)[24] and by the upfield shift of the HC=N proton resonance in the ^{1}H NMR spectrum *ca.* 0.7 ppm from its position in the spectrum of the free ligand (δ 8.00 and δ 8.64, respectively).[25] In the ^{1}H NMR spectrum, two doublets at δ 6.06 and δ 6.58 assigned to the H3 and H5 protons [^4J(H3H5) = 2.0 Hz], respectively, evidenced C6–Pd metallation. The IR spectra showed two ν(Pd–Cl) bands, at 295 and 289 cm^{-1}, consistent with an asymmetric Pd$_2$Cl$_2$ bridging unit.[26]

The mononuclear cyclometallated palladium(II) complexes [{Pd[2,4-(OMe$_2$)C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*]}{(Ph$_2$P)$_2$C=CH$_2$-*P*,*P*′}](X) (**2**, X = PF$_6$; **3**, X = ClO$_4$) were prepared by treatment of complex **1** with vdpp in 1:2 molar ratio, and ammonium hexafluorophosphate or sodium perchlorate as appropriate, in acetone at room temperature. The IR spectra showed, as the main difference from the starting material, bands at 850 br and 1080 s cm^{-1}, arising from the corresponding counterions, PF$_6^-$ and ClO$_4^-$, respectively. The FAB-MS spectra showed the corresponding peaks at m/z 748 assigned to [M]$^+$ (M corresponding to the fragment due to the loss of the PF$_6^-$ or ClO$_4^-$ ion), after consideration of the palladium isotopes.[27] The conductivity data (125–150 Ω^{-1} cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solutions in dry acetonitrile) showed them to be 1:1 electrolytes.[28] The HC=N resonance in the ^{1}H NMR spectra at δ 8.45 appeared as a doublet due to coupling with the ^{31}P nucleus *trans* to nitrogen [^4J(PH$_i$) = 8.3 Hz], whilst the H5 resonance appeared as a multiplet by coupling to H3 and to both ^{31}P nuclei, as we have found in related systems.[29] The H5 and 4-OMe proton signals were shifted to lower frequency by *ca.* 0.6 ppm, with respect to their position in the spectrum of the starting product, due to the shielding effect



Scheme 1



Scheme 2

of the phosphine phenyl rings *cis* to the metallated carbon atom. The ^{31}P-{^{1}H} NMR spectra showed two doublets [$^2J(P_AP_B)$ *ca.* 16.5 Hz], indicating the two phosphorus atoms to be non-equivalent in each case; the assignment of the doublets was made in accordance with the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to lower frequency.[30] The ^{13}C-{^{1}H} NMR spectrum of compound **2** showed resonances at δ 170.9 [t, ^3J(PC) = 3.5 Hz] and δ 165.0 [dd, ^2J(PC) = 122.8, 5.0 Hz] assignable to HC=N and C6, respectively, downfield shifted from the spectrum of the free ligand (*ca.* 15 and 35 ppm, also respectively),[23] thereby confirming that cyclometallation was maintained.[31] The C=CH$_2$ resonances appeared at δ 146.6 [dd, ^1J(PC) = 30.2, 20.6 Hz] and δ 138.1 [t, ^2J(PC) = 5.7 Hz], and were assigned to the α- and β-carbon atoms, C13 and C14, respectively. These findings were confirmed by the X-ray crystal structure determination of compound **2** (see below).

Reaction of **2** with acetylacetone, a symmetric 2,4-dicarbonylic derivative, in dry chloroform for 2 hours at 45 °C and inert atmosphere in the presence of anhydrous sodium carbonate yielded the addition product, [Pd{2,4-(MeO)$_2$-C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$CH(COMe)$_2$-*P*,*P′*}](PF$_6$), **4**, quantitatively (yield 95%). Attempts to synthesize **4** in the absence of the carbonate salt failed. The FAB-MS spectra showed a peak corresponding to [M]$^+$ at *m*/*z* 848. Other intense fragmentation peaks at *m*/*z* 537 and 291 were assigned to [Pd(L)(PPh$_2$)]$^+$ and [Pd(PPh$_2$)]$^+$, respectively; they were also present in the spectra of other complexes synthesized from **2** (*vide infra*). The IR absorptions of **4** at 1725 and 1705 cm^{-1} were consistent with the presence of two C=O groups. The ^{1}H NMR spectrum exhibited substantial differences with respect to the starting material. Thus, the resonance of the vinylidene protons in **2** was absent and a multiplet at *ca.* δ 4.80 assignable to the P$_2$C*H* proton appeared; the resonance due to the (Ph$_2$P)$_2$CHC*H*$_2$ protons overlapped with those of the methylene groups from the cyclohexyl ring. The 1,3-dicarbonyl moiety proton resonances were clearly distinguished: a triplet at δ 3.94 [^3J(HH) = 6.8 Hz] assignable to the α-proton H15, and two singlets at δ 1.94 and δ 1.85 assigned to the non-equivalent COMe methyl groups. The ^{31}P-{^{1}H} NMR spectrum showed two doublets assigned to the two inequivalent phosphorus atoms with a greater coupling constant [^2J(PP) = 55.1 Hz] than the one observed for the starting complex, in spite of the fact that the P–C–P carbon atom in **2** shows sp^2 hybridization, as opposed to the sp^3 hybridization of the same carbon atom in **4**; a similar trend has been observed by us in the addition reaction with amines.[22] We reasoned then that the contribution of ^2J(PP) across the metal center (normally of negative sign) is greater in the addition products than in **2**, thus lowering the absolute value of the coupling constant. The ^{13}C-{^{1}H} NMR spectrum confirmed addition showing the C13 and C14, resonances, δ 50.7 and δ 26.9, respectively, shifted to high field and in the expected range for an aliphatic carbon atom consequent on the C=CH$_2$ to CH$_2$CH$_2$ change upon addition. Four singlets, at δ 203.3 and δ 203.1, and at δ 29.7 and δ 29.6, were assigned to the *C*OMe and CO*Me* resonances, respectively. The C15 resonance appeared at δ 64.1 as a triplet [^3J(PC) = 4.3 Hz].

Under similar conditions reaction of **2** with the symmetric 1,3-diester diethyl malonate yielded a 7:3 mixture (as calculated from the integrals in the ^{1}H NMR spectrum) of the desired addition product **5** (in *ca.* 60% yield) and the starting complex, presumably as a consequence of the less acidic character of this nucleophile as compared with acetylacetone. The ^{1}H NMR spectrum of the mixture showed two signals at δ 1.19 and δ 1.15 assignable to the OCH$_2$*Me* methyl group in the addition product.

Treatment of **2** with the β-ketoester methyl acetoacetate afforded [Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$-CHCH$_2$CH-(COMe)(COOMe)-*P*,*P′*}](PF$_6$), **6**, in high yield (90%). The IR spectrum showed two *ν*(C=O) bands: one at 1720 cm^{-1}, assigned to the C(O)Me group, and another one at 1741 cm^{-1}, shifted towards higher wavenumbers, assigned to the C(O)OMe group.[32] The FAB-MS spectrum showed, among others, a peak corresponding to [M]$^+$ at *m*/*z* 864. In the ^{1}H NMR spectrum, four singlets were assigned to the methyl groups of the β-ketoester moiety, instead of the expected two, at δ 3.67 and δ 3.62 (CO$_2$*Me*), and at δ 1.97 and δ 1.80 (CO*Me*). This was also the case for the H5 and 4-MeO proton resonances of the cyclopalladated moiety. Thus, two multiplets at δ 5.69 and δ 5.64 were ascribed to the H5 resonance, and two singlets at δ 3.20 and δ 3.18 to the 4-MeO group. Likewise, the ^{31}P-{^{1}H} NMR spectrum showed two pairs of doublets. These results suggest the presence of optical isomers due to the existence of two chiral carbon atoms, after addition of the asymmetric nucleophile (Ph$_2$P)$_2$*C*HCH$_2$*C*H(COR$_1$)(COR$_2$): one situated in the α position with respect to the phosphorus atoms, and the other one situated in the α position to the carbonyl groups; whereas reaction with symmetric derivatives only produced one chiral center, *i.e.*, the P*C*P carbon atom (see Fig. 1). The relative ratio of the optical isomers was 1:1, as calculated from the integrals in the NMR spectra.

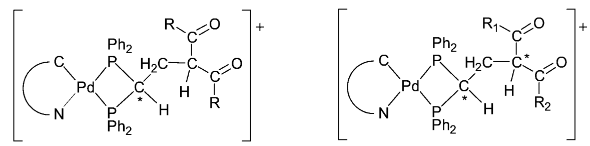


Fig. 1

Other asymmetric nucleophiles were tested, such as ethyl propionylacetate, ethyl acetoacetate and methyl 4-chloroacetoacetate, which yielded the corresponding addition products, **7**–**9**, in good yield (*ca.* 85%). Their mass and NMR spectra showed a similar pattern to that found for compound **6** (see Experimental section). The proposed structure for compound **7** has been confirmed by X-ray diffraction analysis (see below). Treatment of **2** with 1,1,1-trifluoroacetylacetone and thenoyltrifluoroacetone also afforded the corresponding addition products. The ^{31}P-{^{1}H} NMR spectra for compounds **10** and **11** only showed two doublets at *ca.* δ 12 and δ −8, [^2J(PP) *ca.* 53 Hz, see Experimental section], in spite of their asymmetric nature. However, in the corresponding ^{19}F NMR spectra two singlets were ascribed to the CF$_3$ resonance at *ca.* δ −71 and δ −75 in each case.

Reaction of **2** with 1-(2-furyl)-1,3-butanedione, ethyl 2-methylacetoacetate, 3-chloroacetylacetone and methyl 2-chloroacetoacetate gave compounds [Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$C(R$_1$)(COMe)-(COR$_2$)-*P*,*P′*}](PF$_6$) (R$_1$ = H, R$_2$ = 2-OC$_4$H$_3$, **12**; R$_1$ = Me, R$_2$ = OEt, **13**; R$_1$ = Cl, R$_2$ = Me, **14**; R$_1$ = Cl, R$_2$ = OMe, **15**). In the ^{1}H and ^{13}C NMR spectra of compounds **12** and **14** some resonances appeared duplicated, especially those corresponding to the 1,3-dicarbonyl moiety (see Experimental section). The PC*H*P proton resonance was shifted to lower frequency and was overlapped by the cyclohexyl ring signals. The ^{31}P-{^{1}H} NMR spectra of compound **14** showed two doublets, whereas in the case of compounds **12**, **13** and **15** four doublets were observed, as expected. The presence of the neighbouring chlorine atom shifted the phosphorus resonances to lower field with respect to other derivatives (*ca.* 28 and 12 ppm, for P$_A$ and P$_B$, respectively). An interesting feature of these spectra was the $^2J(P_AP_B)$ value, which was smaller in the case of the chlorine derivatives that in the other addition compounds (*ca.* 30 Hz *vs.* > 52 Hz). The FAB-MS spectrum of compounds **12** and **13** showed peaks at *m*/*z* 900 ([M]$^+$), and 892 ([M]$^+$) and 878 ([MH − Me]$^+$), respectively. In the mass spectrum for

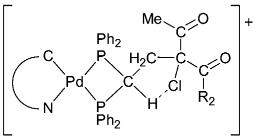


Fig. 2

complex **14** a very weak peak at m/z 882 was assigned to $[M]^+$, and a very intense one at m/z 846 was assigned to $[M - HCl]^+$, the spectrum of compound **15** only registered the peak at m/z 862, corresponding to $[M - HCl]^+$. We performed the electrospray mass spectra for complexes **14** and **15**, thereby confirming the presence of the $[M]^+$ peak. We suggest an additional interaction between the PC*H*P hydrogen atom and the chlorine atom in a five-membered ring, as depicted in Fig. 2, which made reasonable these peculiar findings.

Treatment of **2** with 3-ethylacetylacetone did not give any addition product, regardless of the reaction conditions used, even when a large excess of the nucleophile was added. The presence of the ethyl substituent in the α position to both carbonyl groups did not allow addition to the $C{=}CH_2$ double bond of the coordinated diphosphine, presumably due to steric hindrance by the phenyl rings of the diphosphine ligand, as opposed to the less sterically demanding methyl or chlorine groups, which afforded compounds **13**–**15**. Other bulky substituents, such as *tert*-butyl groups linked to the C(=O) moieties in 2,2,6,6-tetramethyl-3,5-heptanedione, also impeded addition, and no change in the starting complex was observed.

In analogous processes, compound **3** showed similar behavior to compound **2** when treated with the dicarbonyl compounds mentioned above. Furthermore, when **3** was treated with diethylmalonate the desired addition compound **16** could be isolated in pure form, in contrast to the analogous reaction with **2**, in which the corresponding product **5** was contaminated with the starting cyclometallated compound (see above). Reaction of **3** with 3-ethylacetylacetone, which did not react with complex **2**, yielded a mixture of **3** and **17** in 1:1 molar ratio. The effect of the counterion in these type of processes is not clear, but this work is currently being developed by us.

Molecular structures of complexes 2 and 7

Suitable crystals were grown by diffusion of diethyl ether in chloroform solutions of complexes **2** and **7**. The labelling schemes for the complexes are shown in Fig. 3 and 4 (see Experimental section for data). Both structures consist of discrete molecules, separated by normal van der Waals distances. The crystal structure of **2** comprises two molecules per asymmetric unit, both having very similar bond distances and angles; discussion will be limited to only one. The crystal structure of **7** comprises equimolar amounts of the (C16*R*, C18*S*) and (C16*S*, C18*R*) enantiomers. Crystallographic data and selected interatomic distances and angles are listed in Tables 1 and 2.

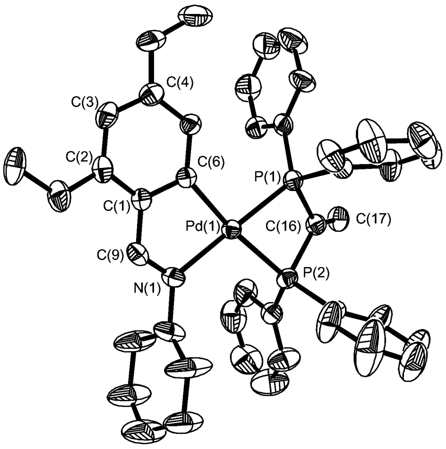


Fig. 3 Molecular structure of the cation for Pd{2,4-$(MeO)_2C_6H_2C(H){=}N(Cy)$-*C*6,*N*}{$(Ph_2P)_2C{=}CH_2$-*P*,*P′*}]$(PF_6)$ (**2**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

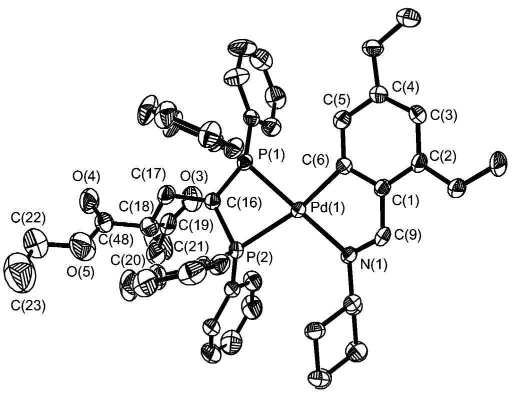


Fig. 4 Molecular structure of the cation for [Pd{2,4-$(MeO)_2C_6H_2C(H){=}N(Cy)$-*C*6,*N*}{$(Ph_2P)_2CHCH_2CH(COEt)(COOEt)$-*P*,*P′*}]$(PF_6)$ (**7**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

The coordination sphere around each palladium atom consists of a nitrogen atom of the imine group, an *ortho* carbon atom of the phenyl ring, and two phosphorus atoms from a chelating diphospine ligand in a slightly distorted square-planar coordination environment. The sums of angles at palladium are 359.97° (**2**) and 359.22° (**7**), with the distortions more noticeable in the somewhat reduced "bite" angles C(6)–Pd(1)–N(1) consequent upon chelation [81.0 (3)° (**2**) and 80.7(2)° (**7**), and P(1)–Pd(1)–P(2) = 73.27(7)° (**2**) and 72.24(6)° (**7**), respectively]. The requirements of the five- and four-membered chelate rings force the bond angles P(1)–Pd(1)–P(2) to 73.27(7)° (**2**) and 72.25(6)° (**7**), P(1)–$C(16)_{sp^2}$–P(2) to 98.4(4)° (**2**) and P(1)–$C(16)_{sp^3}$–P(2) to 95.1(3)° (**7**). The latter ones represent a

Table 1 Crystal and structure refinement data for complexes **2** and **7**

	2	**7**
Formula	$C_{41}H_{42}F_6NO_2P_3Pd$	$C_{48}H_{54}F_6NO_5P_3Pd$
M_r	894.07	1038.23
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P21/c$
Cell dimensions:		
a/Å	16.948(1)	21.054(1)
b/Å	17.549(1)	9.7220(1)
c/Å	18.007(1)	23.338(1)
α/°	61.780(1)	
β/°	64.065(1)	90.661(1)
γ/°	66.171(1)	
V/Å^3	4110.7(1)	4776.7(2)
Z	4	4
Crystal size/mm^3	0.25 × 0.20 × 0.15	0.40 × 0.40 × 0.20
μ/mm^{-1}	0.631	0.558
θ range/°	1.3 to 25.0	0.9 to 25.0
Reflections:		
collected	22085	24121
independent	14094 ($R_{int} = 0.0307$)	8401 ($R_{int} = 0.0670$)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0688, 0.1671	0.0550, 0.1417
R_1, wR_2 (all data)	0.1151, 0.2027	0.1069, 0.1854
max ρ/e Å^{-3}	1.121	0.855

Table 2 Selected bond distances (Å) and angles (°) for complexes **2** and **7**

	2	**7**
C(6)–Pd(1)	2.029(7)	2.035(6)
Pd(1)–N(1)	2.094(6)	2.102(5)
N(1)–C(9)	1.277(10)	1.261(8)
C(9)–C(1)	1.439(10)	1.449(8)
C(1)–C(6)	1.408(9)	1.388(8)
Pd(1)–P(1)	2.257(2)	2.2566(16)
Pd(1)–P(2)	2.370(2)	2.3799(16)
P(1)–C(16)	1.816(8)	1.853(6)
P(2)–C(16)	1.834(8)	1.854(6)
C(16)–C(17)	1.301(10)	1.517(9)
C(17)–C(18)		1.538(9)
C(18)–C(19)		1.499(13)
C(19)–O(3)		1.215(10)
C(18)–C(48)		1.493(11)
C(48)–O(4)		1.194(10)
C(6)–Pd(1)–N(1)	81.0(3)	80.7(2)
C(6)–Pd(1)–P(1)	99.4(2)	98.05(17)
N(1)–Pd(1)–P(2)	106.30(19)	108.54(14)
P(1)–Pd(1)–P(2)	73.27(7)	72.24(6)
P(1)–C(16)–P(2)	98.4(4)	95.1(3)
Pd(1)–P(1)–C(16)	94.1(2)	95.0(2)
Pd(1)–P(2)–C(16)	90.0(2)	91.04(19)
P(1)–C(16)–C(17)	131.0(7)	122.2(5)
P(2)–C(16)–C(17)	129.9(7)	124.8(5)
C(16)–C(17)–C(18)		113.3(6)
C(17)–C(18)–C(19)		114.5(7)
C(19)–C(18)–C(48)		109.2(7)
C(17)–C(18)–C(48)		110.8(7)
C(18)–C(19)–O(3)		122.3(9)
C(18)–C(48)–O(4)		123.6(9)

smaller value than the corresponding one in free vdpp, 118.4°,[33] although some four-membered chelate rings involving coordinated phosphines with a even smaller P–C–P angle have been reported.[34]

The palladium–nitrogen bond lengths, 2.094(6) (**2**) and 2.103(5) Å (**7**), are longer than the single bond predicted value of 2.011 Å, based on the sum of covalent radii for nitrogen (sp^2) and palladium, 0.701 and 1.31 Å, respectively,[35] and reflects the *trans* influence of the phosphorus atom.[29] The palladium–carbon bond length, 2.029(7) (**2**) and 2.035(6) Å (**7**), are within the expected value of 2.081 Å (based on the sum of covalent radii for carbon (sp^2) and palladium, 0.771 and 1.31 Å, respectively), but longer than those found in related complexes where partial multiple-bond character of the Pd–C bond was proposed.[20,36] This suggests some degree of multiple-bond character in the Pd–C(aryl) linkage, and also reflects the *trans* influence of the phosphorus atom for the observed lengthening. The palladium–phosphorus bond distances are shorter than the sum of the single bond radii for palladium and phosphorus, 2.41 Å, suggesting some partial double bond between both atoms and it is similar to others reported earlier.[37] The differing *trans* influence of the phenyl carbon and imine nitrogen atoms is clearly illustrated by the palladium–phosphorus distance *trans* to carbon, Pd(1)–P(1), and *trans* to nitrogen, Pd(1)–P(2), [*i.e.*, Pd(1)–P(1) = 2.257(2) Å *vs.* Pd(1)–P(2) = 2.370(2) Å, **2**; Pd(1)–P(1) = 2.2567(16) Å *vs.* Pd(1)–P(2) = 2.3799(16) Å, **7**].

Except for the methoxy and the cyclohexyl groups, the cyclopalladated moiety is nearly planar. The mean deviations from the least squares planes determined for the metallated phenyl ring (C1, C2, C3, C4, C5, C6; plane 1) and the metallacycle (Pd1, C1, C6, C9, N1; plane 2) are 0.0069 and 0.0074 Å (**2**), respectively; and 0.0029 Å and 0.0208 Å (**7**), also respectively. The angles between these planes are 4.2° (**4**) and 1.2° (**7**). The chelate phosphine ring is not planar, with a mean deviation from the ideal plane of 0.1329 Å (**2**) and 0.1678 Å (**7**). The vinylidene carbon atoms, C(16) and C(17), show a displacement from the plane formed by the metal center and the phosphorus atoms (Pd(1), P(1), P(2), plane 3) of 0.4405 and −1.0606 Å (**2**), respectively; and −0.5583 and −0.3305 Å (2), also respectively. The angles between plane 3 and the previous planes are as follows: plane 1/plane 3:6.0° and plane 2/plane 3:1.8°, for complex **2**; and plane 1/plane 3:12.1°, plane 2/plane 3:9.9°, for complex **7**.

For complex **2**, the C(16)–C(17) bond length is 1.301(10) Å, which is within the range expected for a carbon–carbon double bond and is shorter than the value of 1.34 Å in free vdpp. Its corresponding value in compound **7** is 1.517(9) Å, respectively, consequent upon addition and is within the expected value for a single carbon–carbon bond (*ca.* 1.50 Å). For complex **7** the carbon–oxygen bond lengths are C(19)–O(3) = 1.215(10) Å and C(48)–O(4) = 1.194(10) Å, and are within the expected value for a double bond C=O (*ca.* 1.21 Å), whereas the C(18)–C(19) and C(18)–C(48) bond distances, 1.499(13) and 1.492(11) Å, respectively, are in the corresponding range for a single bond C–C, thereby confirming the presence of the 1,3-dicarbonyl moiety in its keto form.

Experimental section

General remarks

Safety note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.

All manipulations to synthesize the addition compounds were performed under prepurified Ar using standard Schlenk techniques. All solvents were distilled prior to use from appropriate drying agents.[38] $Ph_2PC(=CH_2)PPh_2$ (vdpp) was prepared according to procedures described elsewhere.[39] All other chemicals were used as supplied from commercial sources. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C-{^1H}), 85% H_3PO_4 (^{31}P-{^1H}) or $CFCl_3$ (^{19}F); and were recorded on a Bruker AC-200F spectrometer (200.0 MHz for ^1H, 50.3 MHz for ^{13}C-{^1H}, 81.0 MHz for ^{31}P-{^1H}, 188.3 MHz for ^{19}F). IR spectra were recorded as KBr pellets or Nujol mulls on a Perkin-Elmer 1330 spectrophotometer. Conductivity measurements were made on a Crison GLP 32 conductivimeter using 10^{-3} M solutions in dry acetonitrile at room temperature (298 K). Mass spectra were obtained in a QUATRO mass spectrometer with Cs ion-gun and 3-NBA matrix. Electrospray mass spectra were recorded on a Finnigan Navigator spectrometer with acetonitrile as the solvent. The synthesis of [{Pd-[2,4-$(OMe)_2C_6H_2C(H)=N(Cy)$-*C*6,*N*]}(μ-$MeCO_2$)]$_2$ was reported in a recent paper from this laboratory.[23]

Syntheses of the addition compounds

[{Pd[2,4-$(OMe)_2C_6H_2C(H)=N(Cy)$-*C*6,*N*]}{μ-Cl)]$_2$, 1. An aqueous solution of 10^{-2} M NaCl (*ca.* 25 mL) was added dropwise to [{Pd-[2,4-$(OMe)_2C_6H_2C(H)=N(Cy)$-*C*6,*N*]}(μ-$MeCO_2$)]$_2$ (300 mg, 0.364 mmol) in acetone (*ca.* 25 mL). The mixture was stirred for 12 hours after which a pale yellow solid precipitated which was filtered off, washed with water (2 × 3 mL) and dried *in vacuo* over anhidrous $CaCl_2$. Yield: 98%. IR: ν(C=N): 1579 s; $\nu(Pd\text{–}Cl_{trans\text{-}N})$ 295m, $\nu(Pd\text{–}Cl_{trans\text{-}C})$ 280m. FAB-MS: 663 $[MH - Cl - (MeO)_2 - Me]^+$, 647 $[MH - Cl - (MeO)_3]^+$. ^1H NMR: 8.00 (s, *H*i); 6.58 (d, H_5, $^4J(H_3H_5) = 2.0$ Hz); 6.06 (d, H_3); 3.82, 3.76 (s, 2-O*Me*, 4-O*Me*).

Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$C=CH$_2$-*P*,*P*′}](PF$_6$), 2. To a solution of **1** (200 mg, 0.258 mmol) in acetone (*ca.* 25 mL), vdpp (204 mg, 0.516 mmol) was added. The mixture was stirred for 30 minutes at room temperature, after which ammonium hexafluorophosphate (85 mg, 0.521 mmol) was added, the resultant solution stirred for a further 30 minutes, water (*ca.* 25 mL) added dropwise and the resulting mixture stirred for 12 hours. A pale yellow precipitate which formed was filtered off, washed with water (2 × 3 mL) and dried *in vacuo* over anhydrous CaCl$_2$. The desired complex was recrystallized from a chloroform solution by gaseous diffusion of diethyl ether. Yield: > 95%. IR: ν(C=N): 1579 s. FAB-MS: 748 [M]$^+$. ^{1}H NMR: 8.45 (d, *H*i, ^4J(PH$_i$) = 8.3 Hz); 6.36 (m, C=C*H*$_2$); 6.11 (d, H_3, ^4J(H$_3$H$_5$) = 2.0 Hz); 5.94 (m, H_5); 3.81 (s, 2-O*Me*); 3.25 (s, 4-O*Me*). ^{31}P-{^{1}H} NMR: 12.75 (d, P_A, ^2J(P$_A$P$_B$) = 16.9 Hz); –4.05 (d, P_B). ^{13}C NMR: 170.9 (t, *C*=N, ^3J(PC = 3.5 Hz); 165.0 (dd, C_6, ^2J(P$_{trans}$C$_6$) = 122.8 Hz, ^2J(P$_{cis}$C$_6$) = 5.0 Hz); 163.7 (dd, C_4, ^4J(P$_{trans}$C$_4$) = 13.5 Hz, ^4J(P$_{cis}$C$_4$) 8.5 Hz); 160.3 (d, C_2, ^4J(PC$_2$) = 10.6 Hz); 146.6 (dd, C_{13}, ^1J(P$_{trans}$C$_{13}$) = 30.2 Hz, ^1J(P$_{cis}$C$_{13}$) = 20.6 Hz); 138.1 (t, C_{14}, ^2J(PC$_{14}$) = 5.7 Hz); 128.6 (d, C_1, ^3J(PC$_1$) = 2.1 Hz); 115.7 (dd, C_5, ^3J(P$_{trans}$C$_5$) = 14.2 Hz, ^3J(P$_{cis}$C$_5$) = 2.8 Hz); 95.7 (s, C_3); 70.0 (d, C_7, ^3J(PC$_7$) = 4.3 Hz); 55.6, 55.2 (s, O*Me*); 33.8 (s, C_8, C_{12}); 24.9, 24.5 (s, C_9–C_{11}).

Compound **3** was prepared similarly to compound **2** and isolated as a pale yellow solid, but using sodium perchlorate as appropiate.

Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$C=CH$_2$-*P*, *P*′}](ClO$_4$), 3. Yield: > 95%. IR: ν(C=N): 1575 s. FAB-MS: 748 [M]$^+$. ^{1}H NMR: 8.45 (d, *H*i, ^4J(PH$_i$) = 8.3 Hz); 6.35 (m, C=C*H*$_2$); 6.10 (d, H_3, ^4J(H$_3$H$_5$) = 2.0 Hz); 5.94 (m, H_5); 3.81 (s, 2-O*Me*); 3.25 (s, 4-O*Me*). ^{31}P-{^{1}H} NMR: 12.58 (d, P_A, ^2J(P$_A$P$_B$) = 16.1 Hz); –4.27 (d, P_B).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$-CH(COMe)$_2$-*P*,*P*′}](PF$_6$), 4. Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$=CH$_2$-*P*,*P*′}](PF$_6$), **2** (50 mg, 0.056 mmol) and acetylacetone (11 μL, 0.112 mmol) were heated at 45 °C in dry chloroform (*ca.* 5 mL) for 2 hours under Ar in the presence of anhydrous sodium carbonate (catalytic amount). The solution was cooled to room temperature, filtered through Celite, and the solvent removed under reduced pressure to give an oily product. The residue was triturated with diethyl ether, filtered off, washed with cold diethyl ether and dried *in vacuo* to yield the desired product as a yellow solid. Yield: 95%. IR: ν(C=O): 1705 s, 1725 s; ν(C=N): 1578 s. FAB-MS: 848 [M]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 291 [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 7.8 Hz); 6.04 (d, H_3, ^4J(H$_3$H$_5$) = 2.0 Hz); 5.67 (m, H_5); 4.69 (m, PC*H*P); 3.94 (t, H_{15}, ^3J(H$_{15}$H$_{14}$) = 6.8 Hz); 3.78 (s, 2-O*Me*); 3.14 (s, 4-O*Me*); 1.94 s, 1.85 (s, CO*Me*). ^{31}P-{^{1}H} NMR: 12.36 (d, P_A, ^2J(P$_A$P$_B$) = 55.1 Hz); –8.66 (d, P_B). ^{13}C NMR: 203.3, 203.1 (s, *C*OMe); 171.0 (t, *C*=N, ^3J(PC) = 3.5 Hz); 166.1 (dd, C_6, ^2J(P$_{trans}$C$_6$) = 125.6 Hz, ^2J(P$_{cis}$C$_6$) = 8.5 Hz); 163.7 (dd, C_4, ^4J(P$_{trans}$C$_4$) = 13.5 Hz, ^4J(P$_{cis}$C$_4$) = 8.5 Hz); 160.1 (d, C_2, ^4J(PC$_2$) = 10.6 Hz); 128.6 (d, C_1, ^3J(PC$_1$) = 2.0 Hz); 114.3 (dd, C_5, ^3J(P$_{trans}$C$_5$) = 13.5 Hz, ^3J(P$_{cis}$C$_5$) = 3.5 Hz); 95.9 (s, C_3); 69.1 (d, C_7, ^3J(PC$_7$) = 4.3 Hz); 64.1 (t, C_{15}, ^3J(PC$_{15}$) = 4.3 Hz); 55.5, 55.1 (s, O*Me*); 50.7 (dd, C_{13}, ^1J(P$_{trans}$C$_{13}$) = 22.7 Hz, ^1J(P$_{cis}$C$_{13}$) = 16.3 Hz); 33.8, 33.3 (s, C_8, C_{12}); 29.7, 29.6 (s, CO*Me*); 26.9 (t, C_{14}, ^2J(PC$_{14}$) = 4.9 Hz); 25.0, 24.9, 24.6 (s, C_9–C_{11}).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$-CH(COOEt)$_2$-*P*,*P*′}](PF$_6$), 5. A mixture of **2** (0.025 g, .028 mmol) and diethylmalonate (9 μL, 0.056 mmol) was treated in a similar fashion to the above complex. The final residue was shown to consist of a 7:3 mixture (as calculated from the integrals in the ^{1}H NMR spectra) of the desired addition product **5** and the starting complex **2**. It was not possible to obtain **5** in pure form by either recrystallization or column chromatography. Overall yield: 86%, *ca.* 60% relative to **5**. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 8.3 Hz); 6.07 (d, H_3, ^4J(H$_3$H$_5$) = 2.0 Hz); 5.66 (m, H_5); 4.80 (m, PC*H*P); 4.12 (m, CO$_2$C*H*$_2$); 3.79 (s, 2-O*Me*); 3.23 (s, 4-O*Me*); 3.01 (t, H_{15}, ^3J(H$_{15}$H$_{14}$) = 7.3 Hz); 1.19 (dd, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 7.3, 3.9); 1.15 (dd, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 6.8, 3.9). ^{31}P-{^{1}H} NMR: 11.20 (d, P_A, ^2J(P$_A$P$_B$) = 53.4 Hz); –9.26 (d, P_B).

Compounds **6**–**8** were prepared as white solids in a similar manner to **4**, but using methyl acetoacetate (**6**), ethyl propionylacetate (**7**) and ethyl acetoacetate (**8**) as appropriate.

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$ CH(COMe)(COOMe)-*P*,*P*′}](PF$_6$), 6. Yield: 90%. IR: ν(C=O): 1720 s, 1741 s; ν(C=N): 1579 s. FAB-MS: 864 [M]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 291 [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 7.8 Hz); 6.06 (d, H_3, ^4J(H$_3$H$_5$) = 1.0 Hz); 5.69, 5.64 (m, H_5); 4.69 (m, PC*H*P); 3.79 (s, 2-O*Me*); 3.67, 3.62 (s, CO$_2$*Me*); 3.20, 3.18 (s, 4-O*Me*); 1.97, 1.80 (s, CO*Me*). ^{31}P-{^{1}H} NMR: 12.36, 11.70 (d, P_A, ^2J(P$_A$P$_B$) = 54.2, 54.2 Hz); –7.99, –9.29 (d, P_B).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$ CH(COEt)(COOEt)-*P*,*P*′}](PF$_6$), 7. Yield: 83%. IR: ν(C=O): 1720 s, 1740 s; ν(C=N): 1579 s. FAB-MS: 892 [M]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 291 [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 8.8 Hz); 6.06 (d, H_3, ^4J(H$_3$H$_5$) = 1.0 Hz); 5.67, 5.63 (m, H_5); 4.70 (m, PC*H*P); 4.12 (m, CO$_2$C*H*$_2$); 3.79 (s, 2-O*Me*); 3.21, 3.18 (s, 4-O*Me*); 1.20 (dd, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 7.3, 4.4); 1.16 (dd, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 6.8, 4.4); 0.87 (m, COCH$_2$*Me*). ^{31}P-{^{1}H} NMR: 11.95, 11.68 (d, P_A, ^2J(P$_A$P$_B$) = 54.3, 55.1 Hz); –8.11, –9.51 (d, P_B).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$-CH(COMe)(COOEt)-*P*,*P*′}](PF$_6$), 8. Yield: 87%. IR: ν(C=O): 1720 s, 1740 s; ν(C=N): 1579 s. FAB-MS: 878 [M]$^+$, 632 [M – L]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 291 [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 8.8 Hz); 6.06 (d, H_3, ^4J(H$_3$H$_5$) = 1.5 Hz); 5.68, 5.64 (m, H_5); 4.70 (m, PC*H*P); 4.13 (m, CO$_2$C*H*$_2$); 3.79 (s, 2-O*Me*); 3.21, 3.18 (s, 4-O*Me*); 1.95, 1.81 (s, CO*Me*); 1.21 (dd, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 7.3, 3.9); 1.17 (dd, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 6.8, 3.9). ^{31}P-{^{1}H} NMR: 11.85, 11.80 (d, P_A, ^2J(P$_A$P$_B$) = 53.4, 54.2 Hz); –7.89, –9.01 (d, P_B).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$-CH(COCH$_2$Cl)(COOMe)-*P*,*P*′}](PF$_6$), 9. This was prepared by treating a mixture of **2** and methyl 4-chloroacetoacetate similarly to **4**, except that a reaction time of 4 hours was used. Yield: 54%. IR: ν(C=O): 1729 s; ν(C=N): 1577 s. FAB-MS: 898 [M]$^+$, 862 [M – HCl]$^+$, 431 [M – HCl]$^{2+}$. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 8.3 Hz); 6.04 (d, H_3, ^4J(H$_3$H$_5$) = 1.5 Hz); 5.64 (m, H_5); 4.65 (m, PC*H*P); 3.78 (s, 2-O*Me*); 3.18, 3.14 (s, 4-O*Me*); 3.69, 3.63 (s, CO$_2$*Me*), 2.30 (b, C*H*$_2$Cl). ^{31}P-{^{1}H} NMR: 12.86, 12.39 (d, P_A, ^2J(P$_A$P$_B$) = 54.3, 55.9 Hz); –7.31, –8.87 (d, P_B).

Compounds **10** and **11** were prepared analogously to **4** by treatment of **2** with 1,1,1-trifluoroacetylacetone (**10**) and thenoyltrifluoroacetone (**11**), and isolated as white and yellow solids, respectively.

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C*6,*N*}{(Ph$_2$P)$_2$CHCH$_2$-CH(COMe)(COCF$_3$)-*P*,*P*′}](PF$_6$), 10. Yield: 88%. IR: ν(C=O): 1720 s; ν(C=N): 1579 s. FAB-MS: 806 [MH – CF$_3$CO]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 291, [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 8.3 Hz); 6.05 (d, H_3, ^4J(H$_3$H$_5$) = 2.0 Hz); 5.70 (m, H_5); 4.96 (m, PC*H*P); 3.78 (s, 2-O*Me*); 3.17 (s, 4-O*Me*); 2.45 (t, H_{15}, ^3J(H$_{15}$H$_{14}$) = 6.3 Hz); 1.74 (b, CO*Me*).

^{31}P-{^{1}H} NMR: 11.40 (d, P_A, $^2J(P_AP_B) = 53.4$ Hz); −8.90 (d, P_B). ^{19}F NMR: −71.47 (s, CF$_3$), −75.23 (s, CF$_3$).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$P)$_2$CHCH$_2$-CH(COCF$_3$)(CO{2-SC$_4$H$_3$})-*P,P′*}](PF$_6$), 11. Yield: 80%. IR: ν(C=O): 1740 s; ν(C=N): 1579 s. FAB-MS: 970 [M]$^+$, 874 [MH − CF$_3$CO]$^+$, 748 [Pd(L)(vdpp)]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 291 [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 7.8 Hz); 6.04 (d, H_3, $^4J(H_3H_5) = 2.0$ Hz); 5.71 (m, H_5); 5.17 (m, PC*H*P); 3.78 (s, 2-O*Me*); 3.14 (s, 4-O*Me*); 2.96 (t, H_{15}, $^3J(H_{15}H_{14}) = 6.4$ Hz). ^{31}P-{^{1}H} NMR: 12.18 (d, P_A, $^2J(P_AP_B) = 52.6$ Hz); -7.69 (d, P_B). ^{19}F NMR: −71.29 (s, CF$_3$), −75.07 (s, CF$_3$).

Compounds **12**–**15** were synthesized similarly, using 1-(2-furyl)-1,3-butanedione (**12**), ethyl 2-methylacetoacetate (**13**), 3-chloroacetylacetone (**14**) and methyl 2-chloroacetoacetate (**15**) as appropriate, and isolated as white solids.

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$P)$_2$CHCH$_2$-CH(COMe)(CO{2-OC$_4$H$_3$})-*P,P′*}](PF$_6$), 12. Yield: 77%. IR: ν(C=O): 1720 s; ν(C=N): 1576 s. FAB-MS: 900 [M]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 291 [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.41 (d, *H*i, ^4J(PH$_i$) = 7.8 Hz); 7.16 (d, H_b, $^3J(H_bH_c) = 3.4$ Hz); 6.54 (dd, H_c, $^3J(H_cH_d) = 1.5$ Hz); 6.03 (d, H_3, $^4J(H_3H_5) = 2.0$ Hz); 5.63 (m, H_5); 4.80 (m, PC*H*P); 4.30 (m, H_{15}); 3.77 (s, 2-O*Me*); 3.15 (s, 4-O*Me*); 2.01, 1.90 (s, CO*Me*). ^{31}P-{^{1}H} NMR: 13.38, 12,83 (d, P_A, $^2J(P_AP_B) = 53.4$, 55.1 Hz); −6.74, −7.60 (d, P_B). ^{13}C NMR: 201.6 (s, *C*OMe); 182.3 (s, *C*O$_{\text{furyl}}$); 170.8 (d, *C*=N, ^3J(PC) = 5.7 Hz); 164.0 (m, C_4); 160.0 (d, C_2, $^4J(PC_2) = 10.6$ Hz); 150.9, 150.8 (s, C_a); 148.5, 148.3 (s, C_d); 128.5 (s, C_1); 120.7 (b, C_b); 114.2 (b, C_5); 113.5, 113.4 (s, C_c); 96.0 (s, C_3); 69.2 (s, C_7); 59.3 (s, C_{15}); 55.5, 55.2 (s, O*Me*); 49.0 (m, C_{13}); 33.8, 33.2 (s, C_8, C_{12}); 29.4 (s, CO*Me*); 27.3 (b, C_{14}); 25.0, 24.8, 24.5 (s, C_9–C_{11}).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$P)$_2$CHCH$_2$-C(Me)(COMe)(COOEt)-*P,P′*}](PF$_6$), 13. Yield: 65%. IR: ν(C=O): 1730 b,m; ν(C=N): 1579 s. FAB-MS: 892 [M]$^+$, 878 [MH − Me]$^+$, 748 [Pd(L)(vdpp)]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 505 [Pd(L)(PPh$_2$) − MeO]$^+$, 291 [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.41 (d, *H*i, ^4J(PH$_i$) = 7.8 Hz); 6.04 (d, H_3, $^4J(H_3H_5) = 1.9$ Hz); 5.69, 5.65 (m, H_5); 4.56 (m, PC*H*P); 3.78 (s, 2-O*Me*); 3.72 (m, CO$_2$C*H*$_2$); 3.20, 3.19 (s, 4-O*Me*); 1.76, 1.78 (s, CO*Me*); 1.08 (t, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 7.1 Hz); 1.07 (s, COC-*Me*CO). ^{31}P-{^{1}H} NMR: 16.08, 15.54 (d, P_A, $^2J(P_AP_B)$ = 61.04, 61.89 Hz); −4.29, −4.63 (d, P_B).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$P)$_2$CHCH$_2$-C(Cl)(COMe)$_2$-*P,P′*}](PF$_6$), 14. Yield: 85%. IR: ν(C=O): 1705 s; ν(C=N): 1579 s. FAB-MS: 882 [M]$^+$, 846 [M − HCl]$^+$, 537 [Pd(L)(PPh$_2$)]$^+$, 291 [Pd(PPh$_2$)]$^+$. ^{1}H NMR: 8.39 (d, *H*i, ^4J(PH$_i$) = 8.8 Hz); 6.03 (d, H_3, $^4J(H_3H_5) = 2.0$ Hz); 5.65 (m, H_5); 3.77 (s, 2-O*Me*); 3.14 (s, 4-O*Me*); 2.30 (m, C*H*$_2$CCl); 1.97, 1.80 (s, CO*Me*). ^{31}P-{^{1}H} NMR: 31.3 (d, P_A, $^2J(P_AP_B) = 28.8$ Hz); 15.8 (d, P_B). ^{13}C NMR: 200.6, (d, *C*OMe, ^4J(PC) = 3.5 Hz); 200.3 (d, *C*OMe, ^4J(PC) = 2.8 Hz); 171.4 (t, *C*=N, ^3J(PC) = 5.0 Hz); 168.5 (dd, C_6, $^2J(P_{\text{trans}}C_6) = 124.2$ Hz, $^2J(P_{cis}C_6) = 8.5$ Hz); 163.6 (dd, C_4, $^4J(P_{trans}C_4) = 13.5$ Hz, $^4J(P_{cis}C_4) = 8.5$ Hz); 160.0 (d, C_2, $^4J(PC_2) = 10.0$ Hz); 129.0 (s, C_1); 114.4 (dd, C_5, $^3J(P_{trans}C_5) = 10.6$ Hz, $^3J(P_{cis}C_5) = 3.5$ Hz); 95.8 (s, C_3); 67.7 (d, C_7, $^3J(PC_7) = 5.7$ Hz); 57.6 (t, C_{15}, $^3J(PC_{15}) = 2.8$ Hz); 55.4, 54.9 (s, O*Me*); 43.5 (dd, C_{13}, $^1J(P_{trans}C_{13}) = 17.8$ Hz, $^1J(P_{cis}C_{13}) = 3.5$ Hz); 33.9, 33.6 (s, C_8, C_{12}); 30.2, 29.8 (s, CO*Me*); 26.5 (b, C_{14}); 25.4, 25.2, 24.9 (s, C_9–C_{11}).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$P)$_2$CHCH$_2$-C(Cl)(COCH$_3$)(COOMe)-*P,P′*}](PF$_6$), 15. Yield: 58%. IR: ν(C=O): 1730 s,1704 s; ν(C=N): 1577 s. FAB-MS: 862 [M − HCl]$^+$, 748 [Pd(L)(vdpp)]$^+$. ^{1}H NMR: 8.38 (d, *H*i, ^4J(PH$_i$) = 8.3 Hz); 6.02 (d, H_3, $^4J(H_3H_5) = 2.0$ Hz); 5.58 (m, H_5); 3.75 (s, 2-O*Me*); 3.20 (s, 4-O*Me*); 3.44, 3.40 (s, CO$_2$*Me*); 2.12, 2.05 (s, CO*Me*). ^{31}P-{^{1}H} NMR: 28.39, 27.54 (d, P_A, $^2J(P_AP_B)$ = 30.5, 30.5 Hz); 12.56, 10.98 (d, P_B). ^{13}C NMR: 199.0, 198.8 (s, *C*OMe); 171.5 (m, *C*=N); 169.0 (m, C_6); 166.2 (s, *C*OOMe); 163.8 (m, C_4); 160.0 (d, C_2, $^4J(PC_2) = 9.9$ Hz); 114.2 (dd, C_5, $^3J(P_{trans}C_5) = 11.2$ Hz, $^3J(P_{cis}C_5) = 4.2$ Hz); 95.7 (s, C_3); 67.7 (b, C_7); 50.9 (s, C_{15}); 44.2 (m, C_{13}); 34.0, 33.9, 33.7, 33.4 (s, C_8, C_{12}); 30.5, 29.9 (s, CO*Me*); 29.2 (b, C_{14}); 25.4, 25.3, 24.8 (b, C_9–C_{11}); 55.4, 55.1, 55.0, 53.6 (s, O*Me*, COO*Me*)

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$P)$_2$CHCH$_2$-CH(COOEt)$_2$-*P,P′*}](ClO$_4$), 16. Treatment of Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$P)$_2$=CH$_2$-*P,P′*}](ClO$_4$), **3**, with diethylmalonate analogously to **4**, but using a reaction time of 15 hours afforded the desired addition product in pure form as a white solid. Yield: 77%. IR: ν(C=O): 1743 s, 1730 s; ν(C=N): 1577 s. FAB-MS: 908 [M]$^+$, 748 [Pd(L)(vdpp)]$^+$. ^{1}H NMR: 8.43 (d, *H*i, ^4J(PH$_i$) = 8.3 Hz); 6.08 (d, H_3, $^4J(H_3H_5) = 2.0$ Hz); 5.66 (m, H_5); 4.82 (m, PC*H*P); 4.11 (m, CO$_2$C*H*$_2$); 3.79 (s, 2-O*Me*); 3.24 (s, 4-O*Me*); 3.02 (t, H_{15}, $^3J(H_{14}H_{15}) = 7.3$ Hz); 1.19 (dd, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 7.3, 3.9); 1.15 (dd, CO$_2$CH$_2$*Me*, ^3J(CH$_2$Me) = 6.8, 3.9). ^{31}P-{^{1}H} NMR: 11.10 (d, P_A, $^2J(P_AP_B) = 53.4$ Hz); −9.25 (d, P_B).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(Cy)-*C6,N*}{(Ph$_2$P)$_2$CHCH$_2$-C(Et)(COMe)$_2$-*P,P′*}](ClO$_4$), 17. Treatment of **3** and 3-ethylacetylacetone in a similar fashion to **16**, but using a reaction time of 20 hours yielded a 1:1 mixture of the desired addition product **17** and the starting complex **3**. It was not possible to obtain **17** in pure form by either by recrystallization or column chromatography. Overall yield: 74%, *ca.* 37% relative to **17**. FAB-MS: 875 [M]$^+$. ^{1}H NMR: 8.44 (d, *H*i, ^4J(PH$_i$) = 8.3 Hz); 6.03 (d, H_3, $^4J(H_3H_5) = 2.0$ Hz); 5.63 (m, H_5); 4.46 (m, PC*H*P); 3.78 (s, 2-O*Me*); 3.09 (s, 4-O*Me*); 1.61, 1.58 (s, CO*Me*). ^{31}P-{^{1}H} NMR: 12.36 (d, P_A, $^2J(P_AP_B) = 64.4$ Hz); −10.04 (d, P_B).

X-Ray crystallographic study

Three-dimensional, room temperature X-ray data were collected on a Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo-Kα radiation. All the measured reflections were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least squares on F^2. The F1, F2, F4 and F5 fluorine atoms of the hexafluorophosphate counterion in compound **7** were found to be disordered over two positions (48 and 52% occupancy). The refinement was carried out taking into account the minor components of the disorder. The C21 and C23 carbon atoms of compound **7** showed high displacement parameters, probably indicating partial disorder, however we could not find a reasonable model for it. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0688$ and 0.0550 (for complexes **2** and **7**, respectively, observed data, *F*) and $wR_2 = 0.2027$ and 0.1854 (for complexes **2** and **7**, respectively, unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97.[40]

CCDC reference numbers 190097 and 190098. See http://www.rsc.org/suppdata/nj/b2/b203864a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the DGES (Proyecto PB98-0638-C02-01/02) for financial support. RM acknowledges a fellowship from the Ministerio de Ciencia y Tecnología (Spain).

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