Intermediates in the palladium-catalysed reaction of 1,3-dienes Part 8*. The reaction of palladium–butadiene complexes with ethyl methylacetoacetate

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(Received January 25, 1994)

Abstract

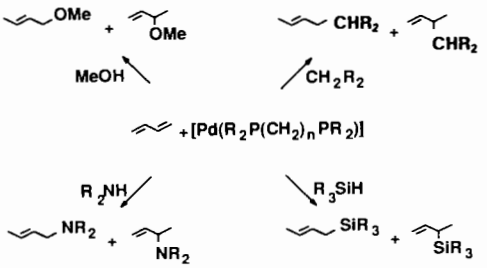
The catalytic reaction of 1,3-butadiene with ethyl methylacetoacetate in the presence of (η^2-1,3-butadiene)Pd($R_2P(CH_2)_nPR_2$) compounds has been investigated. The product is a mixture of 1:1 adducts and the rate of reaction is highest when $n=2$, R = Pr^i and in dichloromethane as solvent. Insight into the mechanism has been obtained by studying the stoichiometric reaction of (η^2-1,3-butadiene)Pd($Pr^i_2PC_2H_4PPr^i_2$) with the ester using variable temperature NMR spectroscopy and it has been shown that initially an [(η^3-1-MeC_3H_4)-Pd($Pr^i_2PC_2H_4PPr^i_2$)]$^+$ species is formed which reacts further to give (η^2-alkene)Pd($Pr^i_2PC_2H_4PPr^i_2$) compounds in which the product of the catalysis is complexed to the palladium atom. The crystal structures of three side products, viz. $Pd_2(Pr^i_2PCH_2PPr^i_2)_2$, [($\eta^1$,$\eta^3$-$C_8H_{12}$)Pd]$_2$($Me_2PC_2H_4PMe_2$) and $ClCH_2Pd(Cy_2PC_2H_4PCy_2)Cl$, have been determined by X-ray diffraction.

Key words: Crystal structures; Catalysis; Diene complexes; Palladium complexes; Methylacetoacetate complexes

Introduction

In a recent publication we reported that the palladium-catalysed reaction between 1,3-dienes and nucleophiles can be selectively directed towards the formation of 1:1 adducts by modification of the metal with an alkyl-substituted bidentate phosphine (Scheme 1); see ref. 2 and references therein.

Although the course of related reactions catalysed by nickel (in particular those involving HCN) have been investigated in considerable detail [3], surprisingly little information is available on the mechanism of the palladium-catalysed reaction [4]. Here we report the results of an optimisation study of the Pd-catalysed reaction between butadiene and ethyl 2-methylacetoacetate and discuss the mechanistic relevance of the reaction of the latter compound with (η^2-1,3-butadiene)Pd-($Pr^i_2PC_2H_4PPr^i_2$).



Scheme 1.

Results

Optimisation experiments

We have already shown that 1,3-butadiene and ethyl methylacetoacetate are converted in the presence of (η^2-1,3-butadiene)Pd($Pr^i_2PC_2H_4PPr^i_2$) in THF at 20 °C within 20 h completely and selectively into a mixture of the three adducts **1**, **2** and **3** whereby **1** predominates (eqn. (1)) [2].

*For Part 7 see ref. 1.
**Part of the doctoral thesis submitted to Ruhr-Universität, Bochum, Germany, 1992.
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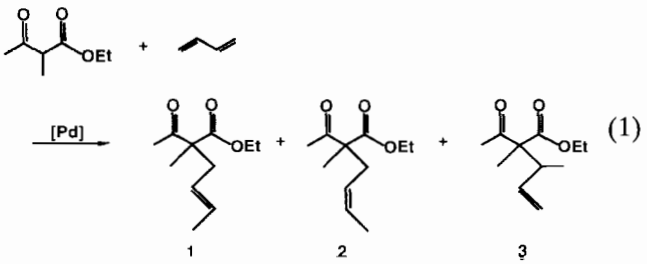
SSDI 0020-1693(94)03907-6



(1)

Optimisation experiments were carried out under standard conditions in a solvent at 20 °C with a 1,3-butadiene:ethyl methylacetoacetate:[Pd] ratio of 300:100:1 using (η^2-1,3-butadiene)Pd($R_2P(CH_2)_nPR_2$) compounds as the catalyst. Complete conversion of the ester corresponds to 100 catalytic cycles and no attempt was made to determine the life of the catalyst. The following parameters were varied: the solvent, the alkyl substituents (R) for a series of $R_2PC_2H_4PR_2$-modified catalysts and the length of the bridge for a series of $R_2P(CH_2)_nPR_2$-modified catalysts where R = Pr^i, Cyp (Cyp = cyclopentyl). In addition, the reaction was extended to nickel catalysts.

A marked solvent dependence is observed for the reactions catalysed by (η^2-1,3-C_4H_6)Pd($Pr^i_2PC_2H_4PPr^i_2$) and the rate of reaction was found to decrease in the order CH_2Cl_2 > MeCN ~ PhCl ~ Me_2CO > $MeOC_2H_4OMe$ > THF ~ diethyl ether whereby the reaction in dichloromcthanc is an order of magnitude faster than that in diethyl ether. No effect, however, was observed upon the distribution of the products (**1**:**2**:**3** = 77:8:15). The remaining optimisation experiments were carried out in dichloromethane.

The rate of reaction in the presence of $R_2PC_2H_4PR_2$-modified catalysts decreases in the order $Pr^i_2PC_2H_4PPr^i_2$ > $Cyp_2PC_2H_4PCyp_2$ > $Cy_2PC_2H_4PCy_2$ ≫ $Bu^t_2PC_2H_4PBu^t_2$ whereby the system containing isopropyl substituents is almost three times more active than that containing t-butyl groups. A catalyst containing 1,2-$(Pr^i_2P)_2C_6H_4$ was found to be slightly less active than that involving bis(dicyclohexylphosphino)ethane. The nature of the substitucnts has only a slight influence upon the product distribution and only in the case of the catalyst containing $Bu^t_2PC_2H_4PBu^t_2$ was significantly more of **2** formed at the expense of **1** (**1**:**2**:**3** = 67:20:13). Attempts to extend the investigations to catalysts containing methyl or ethyl substituted bidentate ligands were hindered by our inability to prepare the required (η^2-1,3-butadiene)Pd species: the product of the reaction between (η^3-2-MeC_3H_4)$_2$Pd, butadiene and $Me_2PC_2H_4PMe_2$ or $Et_2PC_2H_4PEt_2$ contains two (η^1,η^3-C_8H_{12})Pd fragments bridged by the bidentate ligand (see below) while the combination of the reactants catalytically converts butadiene and ethyl methylacetoacetate into a mixture of products consisting mainly of telomers derived from two molecules of butadiene.

The length of the hydrocarbon chain bridging the two phosphorus atoms effects both the rate of reaction and the distribution of the products. Where R is Pr^i or Cyp, the rate decreases in the order $R_2PC_2H_4PR_2$ > $R_2PC_3H_6PR_2$ > $R_2PC_4H_8PR_2$ with the catalyst containing the ethano-bridged ligands being some five times more active than those containing a butano bridge. Increasing the length of the hydrocarbon chain increases the proportion of **3** in the product mixture at the expense of **1**, reaching a maximum of 56:40 (**3**:**1**) for the system containing $Cyp_2PC_4H_8PCyp_2$.

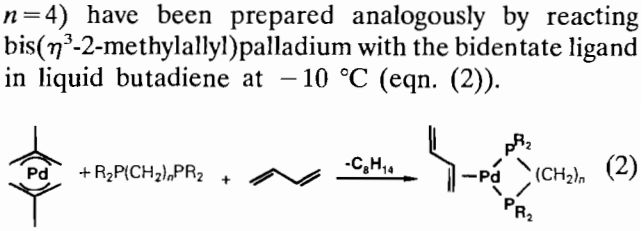
Summarising: the preferred catalyst is (η^2-1,3-butadiene)Pd($Pr^i_2PC_2H_4PPr^i_2$) with dichloromethane as the solvent of choice. This combination is able to convert 1,3-butadiene and ethyl methylacetoacetate at 20 °C into a mixture of adducts which consists of *c.* 80% of the *trans*-2-butenyl derivative **1**.

We have also investigated the effect of the bidentate ligand $R_2PC_2H_4PR_2$ (R = Cyp, Cy) upon the same reaction in the presence of a nickel catalyst and to our surprise instead of the anticipated mixture of telomers and adducts, we observed that (η-1,3-butadiene)-Ni($R_2PC_2H_4PR_2$) complexes in dichloromethane show a similar activity to the related palladium species giving the adducts **1**, **2** and **3** as the sole products in the ratio 63:1:27 (R = Cy) or 51:8:41 (R = Cyp). The implications of these observations will be investigated further.

Preparation of the catalyst

In the discussion of the mechanism of the palladium-catalysed reaction between nucleophiles and 1,3-dienes to give 1:1 adducts which follows, we have assumed that the initial step in the reaction is the formation of an (η^2-1,3-diene)Pd($R_2PC_2H_4PR_2$) species which then reacts further with the nucleophile. It was therefore logical to use these compounds as the catalyst; particularly since it was anticipated that valuable mechanistic information could be obtained by studying their stoichiometric reactions with the nucleophile.

We have previously reported the preparation of the (η^2-1,3-butadiene)Pd($R_2PC_2H_4PR_2$) compounds where R is Pr^i, Bu^t, Cy and Ph and in two cases (R = Bu^t, Cy), the single *trans*, η^2-coordination of the butadiene molecule to the metal atom has been confirmed by X-ray diffraction [5, 6]. The additional examples reported here (where R = Cyp and *n* = 3 or 4; where R = Pr^i and *n* = 4) have been prepared analogously by reacting bis(η^3-2-methylallyl)palladium with the bidentate ligand in liquid butadiene at −10 °C (eqn. (2)).

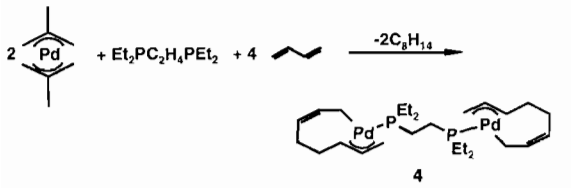


(2)

A related compound containing isoprene, viz. (η^2-CH_2:CHCMe:CH_2)Pd($Pr^i_2PC_2H_4PPr^i_2$), has been de-

scribed previously [6] and we report the analogous compound of 2,3-dimethylbutadiene here. (η^2-1,3-Butadiene)Pd(1,2-($Pr^i_2P)_2C_6H_4$) has been prepared similarly by reacting 1,2-bis(diisopropylphosphino)benzene.

The reaction leading to the formation of the (η^2-1,3-butadiene)Pd($R_2P(CH_2)_nPR_2$) compounds is not, however, general and requires the presence of relatively large substituents on the P atoms and favourable chelating properties of the bidentate ligand. The presence of the sterically undemanding substituents in bis(diethylphosphino)ethane apparently facilitates the reaction of the (η^2-1,3-C_4H_6)Pd species with further butadiene to give [(η^1,η^3-C_8H_{12})Pd]$_2$($Et_2PC_2H_4PEt_2$) (**4**) (eqn. (3)).



(3)

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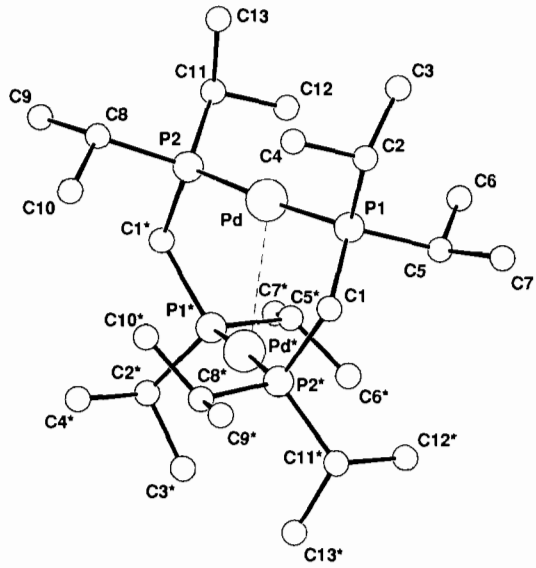
A compound related to **4** involving bis(dimethylphosphino)ethane has been prepared by reacting (η^1,η^3-C_8H_{12})$PdPMe_3$ [7] with the bidentate ligand and its crystal structure has been confirmed by X-ray diffraction – although disorder in the C_8 chain complicated refinement of the data (see 'Experimental'). The crystal structures of a number of structurally related compounds containing Ni [8], Pd [7] and Pt [9] have been reported.

The length of the carbon chain bridging the two P atoms also effects the course of reaction and best results are obtained for systems containing bridging ethano or propano groups. Ligands containing either shorter or longer chains prefer to bond in a monodentate manner either because of an unfavourable 'bite' angle or because the chelate effect is weakened. Thus, bis(diisopropylphosphino)methane reacts to give (η^3-2-MeC_3H_4)(η^1-2-MeC_3H_4)$PdPPr^i_2CH_2PPr^i_2$ (**5**) at −30 °C while at −10 °C the binuclear compound $Pd_2(Pr^i_2PCH_2PPr^i_2)_2$ (**6**) is formed. **6** may also be prepared by reacting $Pd(Pr^i_2PCH_2PPr^i_2)Cl_2$ with Mg(butadiene) in the presence of butadiene and its crystal structure has been confirmed by X-ray diffraction (Fig. 1; see also 'Experimental'). The two Pd atoms are bridged by two bis(diisopropylphosphino)methane molecules and as a result the metal atoms are within 2.83 Å of each other. Although popular prejudice would attribute the dark red colour of **6** (in contrast to the pale yellow of the zerovalent palladium–η^2-butadiene compounds) to a Pd–Pd interaction, the relatively large distance separating these atoms (that for metallic Pd is 2.75 Å and that in, for example, $Pd_2(Ph_2PCH_2PPh_2)_2(SnCl_3)Cl$ is 2.644 Å [10]) and the near linearity (176.6°) of the P–Pd–P fragments suggest that

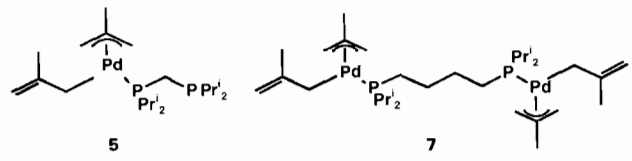


Pd---Pd* 2.828(1), Pd–P1 2.265(1), Pd–P2 2.249(1), P1–C1 1.860(2), P2–C1* 1.850(2), P1–C2 1.860(2), P1–C5 1.845(3), P2–C8 1.857(3), P2–C11 1.855(3), P1–Pd–Pd* 88.1(1), P2–Pd–Pd* 95.0(1), P1–Pd–P2 176.6(1), P1–C1–P2* 114.1(1), Pd–P1–C1 116.2(1), Pd–P2–C1* 114.5(1), P1–Pd–Pd*–P2* (twist) 25.7(2).

Fig. 1. The molecular structure of $Pd_2(Pr^i_2PCH_2PPr^i_2)_2$ (**6**) with selected bond distances (Å) and angles (°). The molecule contains an exact two-fold axis of symmetry perpendicular to both the Pd---Pd* and C1---C1* vectors.

this is probably weak in nature. A practically identical angle (175.7°) has been reported for $Pd[P(C_4H_9\text{-}t)_2Ph]_2$ [11]. Recently a structurally related complex containing bidentate ligand molecules having an ethano bridge, viz. $Pd_2(Cy_2PC_2H_4PCy_2)_2$, was prepared. The Pd–Pd distance in this compound, which is also red, of 2.7611 Å is suggested to indicate a 'significant bonding interaction' [12].

The product of the reaction of (η^3-2-$MeC_3H_4)_2Pd$ with bis(diisopropylphosphino)butane and 1,3-butadiene is a mixture of the expected (η^2-1,3-butadiene)Pd species and the dinuclear compound **7** while bis(diisopropylphosphino)pentane reacts at −30 °C to give a mixture of compounds whose ^{31}P NMR spectrum contains at least 20 individual peaks none of which is part of the AB system expected for species in which the ligand is acting in a chelate manner.



Mechanistic investigations

We have assumed that the key intermediate in the formation of the 1:1 adducts is an (η^2-1,3-diene)-

$Pd(R_2P(CH_2)_nPR_2)$ species which reacts further with the nucleophile. Attempts to test an alternative mechanism in which the nucleophile adds in an oxidative manner to a $[Pd(R_2P(CH_2)_nPR_2)]$ species to give a palladium hydride which then adds to the diene were stymied by our inability to prepare a suitable hydride; for example, by reacting $Pd(Pr^i_2PC_2H_4PPr^i_2)Cl_2$ with $NaBH_4$.

We have devoted most attention to the stoichiometric reaction of (η^2-1,3-butadiene)$Pd(Pr^i_2PC_2H_4PPr^i_2)$ with ethyl methylacetoacetate which has been studied with the help of variable temperature NMR spectroscopy. Representative ^{31}P NMR spectra are shown in Fig. 2. At -80 °C, the spectrum of the starting material consists of two doublets as a result of the inequivalence of the two P atoms (δ 63.4, 55.2, J(P,P) 51). Addition of a stoichiometric amount of ethyl methylacetoacetate at -80 °C is accompanied by the generation of two additional sets of doublets (δ 84.7, 76.3, J(P,P) 26.8; δ 86.7, 79.2, J(P,P) 27.5) in the ratio 29:71 (as well as a trace of a species formed by the oxidative addition of CH_2Cl_2 to the Pd(0) complex; see below). Upon warming, the intensity of the high field component increases at the expense of the low field component and at -30 °C the ratio of the two is 87:13. In addition, at -30 °C further species are formed which have ^{31}P NMR signals at *c.* 58 ppm. The expanded spectrum (Fig. 3) of this complex indicates that it is the result of the superimposition of two groups of signals of almost equal intensity. The spectra are second order ($\Delta\nu/J < 10$) and the almost identical chemical shifts and coupling constants suggests that they are associated with species having very similar structures.

Attempts to follow the reaction to completion by raising the temperature further were thwarted by reaction with the solvent to give $ClCH_2Pd(Pr^i_2PC_2H_4PPr^i_2)Cl$ (δ (-10 °C) 81.5, 73.8, J(P,P) 18.3). A related complex has been prepared by reacting (η^3-2-$MeC_3H_4)_2Pd$ with $Cy_2PC_2H_4PCy_2$ in CH_2Cl_2 and its crystal structure confirmed by X-ray diffraction (see 'Experimental').

We were unable to isolate the η^3-allyl–Pd intermediates directly out of the reaction mixture and therefore resorted to preparing them by independent routes and to comparing their spectral data. The initial products of the reaction were shown to be the *anti* and *syn* isomers of $[(\eta^3\text{-}1\text{-}MeC_3H_4)Pd(Pr^i_2PC_2H_4PPr^i_2)]^+$ by isolating these species from the reaction of the chelating ligand with $[(\eta^3\text{-}1\text{-}MeC_3H_4)PdCl]_2$ (eqn. (4)).

$$[(\eta^3\text{-}1\text{-}MeC_3H_4)PdCl]_2 + 2Pr^i_2PC_2H_4PPr^i_2 \longrightarrow 2[(\eta^3\text{-}1\text{-}MeC_3H_4)Pd(Pr^i_2PC_2H_4PPr^i_2)]^+Cl^- \quad (4)$$

The ^{31}P NMR spectrum of this species is practically identical with that of the reaction mixture formed at -30 °C (Fig. 2) and the ^1H NMR spectrum confirms that at this temperature the main component contains

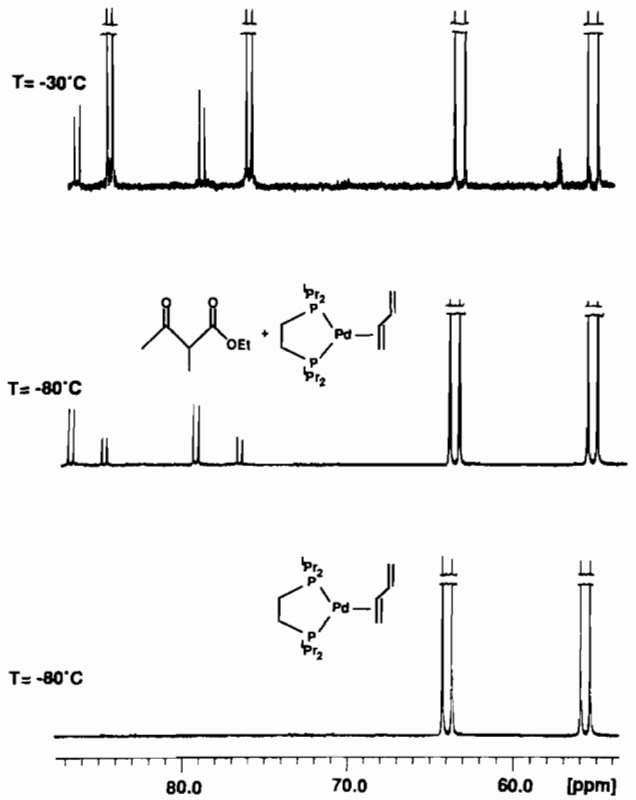


Fig. 2. Variable temperature ^{31}P NMR spectroscopic investigation of the reaction between (η^2-1,3-C_4H_6)$Pd(Pr^i_2PC_2H_4PPr^i_2)$ and ethyl methylacetoacetate in CH_2Cl_2.

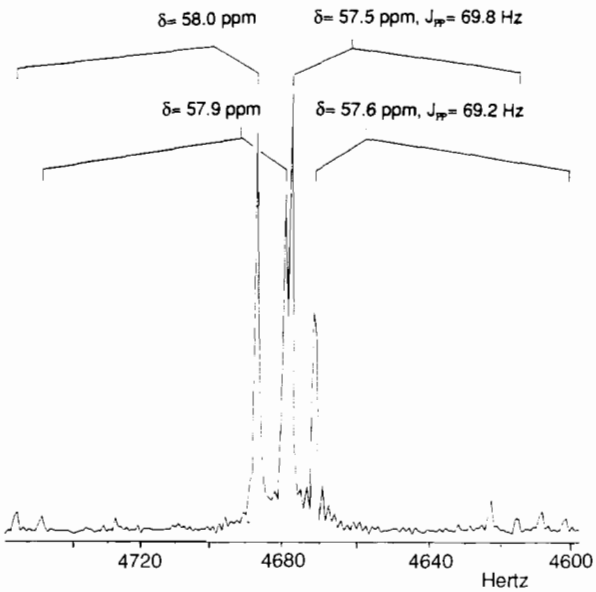
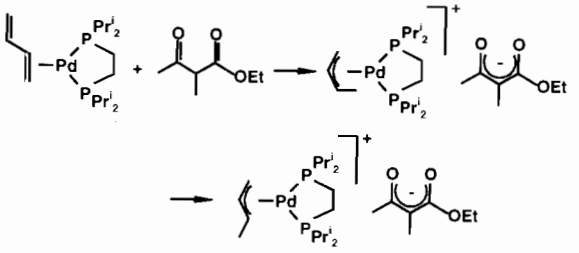


Fig. 3. Expanded ^{31}P NMR spectrum of the product of the reaction between (η^2-1,3-C_4H_6)$Pd(Pr^i_2PC_2H_4PPr^i_2)$ and ethyl methylacetoacetate at -30 °C in CH_2Cl_2.

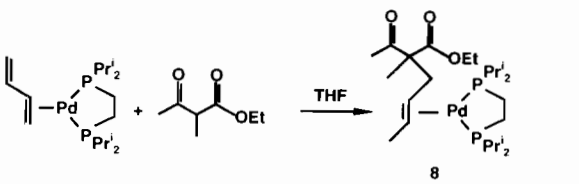
a *syn*-substituted 1-methylallyl group. In other words, the initial product of the reaction shown in Fig. 2 contains an *anti*-substituted 1-methylallyl group and upon raising the temperature this isomerises to the thermodynamically more stable *syn* isomer (eqn. (5)).



(5)

Isomerisations of this type are not uncommon and have, for example, been observed in the reaction between $[HPd(Ph_2PC_2H_4PPh_2)]^+$ and isoprene [13] and have been studied in some detail for the reaction between $[HNi(P(OEt)_3)_3]^+$ and 1,3-butadiene [14].

The ^{13}P NMR chemical shift of the second class of intermediates (Fig. 3) suggests that they contain zero-valent palladium and they were shown to be (η^2-alkene)$Pd(Pr^i_2PC_2H_4PPr^i_2)$ species (**8**), containing the principal adduct **1**, formed from 1,3-butadiene and ethyl methylacetoacetate, by reacting $(\eta^2\text{-}1,3\text{-}C_4H_6)Pd(Pr^i_2PC_2H_4PPr^i_2)$ with ethyl methylacetoacetate in THF (eqn. (6)) or by reacting $[(\eta^3\text{-}1\text{-}MeC_3H_4)Pd(Pr^i_2PC_2H_4PPr^i_2)]^+Cl^-$ with the potassium salt of the ester in THF. The ^{31}P NMR spectral data for **8** confirms



(6)

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not only the identity of the second intermediate but also shows that the two species present (Fig. 3) are indeed diastereomers arising from the chirality of the Pd-bonded alkene.

These results suggest that the three olefinic products of the catalytic reactions between 1,3-butadiene and ethyl methylacetoacetate are the products of reductive coupling reaction between the *syn*- and *anti*-1-methylallylpalladium species and the ethyl methylacetoacetate anion. A mechanism which takes these observations into account is shown in Fig. 4. The initial product of the reaction contains an *anti*-substituted 1-methylallyl group, from which the *cis*-substituted 2-butene derivative is derived, and this isomerises to the *syn* form, from which the *trans*-substituted 2-butene derivative is derived. The 1-butene derivatives could be produced from either the *anti*- or *syn*-substituted 1-methylallyl species. The final step in the catalytic cycle, the displacement

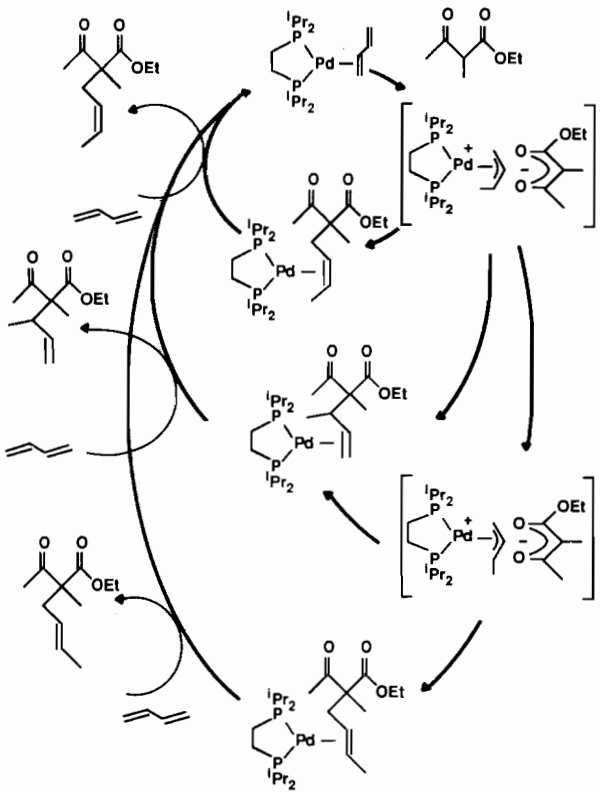
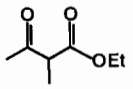
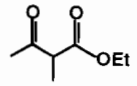


Fig. 4. A simplified mechanism for the $[Pd(Pr^i_2PC_2H_4PPr^i_2)]$-catalysed reaction between 1,3-butadiene and ethyl methylacetoacetate.

of the alkene from the metal by exchange with butadiene, has been confirmed by reacting the alkene–Pd complex **8** with butadiene: complete (^{31}P NMR) exchange occurs. Interestingly, the reverse reaction (displacement of butadiene from palladium by reaction with the adduct **1**) does not occur. In the absence of butadiene, **8** reacts further at room temperature to give a dark red compound whose ^{31}P NMR spectrum and mass spectrum suggest the formation $Pd_2(Pr^i_2PC_2H_4PPr^i_2)_2$ (MS (105 °C): *m/e* 736 (M^+); ^{31}P NMR (d_8-THF, −30 °C): 30.09 ppm) and whose structure is presumably analogous to that of $Pd_2(Cy_2PC_2H_4PCy_2)_2$ (see above and ref. 12).

Satisfying as the above mechanism may be, a number of details warrant further discussion. The nature of the bond between the metal and the ethyl methylacetoacetate group in the initial (η^3-1-methylallyl)palladium species has been explored by carrying out conductivity measurements on the reaction mixture and by comparing the results with those obtained for isolated compounds (Table 1). The molar conductivity of the reaction mixture lies between that of the fully dissociated PF_6 species and the non-ionic $(\eta^2\text{-}1,3\text{-}C_4H_6)Pd$ compound suggesting that we are dealing here with a close ion-pair. A similar effect has been observed previously for $[(\eta^3\text{-}C_3H_5)Ni(P(OPh)_3)_2]X$ species (Table 1) [15] while a

TABLE 1. Molar conductivity measurements (acetonitrile, −10 °C, $c = 0.008$ mol^{-1})

Compound	Λ (cm^2 Ω^{-1} mol^{-1})
	0.01
$(\eta^2$-1,3-$C_4H_6)Pd(Pr^i_2PC_2H_4PPr^i_2)$	0.04
$(\eta^2$-1,3-$C_4H_6)Pd(Pr^i_2PC_2H_4PPr^i_2)$ + 	4.20
$[(\eta^3$-1-$MeC_3H_4)Pd(Pr^i_2PC_2H_4PPr^i_2)]^+Cl^-$	96.93
$[(\eta^3$-1-$MeC_3H_4)Pd(Pr^i_2PC_2H_4PPr^i_2)]^+PF_6^-$	141.63
$[(\eta^3$-$C_3H_5)Ni(P(OPh)_3)_2]^+PF_6^-$	124.10 [15]
$[(\eta^3$-$C_3H_5)Ni(P(OPh)_3)_2]^+MeC_6H_4SO_3^-$	3.77 [15]

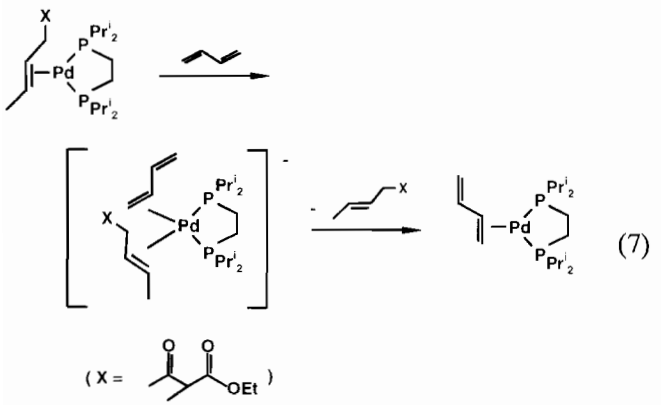
crystal structure determination for $(\eta^3$-2-$MeC_3H_4)$-$Ni(Ph_2PC_2H_4PPh_2)Br$ indicates that the Br atom in this compound occupies a coordination position at the Ni atom without forming a direct bond to the metal atom (Ni---Br 2.671(2) Å) [16].

It should be stressed that the mechanism shown in Fig. 3 is based upon the characterisation of a number of relatively stable organopalladium compounds and although these are probably stations on the reaction path, they will certainly not be true intermediates and the following processes need to be considered further:

(i) the preferential formation of the *anti*-1-methylallyl-palladium species and its isomerisation to the *syn* isomer.

(ii) the coupling of the 1-methylallyl group with the ester which leads to formation of the alkene.

A detailed mechanism which takes into account these processes is shown in Fig. 5 whereby the final step in the catalytic cycle, the displacement of the alkene from the metal, presumably proceeds through the intermediacy of a bis(alkene)Pd species (e.g. eqn. (7)).



(7)

The kinetically controlled formation of an *anti*-substituted 1-methylallylpalladium species suggests that the initial reaction of the (1,3-butadiene)Pd complex with the nucleophile takes place from an isomer in which the 1,3-butadiene molecule is bonded in a single *cis*-η^2 manner. Species of this type have not been isolated for palladium but they have been proposed as intermediates to explain the fluxional behaviour observed

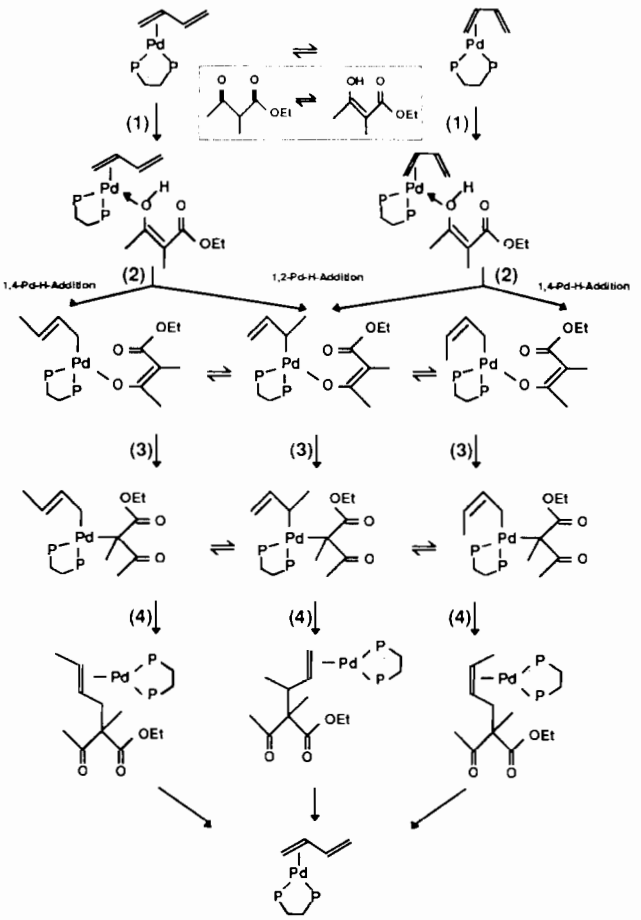
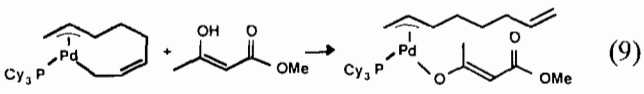


Fig. 5. Fundamental steps in the $[Pd(Pr^i_2PC_2H_4PPr^i_2)]$-catalysed reaction between 1,3-butadiene and ethyl methylacetoacetate.

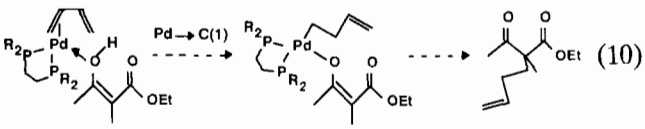
for the (η^2-1,3-C_4H_6)Pd($R_2P(CH_2)_nPR_2$) compounds at elevated temperatures (eqn. (8)) [5, 6].


(8)

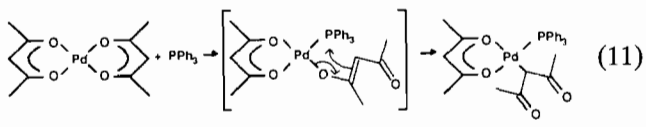
The reaction of the (η^2-1,3-butadiene)palladium species with ethyl methylacetoacetate (Fig. 5, step 1) presumably takes place through the enol form; a ^{1}H NMR spectroscopic investigation indicates that the enol form (δ (OH, d_8-THF, 30 °C): 12.69 ppm) is present to *c.* 2%. A preferential reaction of the enol form has also been observed upon reacting (η^1,η^3-C_8H_{12})PdPCy$_3$ with methyl acetoacetate (eqn. (9)) [17].


(9)

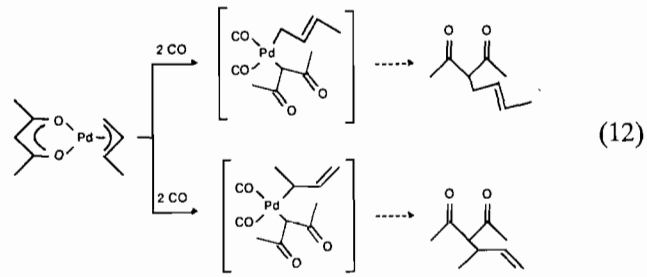
The protonation of the complexed butadiene molecule (Fig. 5, step 2) could proceed either directly or though the intermediacy of a Pd–H species: from the structure of the products it follows that either a 1,4-addition or a 1,2-addition with the Pd atom adding to C(2) has occurred; a 1,2-addition with the Pd atom adding to C(1) would lead to the formation of a 1-butenyl-substituted species (eqn. (10)) and this is not observed among the products. The rearrangement of the Pd–alkoxy intermediates to species containing a Pd–C


(10)

bond (Fig. 5, step 3) has precedence in the literature and, for example, Pd(acac)$_2$ reacts with triphenylphosphine as shown in eqn. (11) [18]. The further reaction of the resulting dialkyl–Pd species with


(11)

reductive coupling (Fig. 5, step 4) is presumably induced by butadiene complexation and has a close analogy in the reaction of (η^3-1-MeC_3H_4)Pd(acac) with CO which also occurs with coupling of the organic ligands (eqn. (12)) [19].


(12)

The formulation of a detailed mechanism for the palladium-catalysed reaction of 1,3-butadiene with ethyl methylacetoacetate is complicated by the fact that all three groups bonded to the metal atom can vary their hapticity: the 1-methylallyl group can bond either in an η^3 or η^1 manner, the chelate phosphine can act either as a monodentate or bidentate ligand while the ethyl methylacetoacetate group can complex to the metal either through one or two oxygen atoms or can form an anion. The η^1–η^3 rearrangement of the 1-methylallyl group provides a path for *anti–syn* isomerisation (eqn. (13)). A consequence of this rearrangement is that the (η^1-1-methylallyl)palladium species shown in

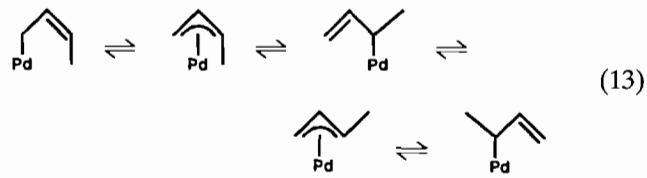
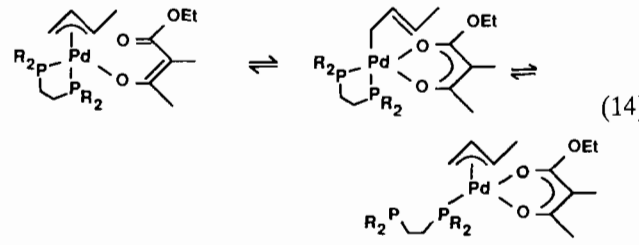
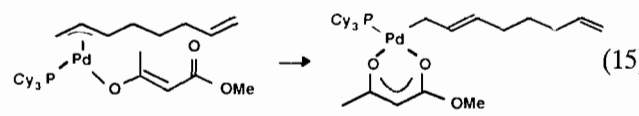

(13)

Fig. 5 are in equilibrium with each other and hence a 1,2-addition (Fig. 5, step 2) is not a necessity since the same result would be obtained by a 1,4-addition with subsequent isomerisation. The η^1–η^3 rearrangement can be induced by a change in hapticity of either the diketoester or of the chelating ligand (eqn. (14)). Precedence is found in the rearrangement of the


(14)

methyl acetoacetate derivative shown below (eqn. (15)) [17].


(15)

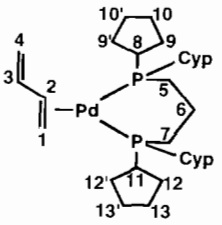
We should also mention that the changes in hapticity which have been discussed above can also be induced by complexation of butadiene molecules to the palladium.

Experimental

The organometallic compounds described below and the intermediates formed in the catalytic reactions are air sensitive and hence all reactions were carried out in an atmosphere of argon. $Pr^i_2PCH_2PPr^i_2$ was kindly donated by Professor K. Jonas [20]. The $R_2PC_2H_4PR_2$ ligands were either commercially available (R = Me, Et) or were prepared according to ref. 5 (R = Pr^i, Bu^t) or ref. 21 (R = Cy) or by reacting Cyp_2PH with 1,2-dibromoethane at 150–180 °C [22]. The $Cyp_2P(CH_2)_nPCyp_2$ ligands (n = 3–5) were prepared by reacting Cyp_2PH with $Br(CH_2)_nBr$ (n = 3–5) at 150–200 °C [22]. $Pr^i_2PC_4H_8PPr^i_2$ was prepared similarly from Pr^i_2PH and BrC_4H_8Br [22]. 1,2-$(Pr^i_2P)_2C_6H_4$ was prepared by reacting Mg powder with 1,2-$Br_2C_6H_4$ and Pr^i_2PCl in THF [23]. (η^3-2-$MeC_3H_4)_2Pd$ [24], [(η^3-1-$MeC_3H_4)PdCl]_2$ [25] and (η^2-1,3-C_4H_6)-$Pd(R_2PC_2H_4PR_2)$ (R = Pr^i, Bu^t, Cy) [5] were prepared by published procedures. Microanalyses were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim an der Ruhr. NMR spectra were measured with the following Bruker FT instruments and at room temperature unless otherwise stated: WH-400 FT (^{1}H, ^{13}C, ^{31}P), WM-300 (^{31}P), AM- and AC-200 (^{1}H, ^{13}C, ^{31}P). The molar conductivity measurements were carried out with a Pt electrode using a Philips PW 9512/01 instrument.

(η^2-1,3-C_4H_6)Pd($Cyp_2PC_3H_6PCyp_2$)

1,3-Bis(dicyclopentylphosphino)propane (3.4 g, 9.0 mmol) was dissolved in 1,3-butadiene (20 ml) at −10 °C and added to bis(η^3-2-methylallyl)palladium (1.9 g, 8.8 mmol) at −35 °C. The resulting dark yellow solution was stirred at −10 °C for 58 h and then cooled to −78 °C to give the compound as yellow crystals which were isolated and dried under high vacuum at 0 °C. Yield 3.9 g (93% theory). *Anal.* Found: C, 60.05; H, 9.03; P, 11.32; Pd, 19.58. Calc. for $C_{27}H_{46}P_2Pd$: C, 59.94; H, 8.94; P, 11.45; Pd, 19.67%. IR (KBr): ν(C:C) 1602. MS: *m/e* 486 ($M^+ - C_4H_6$). ^{1}H NMR (d_8-THF, −30 °C, 200.1 MHz): δ 4.71 (m, HC:-2), 3.41 (dbr, HC:-1*Z*), 3.22 (dbr, 3.22, HC:-1*E*), 2.2–1.3. ^{13}C NMR (d_8-THF, −30 °C, 75.5 MHz): δ ~ 102.4 (C-2/3), ~ 70.3 (C-1/4), 41.1 (C-8, J(C,H) 130), 39.1 (C–H, J(C,H) 129), 31.4 (C-9, J(C,H) 127, |J(P,C)|8.3), 30.5 (C-9′, J(C,H) 130, |J(P,C)/10.7), 30.3 (C-12, J(C,H) 128, |J(P,C)|5.4), 29.9 (C-12′, J(C,H)) 126, |J(P,C)|10.3), 27.7 (C-5), 27.2 (C-10′, |J(P,C)|7.4), 27.0 (C-10, |J(P,C)|2.9), 26.9 (C-13, |J(P,C)|3.3), 26.8 (C-13′, |J(P,C)|2.8), 23.9 (C-6, J(C,H) 124), 5.4 (C-7); numbering scheme shown below. ^{31}P NMR (d_8-THF, −30 °C, 121.5 MHz): δ 24.2, 13.1, J(P,P) 16.



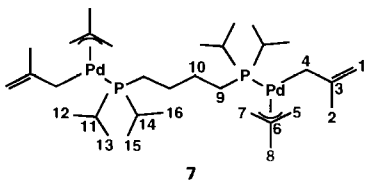
(η^2-1,3-C_4H_6)Pd($Pr^i_2PC_4H_8PPr^i_2$) and [(η^1-2-MeC_3H_4)(η^3-2-MeC_3H_4)Pd]$_2$($Pr^i_2PC_4H_8PPr^i_2$) (7)

1,4-Bis(diisopropylphosphino)butane (1.4 g, 5.0 mmol) was dissolved in 1,3-butadiene (15 ml) at −10 °C and added to bis(η^3-2-methylallyl)palladium (1.1 g, 5.0 mmol) at −78 °C. The reaction mixture was stirred for 3 days at −10 °C, diethyl ether was added and the resulting yellow solution stirred at r.t. The solution was cooled to −25 °C to give **7** as pale yellow crystals which were isolated, washed with pentane and dried in high vacuum at −30 °C (yield 0.9 g, 46% theory, m.p. ~130 °C dec.). The filtrate was cooled to −78 °C to give (η^2-1,3-C_4H_6)Pd($Pr^i_2PC_4H_8PPr^i_2$) as yellow crystals which were washed with cold pentane and dried in high vacuum at 0 °C (yield 0.8 g, 30% theory, m.p. 148 °C dec.).

7. *Anal.* Found: C, 53.16; H, 8.87; P, 5.55; Pd, 29.38. Calc. for $C_{34}H_{64}P_2Pd_2$: C, 53.11; H, 8.91; P, 8.56; Pd, 29.41%. IR (KBr): ν (HC:) 3058, (C:C) 1597. ^{1}H NMR (d_8-toluene, −80 °C, 400.1 MHz): δ 5.17 (m, H-1*Z*), 4.89 (m, H-1*E*), 3.21/3.19 (m, H-5 *syn/anti*, J(5,P) 9/~5), 3.09/2.26 (m, H-7 *syn/anti*) 2.75/2.52 (t, H-4, J(4,P) 4.6/7.6), 2.26 (m, H-2), 1.70 (s, H-8), 1.63 (m, H-10), 1.49 (m, H-9), 1.38 (H-11/14), ~0.94 (dd, H-12/13), ~0.87 (dd, H-15). ^{13}C NMR (d_8-toluene, −80 °C, 100.6 MHz): δ 158.1 (C-3), 131.3 (C-6), 99.3 (C-1, J(C,H) 153), 71.1 (C-5, J(P,C) 3.5, J(C,H) 155), 55.8 (C-7, J(C,H) 155), 29.1 (C-10, J(P,C) 14, J(C,H) 127), 27.3 (C-2, J(C,H) 125), 24.6 (C-14, J(P,C) 20.5, J(C,H) 126), 24.59 (C-8, J(C,H) 126), 20.9 (C-4, J(P,C) ⩾ 10, J(C,H) ~130), 20.9 (C-9), 19.7 (C-12/15), 17.9/17.8 (C-15/18); numbering scheme shown below. ^{31}P NMR (d_8-toluene, −80 °C, 162.0 MHz): δ 44.3.

(η^2-1,3-C_4H_6)Pd($Pr^i_2PC_4H_8PPr^i_2$). Anal. Found: C, 53.43; H, 9.46; P, 13.64; Pd, 23.49. Calc. for $C_{20}H_{42}P_2Pd$: C, 53.27; H, 9.39; P, 13.74; Pd, 23.60%. MS: *m/e* 396 ($M^+ - C_4H_6$). IR (KBr): ν (HC:) 3081/3050, (C:C) 1608. ^{1}H NMR (d_8-THF, −100 °C, 400.1 MHz); δ 5.53 (dt, H-3, J(3,4*Z*) 16.4), 4.61 (dbr, H-4*Z*), 4.26 (dbr, H-4*E*),

3.91 (m, H-2), 2.33 (m, H-1*E*), 2.10 (m, H-1*Z*). ^{13}C NMR (d_8-THF, −80 °C, 75.5 MHz): δ ~145.4 (C-3), 100.9 (C-4), ~41.4 (C-1/2, $|J(P,C)|$ ~20), ~28.7 (C-9), 28.1 (C-19), 27.3 (C-11), 26.5 (C-6), 26.4 (C-7), ~21.8 (C-21), ~20.7 (C-5/8, $|J(P,C)|$ ~7.5), 20.1 (C-10/10′, $|J(P,C)|$ ~6), ~19.7 (C-12/12′), 19.2 (C-20/20′); numbering scheme shown below. ^{31}P NMR (d_8-THF, −30 °C, 162.0 MHz): δ 40.0, 32.5, J(P,P) 22.8.



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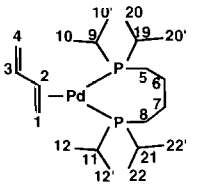
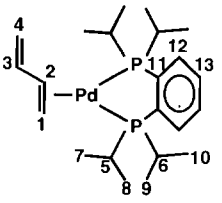


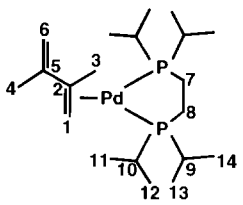
(η^2-1,3-C_4H_6)Pd($Cyp_2PC_4H_8PCyp_2$)

Prepared as described above, by reacting 1,4-bis(dicyclopentylphosphino)butane and 1,3-butadiene with bis(η^3-2-methylallyl)palladium at −10 °C, as a pale yellow crystalline solid. Yield 79% theory. M.p. ~135 °C dec. *Anal.* Found: C, 60.68; H, 9.15; P, 10.88; Pd, 19.26. Calc. for $C_{28}H_{50}P_2Pd$: C, 60.59; H, 9.08; P, 11.16; Pd, 19.17. MS: *m/e* 500 ($M^+ - C_4H_6$), 431, 362. IR (KBr): ν (HC:) 3077/3035, (C:C) 1602. ^1H NMR (d_8-THF, −30 °C, 200.1 MHz): δ 4.69 (br, H-2), 3.44 (br, H-1*Z*), 3.25 (br, H-1*E*), 2.2–1.3 m. ^{31}P NMR (d_8-THF, −30 °C, 81.0 MHz): δ 30.6, 19.8, J(P,P) 28.1.

(η^2-1,3-C_4H_6)Pd(1,2-(Pr^i_2P)$_2C_6H_4$)

Prepared as described above, by reacting 1,2-bis(diisopropylphosphino)benzene and 1,3-butadiene with bis(η^3-2-methylallyl)palladium at −10 °C, as a yellow crystalline solid. Yield 81% theory. M.p. ~85 °C dec. *Anal.* Found: C, 56.21; H, 7.71; P, 13.29: Pd, 22.81. Calc. for $C_{22}H_{36}P_2Pd$: C, 56.35; H, 7.74; P, 13.21; Pd, 22.70. MS: *m/e* 470 (M^+), 416 ($M^+ - C_4H_6$), 373, 267. IR: ν (HC:) 3071, 3053, 3034, (C:C) 1601. ^1H NMR (d_8-THF, −30 °C, 200.1 MHz): δ 7.86 (m, H-12), 7.52 (m, H-13), 5.01 (m, H-2), 3.62 (dd, H-1*Z*, J(1*Z*,2) ~15), 3.41 (dd, H-1*E*, J(1*E*,1*Z*) 3.9, J(1*E*,2) 8.7), 2.4 (m, H-5/6), 1.18 (dd, H-8, J(8,P) 15.0), 1.10 (dd, H-7, J(7,P) 14.9), 0.81 (dd, H-9, J(9,P) 13.7), 0.75 (dd, H-10, J(10,P) 14.2); numbering scheme shown below. ^{31}P NMR (d_8-THF, −30 °C, 81.0 MHz): δ 64.9, 55.6, J(P,P) 49.





(η^2-2,3-$Me_2C_4H_4$)Pd($Pr^i_2PC_2H_4PPr^i_2$)

Prepared as described above, by reacting 1,2-bis(diisopropylphosphino)ethane and 2,3-dimethyl-1,3-butadiene with bis(η^3-2-methylallyl)palladium at 0 °C, as a brown powder. Yield 84% theory. M.p. 45 °C dec. *Anal.* Found: C, 53.22; H, 9.36; P, 13.81; Pd, 23.54. Calc. for $C_{20}H_{42}P_2Pd$: C, 53.27; H, 9.39; P, 13.74; Pd, 23.60. MS: *m/e* 450 (M^+), 368 ($M^+ - Me_2C_4H_4$). IR (KBr): ν (HC:) 3093/3038, (C:C) 1599. ^1H NMR (d_8-THF, −30 °C, 400.1 MHz): δ 3.56 (sbr, H-1*Z*), 3.35 (sbr, H-1*E*), 1.95/1.94 (m, H-9/10), 1.74 (d, H-3, J(3,P) 2.6), 1.58 (m, H-7/8), 1.07 (dd, H-11), 1.00 (dd, H-12), 0.98 (dd, H-13), 0.97 (dd, H-14). ^{13}C NMR (d_8-THF, −30 °C, 100.6 MHz): δ ~152.3 (C-2/5), ~97.5 (C-1/6), ~ 44.2 (br, C-3/4), ~26.2 (C-10), 26.0 (C-9) 22.2 (C-7/8, J(7,P) 17.6, J(7,P′) ~5), 22.0 (C-8/7, J(8,P) 17.6, J(8,P′) ~7), 20.4 (C-14), ~19.3 (C-12), ~19.1 (C-13), ~19.0 (C-11), numbering scheme shown above. ^{31}P NMR (d_8-THF, −30 °C, 162.0 MHz): δ 62.2, 52.9, J(P,P) 59.

[(η^1,η^3-C_8H_{12})Pd]$_2$($Me_2PC_2H_4PMe_2$)

(η^1,η^3-C_8H_{12})PdPMe_3 (2.13 g, 7.32 mmol) [7] was dissolved in diethyl ether (150 ml) and treated with bis(dimethylphosphino)ethane (1.12 g, 7.47 mmol) in diethyl ether (50 ml) at −50 °C. The reaction mixture was stirred overnight, the solvent removed under high vacuum and the yellow residue washed with pentane (2×60 ml) at −70 °C and treated with a butadiene/ether solution (100 ml, 1:3). A dark brown reaction mixture was formed. The solvent was distilled off and the residue dissolved in a toluene/butadiene mixture to give a dark red solution which was filtered and cooled to 10 °C. The resulting dark brown crystals were isolated and washed with butadiene. Yield 1.0 g (44% theory). M.p. ~60 °C dec. *Anal.* Found: P, 10.63; Pd, 38.86. Calc. for $C_{22}H_{40}Pd_2P_2$: P, 10.71; Pd, 36.77. IR (KBr): ν (C:C) 1593. ^{31}P NMR (d_8-THF, −30 °C): δ 2.87.

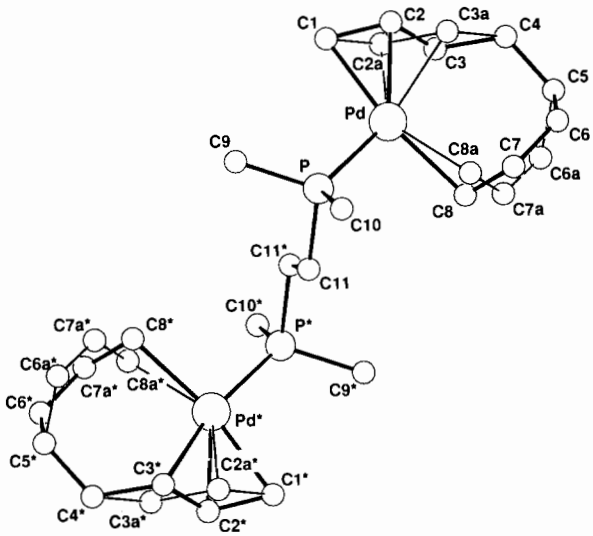
Crystal structure analysis: molecular formula $C_{22}H_{40}P_2Pd_2$, molecular weight 578.6 g mol^{-1}, crystal colour light brown, crystal size 0.36×0.36×0.14 mm, a = 15.832(3), b = 9.695(1), c = 16.219(4) Å, V = 2489.5 Å^3, T = 293 K, D_{calc} = 1.54 g cm^{-3}, μ = 15.53 cm^{-1}, Z = 4, orthorhombic, space group *Pbcn* (No. 60), Enraf-Nonius

TABLE 2. Atomic fractional coordinates and equivalent isotropic thermal parameters (Å^2) of $[(\eta^1,\eta^3\text{-}C_8H_{12})Pd]_2(Me_2PC_2H_4PMe_2)$ with standard deviations in parentheses

Atom	x	y	z	U_{eq}[a]
Pd	0.1769(1)	0.1372(1)	0.0972(1)	0.050(1)
P	0.0588(1)	0.2020(2)	0.0312(1)	0.055(1)
C(1)	0.2748(4)	0.1746(8)	0.0061(4)	0.077(4)
C(2)	0.3097(5)	0.159(1)	0.0827(8)	0.076(8)
C(3)	0.3056(5)	0.055(1)	0.1326(8)	0.072(7)
C(4)	0.3373(4)	0.0323(7)	0.2168(4)	0.077(4)
C(5)	0.2778(5)	−0.003(1)	0.2845(5)	0.104(6)
C(6)	0.215(1)	0.079(1)	0.3054(6)	0.098(9)
C(7)	0.1404(7)	0.100(1)	0.2621(8)	0.086(8)
C(8)	0.1119(5)	0.034(1)	0.1993(6)	0.075(7)
C(9)	0.0694(4)	0.2653(7)	−0.0720(5)	0.082(5)
C(10)	−0.0018(4)	0.3368(6)	0.0806(5)	0.081(5)
C(11)	−0.0187(3)	0.0649(5)	0.0199(4)	0.057(3)
C(2a)	0.302(1)	0.069(2)	0.064(1)	0.045(5)
C(3a)	0.310(1)	0.137(2)	0.154(1)	0.050(5)
C(6a)	0.196(1)	−0.053(2)	0.276(1)	0.044(4)
C(7a)	0.131(1)	−0.013(2)	0.242(1)	0.045(5)
C(8a)	0.114(1)	0.146(2)	0.214(1)	0.039(4)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

CAD 4 diffractometer, $\lambda = 0.71069$ Å, scan mode ω–2θ, 4847 measured reflections $(+h, +k, +l)$, $[(\sin\theta/\lambda]_{max}$ 0.75 Å^{-1}, 4327 independent reflections, 2398 observed reflections ($I > 2\sigma(I)$) for 138 refined parameters, structure solved by heavy atom method, H atom positions calculated and fixed in the final refinement stages, $R = 0.053$, $R_w = 0.050$, residual electron density 0.90 e Å^{-3}. Atomic positional parameters and equivalent isotropic thermal parameters are listed in Table 2 and the molecular structure with selected bond distances and angles in Fig. 6.

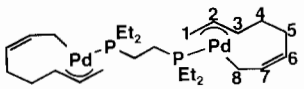


Pd–P 2.245(1), Pd–C1 2.173(6), Pd–C2 2.128(7), Pd–C3 2.262(8), Pd–C8 2.19(1), P–C11 1.820(5), C11–C11* 1.534(7), P–Pd–C1 102.9(2), P–Pd–C8 95.6(2), Pd–P–C11 113.9(2), P–C11–C11* 112.4(3).

Fig. 6. The molecular structure of $[(\eta^1,\eta^3\text{-}C_8H_{12})Pd]_2$-$(Me_2PC_2H_4PMe_2)$ with selected bond distances (Å) and angles (°). The octadienediyl fragment is disordered (C2a, C3a, C6a, C7a, C8a 30%).

$[(\eta^1,\eta^3\text{-}C_8H_{12})Pd]_2(Et_2PC_2H_4PEt_2)$ (4)

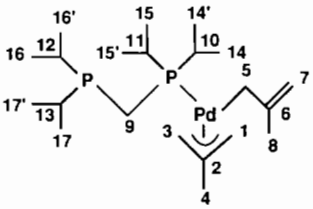
1,2-Bis(diethylphosphino)ethane (0.8 g, 4.0 mmol) was dissolved in 1,3-butadiene (15 ml) at −25 °C and added to bis(η^3-2-methylallyl)palladium (0.9 g, 4.0 mmol) at −78 °C. The reaction mixture was stirred at −10 °C for 24 h to give an orange–yellow suspension. Toluene was added and the mixture stirred at room temperature to give a clear solution which was cooled to −78 °C. Orange crystals precipitated and were isolated, washed with cold pentane and dried under high vacuum at −30 °C. Yield 0.8 g (65% theory). M.p. ~60 °C dec. *Anal.* Found: C, 49.12; H, 7.70; P, 33.28; Pd, 9.84. Calc. for $C_{26}H_{48}P_2Pd$: C, 49.14; H, 7.61; P, 33.49; Pd, 9.75%. IR (KBr): ν (HC:) 3052/3008, (C:C) 1601. ^{1}H NMR (d_8-toluene, −30 °C, 200.1 MHz): δ ~6.32 (m, H-7), 4.75 (q, H-6, $J(6,7) = J(6,5)$ 8.6), 4.22 (ddd, H-2, $J(2,3)$ 7.6), 3.37 (d, H-1*E*, $J(1E,2)$ 7.6), 2.39 (q, H-1*Z*, $J(1Z,2)$ 13.0); numbering scheme shown below. ^{13}C NMR: the compound was not sufficiently soluble. ^{31}P NMR (d_8-toluene, −30 °C, 81.0 MHz): δ 27.23, 27.27 (diastereomers).



$(\eta^1\text{-}2\text{-}MeC_3H_4)(\eta^3\text{-}2\text{-}MeC_3H_4)PdPr^i_2PCH_2PPr^i_2$ (5)

Bis(diisopropyl)phosphinomethane (0.79 g, 3.2 mmol) was dissolved in 1,3-butadiene (15 ml) at −20 °C and added to bis(η^3-2-methylallyl)palladium (0.68 g, 3.2 mmol) at −30 °C. The pale yellow reaction mixture was stirred at −30 °C for 1 h, concentrated and stirred at −78 °C. Pale yellow, cubic crystals precipitated. The compound decomposes at *c.* −30 °C and the yield was not determined. *Anal.* Found: C, 54.44; H, 9.69; P, 13.13; Pd, 22.71. Calc. for $C_{21}H_{44}P_2Pd$: C, 54.25; H, 9.54; P, 13.32; Pd, 22.89%. IR (KBr): ν (HC:) 3058, (C:C) 1597. ^{1}H NMR (d_8-THF, −80 °C, 300.1 MHz): δ 4.22 (d, H-7*Z*), 3.98 (dd, H-7*E*, $J(7E,7Z$ 3.5), 3.23 (d, H-3*syn*), 2.73 (d, H-1*anti*), J(P,1*anti*) 9), 2.50 (dd, H-1*syn*, $J(1syn,3syn)$ 2.9, J(P,1*syn*) 5.9), 2.27 (m, H-10/11, $J(10,14/14')/J(11,15/15')$ 7, J(P,10)/J(P,11) 7), 2.14 (s, H-3*anti*) 2.06 (dd, H-5, $J(5,5')$ 8.3, J(P,5) 6.0), ~2.04 (m, H-12/13, $J(12,16)$ 7), 1.96 (dd, H-5′, J(P,5′) 6.3), 1.90 (dd, H-9, $J(9,9')$ 14.0, J(P,9) 7.9), 1.84 (dd, H-9′, J(P,9′) 8.4), 1.69 (s, H-8), 1.66 (s, H-4), 1.24 (dd, H-14, J(P,14) 14), 1.20 (dd, H-14′, J(P,14′) ~14), 1.18 (dd, H-15/15′, J(P,15/15′) ~13.5), 1.13 (dd, H-16, J(P,16) ~13.5), 1.10 (dd, H-16′, J(P,16′) ~14), 1.08 (dd, H-

17, J(P,17) ~10.5), 1.05 (dd, H-17', J(P,17') ~10.5). ^{13}C NMR (d_8-THF, −80 °C, 75.5 MHz): δ 158.9 (C-6, J(P,C) 2.5), 131.7 (C-2, J(P,C) 3.8), 98.2 (C-7, J(C,H) 153), 71.5 (C-1, J(C,H) 156, J(P,C) 35.1), 57.0 (C-3, J(C,H) 156), 26.8 (C-8, J(C,H) 128), ~26.6 (C-10, J(P,C) ~20/~4), ~25.5 (C-11, J(P,C) ~20/~4), 24.8 (C-4), 24.7 (C-12/13, J(P,C) 4.8/15.2), 22.2 (C-5, J(P,C) 10.9), 21.8 (C-16', J(P,C) 19.6), 21.2 (C-16, J(P,C) 18.6), 20.3 (C-14'), 19.9 (C-14), 19.6 (C-15', J(P,C) 3.6), 19.4 (C-15), 19.0 (C-17, J(P,C) 9.2), 18.8 (C-17', J(P,C) 8.5), 17.3 (C-9, J(P,C) 12.1/33.3), numbering scheme shown below. ^{31}P NMR (d_8-THF, −80 °C, 121.5 MHz): δ 35.7, −6.1, J(P,P) 48.0.



$Pd_2(Pr^i_2PCH_2PPr^i_2)_2$ (6)

1,1-Bis(diisopropylphosphino)methane (0.91 g, 3.7 mmol) was dissolved in 1,3-butadiene (15 ml) at −25 °C and added to bis(η^3-2-methylallyl)palladium at −78 °C. The reaction mixture was stirred overnight at −10 °C changing from yellow to dark red. The solution was concentrated and cooled to −78 °C to give the product as a red crystalline solid. Yield 0.87 g (66% theory). M.p. ~124 °C. *Anal.* Found: C, 44.12; H, 8.57; P, 17.48; Pd, 29.94. Calc. for $C_{26}H_{60}P_4Pd_2$: C, 44.02, H, 8.52; P, 17.46; Pd, 30.00%. MS: *m/e* 710 (M^+), 205. IR (KBr): no olefinic abs. ^{1}H NMR (d_8-THF, r.t., 200.1 MHz): δ 1.91 (m, CH, J(H,H)+J(H,P) 6.8), 1.74 (m, PCH_2), 1.22 (m, Me). ^{13}C NMR (d_8-THF, r.t., 50.3 MHz): δ 27.10 (Me, |J(P,C)| 4.6), 21.44 (Me), 20.51 (CH_2, |J(P,C)| ~4.2), 19.84 (CH). ^{31}P NMR (d_8-THF, r.t., 81.0 MHz): δ 38.2.

Crystal structure analysis: molecular formula $C_{26}H_{60}P_4Pd_2$, molecular weight 709.5 g mol^{-1}, crystal colour dark red, crystal size 0.18×0.28×0.35 mm, a=18.788(2), b=8.674(1), c=10.711(1) Å, β=102.503(6)°, V=1704.1 Å^3, T=293 K, D_{calc}=1.38 g cm^{-3}, μ=12.40 cm^{-1}, Z=2, monoclinic, space group $C2$ (No. 5), Enraf-Nonius CAD 4 diffractometer, λ=0.71069 Å, scan mode ω–2θ, 10 573 measured reflections (±h, ±k, ±l), $[(\sin\theta)/\lambda]_{max}$ 0.77 Å^{-1}, 6203 independent reflections, 5196 observed reflections ($I>2\sigma(I)$) for 264 refined parameters, structure solved by heavy atom method, H atom positions and isotropic thermal parameters refined, R=0.027, R_w=0.027, residual electron density 0.80 e Å^{-3}. Atomic positional parameters and equivalent isotropic thermal parameters are given in Table 3. The molecular structure with selected bond distances and angles is shown in Fig. 1.

TABLE 3. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of **6** with standard deviations in parentheses

Atom	x	y	z	U_{eq}[a]
Pd	0.0767(1)	0.0000	0.0413(1)	0.040(1)
P(1)	0.0837(1)	0.0611(1)	−0.1612(1)	0.036(1)
P(2)	0.0763(1)	−0.0545(1)	0.2464(1)	0.036(1)
C(1)	0.0124(1)	−0.0236(5)	−0.2909(2)	0.045(2)
C(2)	0.1674(1)	0.0024(8)	−0.2152(2)	0.057(1)
C(3)	0.2343(2)	0.0858(6)	−0.1378(5)	0.083(3)
C(4)	0.1772(3)	−0.1712(6)	−0.1991(6)	0.089(3)
C(5)	0.0714(2)	0.2694(4)	−0.1933(6)	0.055(2)
C(6)	0.1122(4)	0.3654(5)	−0.0802(5)	0.086(3)
C(7)	0.0859(3)	0.3269(5)	−0.3201(4)	0.079(3)
C(8)	0.0954(2)	−0.2602(4)	0.2886(3)	0.055(2)
C(9)	0.0916(3)	−0.3070(6)	0.4242(5)	0.080(3)
C(10)	0.0485(3)	−0.3612(5)	0.1884(5)	0.090(3)
C(11)	0.1409(1)	0.0474(4)	0.3757(3)	0.054(2)
C(12)	0.1322(3)	0.2219(5)	0.3567(5)	0.073(3)
C(13)	0.2193(2)	0.0020(9)	0.3745(5)	0.088(3)

[a] $U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i\mathbf{a}_j$.

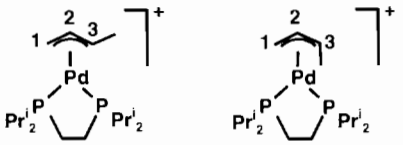
$[(\eta^3$-1-$MeC_3H_4)Pd(Pr^i_2PC_2H_4PPr^i_2)]^+Cl^-$

A solution of $[(\eta^3$-1-$MeC_3H_4)PdCl]_2$ (0.60 g, 1.5 mmol) in dichloromethane (5 ml) was cooled to −30 °C and treated with 1,2-bis(diisopropylphosphino)ethane (0.9 ml, 0.79 g, 3.0 mmol) in dichloromethane (1 ml). The yellow solution was evaporated to dryness and the resulting oil dissolved in acetone/ether and cooled to −30 °C to give the compound as pale yellow crystals (yield 1.16 g, 83% theory, m.p. ~85 °C). *Anal.* Found: C, 46.98; H, 8.63; Cl, 7.66; P, 13.41; Pd, 23.24. Calc. for $C_{18}H_{39}ClP_2Pd$: C, 47.07; H, 8.56; Cl, 7.72; P, 13.49; Pd, 23.17%. IR (KBr): ν (HC:) 30.52, (C:C) 1515. ^{1}H NMR (d_6-acetone, −80 °C): δ 5.58 (q, H-2, J(1,2)+J(2,3) 11.4), 4.58 (sbr, H-1*syn*), 4.40 (dq, H-3*anti*, J(2,3*anti*)/J(3*anti*,4) 6.0), 2.88 (d, H-1*anti*, J(1*anti*,2) ~7)-allyl group; 2.48 (sbr, CH), 2.10 (d, CH_2, J(H,H) 6.2), 1.12 (m, Me) $Pr^i_2PCH_2$; numbering scheme shown below. ^{31}P NMR (d_6-acetone, −80 °C): δ 87.4, 79.9, J(P,P) 26.1 1-*syn*-MeC_3H_4 isomer; 85.3, 77.2, J(P,P) 25.5 1-*anti*-MeC_3H_4 isomer (*syn*:*anti*=94.6).

$[(\eta^3$-1-$MeC_3H_4)Pd(Pr^i_2PC_2H_4PPr^i_2)]^+PF_6^-$ [26]

(η^2-1,3-C_4H_6)Pd($Pr^i_2PC_2H_4PPr^i_2$) (2.01 g, 4.75 mmol) was suspended in diethyl ether (30 ml) at 0 °C and treated with acetic acid (0.57 g, 9.49 mmol). The resulting solution was stirred for 5 h and the product extracted with water (10×10 ml). The aq. acetate solution was added to aq. NH_4PF_6 (1.5 g in 10 ml) and the resulting white precipitate isolated, washed with water (3×10 ml) and dried under high vacuum (yield 2.18 g, 84% theory). *Anal.* Found: C, 38.10; H, 7.09; F, 19.94; P,

16.36; Pd, 18.57. Calc. for $C_{18}H_{39}F_6P_3Pd$: C, 38.01; H, 6.91; F, 20.04; P, 16.34; Pd, 18.71%. IR (KBr): ν (allyl) 1505, (PF_6) 840, 560. The compound was shown by NMR spectroscopy to be formed as a mixture of isomers differing in the *syn*- or *anti*-substitution of the 1-methylallyl group (*syn*:*anti* = 9:1). ^{1}H NMR (d_6-acetone, 400.1 MHz): δ 5.83 (m, H-2, *J*(1*syn*,2) 7.4, *J*(1*anti*,2) 13.3, *J*(2,3*anti*) 12.8, *J*(2,P) 0.4), 4.56 (m, H-1*syn*, *J*(1*syn*,1*anti*) 1.6, *J*(1*syn*, P) 6.0/1.2), 4.35 (m, H-3*anti*, *J*(3*anti*,P) 9.6/0.5), 2.83 (m, H-1*anti*, *J*(1*anti*,P) 9.5/1.3), 2.18 (m, Me-*syn*, *J*(Me,3*anti*) 6.2, *J*(Me,P) 9.2/6.4) 1-*syn*-MeC_3H_4 isomer; 6.02 (m, H-3*syn*, *J*(3*anti*,Me) 6.7, *J*(3*anti*,P) 6.1), 5.28 (m, H-2, *J*(2,1*syn*) 8.0, *J*(2,Me) 0.8, *J*(2,3*syn*) 8.0, *J*(2,1*anti*) 14.4), 4.63 (m, H-1*syn*, *J*(1*syn*,1*anti*) 1.8, *J*(1*syn*,3*syn*) 1.3, *J*(1*syn*,P) 0.8/6.1), 3.35 (m, Me-*anti*, *J*(Me,P) ~10) 1-*anti*-MeC_3H_4 isomer; numbering scheme shown below. ^{13}C NMR (d_6-acetone, −10 °C, 75.5 MHz): δ 122.2 (C-2, *J*(P,C) 5.9, *J*(C,H) 158), 88.4 (C-3, *J*(P,C) 29, *J*(C,H) 158), 59.9 (C-1, *J*(P,C) 28, *J*(C,H) 159), 16.8 (Me-*syn*, *J*(P,C) 4.6, *J*(C,H) 128) 1-*syn*-MeC_3H_4 isomer; 116.5 (C-2, *J*(P,C) 5.6), 83.5 (C-3, *J*(P,C) 28), 60.4 (C-1, *J*(P,C) 29), 14.6 (Me-*anti*, *J*(P,C) 5.1) 1-*anti*-MeC_3H_4 isomer; numbering scheme shown below. ^{31}P NMR (d_6-acetone): δ 84.1, 75.7, *J*(P,P)



26.8 1-*syn*-MeC_3H_4 isomer; 86.0, 78.7, *J*(P,P) 28.3 1-*anti*-MeC_3H_4 isomer; −145.1, *J*(P,F) 708 PF_6.

The compound has also been prepared by reacting (η^2-1,3-C_4H_6)Pd($Pr^i_2PC_2H_4PPr^i_2$) with ethyl methylacetoacetate and KPF_6 in acetonitrile at r.t. for 1 h: ^{31}P NMR (d_6-acetone, −30 °C): δ 86.3; 78.2, *J*(P,P) 25.9; −143.1, *J*(P,F) 707.9 1-*syn*-MeC_3H_4 isomer.

(η^2-MeCH:CHCH$_2$C(Me)(CO$_2$Et)C(Me)O)-Pd($Pr^i_2PC_2H_4PPr^i_2$) (8)

(η^2-1,3-C_4H_6)Pd($Pr^i_2PC_2H_4PPr^i_2$) (1.33 g, 3.14 mmol) was dissolved in THF (5 ml) at −78 °C and ethyl methylacetoacetate (0.45 ml, 3.18 mmol) was added dropwise. The reaction mixture was stirred at −20 °C and the course of reaction followed by ^{31}P NMR spectroscopy: the reaction was complete after 48 h. The reaction mixture was evaporated under high vacuum at −20 °C and the product crystallised from pentane/THF at −78 °C. The resulting yellow solid was washed with pentane (2×2 ml) and dried under high vacuum (yield 1.28 g, 71.7% theory). *Anal.* Found: C, 52.78; H, 8.85; P, 11.06; Pd, 18.88. Calc. for $C_{25}H_{50}O_3P_2Pd$: C, 52.95; H, 8.98; P, 10.93; Pd, 18.77%. ^{31}P NMR (d_8-THF, −80 °C): δ 59.4, 59.1, *J*(P,P) 68.2; 59.6; 58.6, *J*(P,P) 67.1 (ratio of isomers 0.7:1).

The compound could also be prepared by carrying out the above reaction in CH_2Cl_2 but was complicated by the further reaction of the product with the solvent (see below) or by reacting [(η^3-1-Me-C_3H_4)Pd($Pr^i_2PC_2H_4PPr^i_2$)]$^+Cl^-$ with the potassium salt of ethyl methylacetoacetate in THF at −50 °C.

The presence of the adduct **1** in the compound was confirmed by treatment with a small excess of $Pr^i_2PC_2H_4PPr^i_2$ in THF at room temperature, vacuum condensation of the organic product and GC identification by comparison with an authentic sample [2]. The compound was also shown by ^{31}P NMR spectroscopy to react with butadiene in THF at −30 °C with displacement of the alkene to give (η^2-1,3-C_4H_6)-Pd($Pr^i_2PC_2H_4PPr^i_2$).

ClCH$_2$Pd($Pr^i_2PC_2H_4PPr^i_2$)Cl

This compound has been isolated as a pale yellow solid (m.p. ~100 °C dec.) as the final product of the reaction between (η^2-1,3-C_4H_6)Pd($Pr^i_2PC_2H_4PPr^i_2$) and ethyl methylacetoacetate in CH_2Cl_2 at r.t. or by refluxing the (η^2-1,3-C_4H_6)Pd species in CH_2Cl_2. *Anal.* Found: C, 39.65; H, 7.59; Cl, 15.71; P, 13.49; Pd, 23.51. Calc. for $C_{15}H_{34}Cl_2P_2Pd$: C, 39.71; H, 7.55; Cl, 15.63; P, 13.65; Pd, 23.46%. MS: *m/e* 403 ($M^+ - CH_2Cl$). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 3.59 (d, $PdCH_2$, *J*(H,H) ~2), 2.36/2.09–1.51/1.40–1.10 (m, $Pr^i_2PCH_2$). ^{31}P NMR (CD_2Cl_2): δ 73.7, 81.5, *J*(P,P) ~19.

The analogous compound *ClCH$_2$Pd($Cy_2PC_2H_4$-PCy$_2$)Cl* was prepared by reacting (η^3-2-MeC_3H_4)$_2$Pd with $Cy_2PC_2H_4PCy_2$ in CH_2Cl_2 at r.t. and the crystal structure confirmed by an X-ray diffraction analysis: molecular formula $C_{27}H_{50}Cl_2P_2Pd \cdot 3CDCl_3$, formula weight 975.1 g mol^{-1}, colourless crystals, crystal size 0.14×0.40×0.22 mm, $a = 10.630(2)$, $b = 15.668(3)$, $c = 13.444(2)$ Å, $\beta = 104.117(7)°$, $V = 2171.4$ Å^3, $T = 293$ K, $D_{calc} = 1.49$ g cm^{-3}, $\mu = 11.97$ cm^{-1}, $Z = 2$, monoclinic, space group $P2_1$ (No. 4), Enraf-Nonius CAD 4 diffractometer, $\lambda = 0.71069$ Å, scan mode ω–2θ, 5329 measured reflections ($\pm h$, $+k$, $+l$), $[(\sin\theta/\lambda)]_{max}$ 0.65 Å^{-1}, 5122 independent reflections, 4102 observed reflections ($I > 2\sigma(I)$) for 396 refined parameters, structure solved by heavy atom method, H atom positions calculated and fixed in the final refinement stages, $R = 0.048$, $R_w = 0.051$, residual electron density 1.07 e Å^{-3}. Atomic positional parameters and equivalent isotropic thermal parameters are given in Table 4. The molecular structure with selected bond distances and angles is shown in Fig. 7: the Pd–C distance (2.101(9) Å) should be compared with that of 2.039(8) Å observed for Cl-$CH_2Pd(Me_2NCH_2CMe_2CH{:}CH_2)Cl$ [27] and that of 2.105(5) Å observed for $Cl_2CHPd(Ph_2PC_2H_4PPh_2)Cl$ [28], the latter compound having been prepared analogously by reacting a [$Pd(Ph_2PC_2H_4PPh_2)$] species with chloroform.

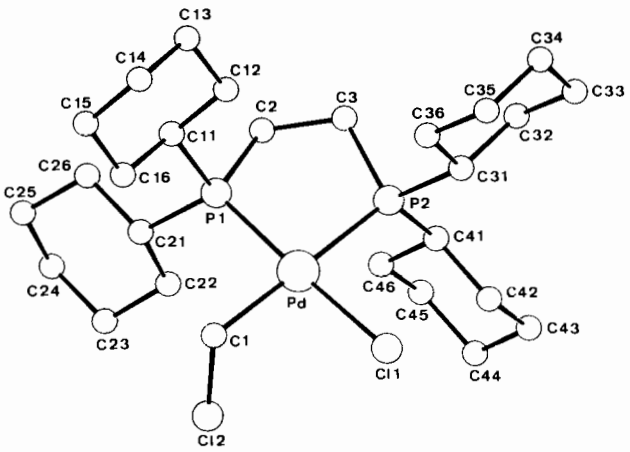
TABLE 4. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of $ClCH_2Pd(Cy_2PC_2H_4PCy_2)Cl$ with standard deviations in parentheses

Atom	x	y	z	U_{eq}[a]
Pd	0.9484(1)	1.0000	0.1140(1)	0.037
Cl1	0.9266(2)	0.9271(2)	−0.0461(2)	0.059
Cl2	0.6928(2)	0.8977(2)	0.1117(3)	0.096
Cl3	0.6316(5)	0.8255(4)	0.6953(4)	0.164
Cl4	0.5456(9)	0.9855(4)	0.7500(7)	0.323
Cl5	0.5063(6)	0.8316(5)	0.8461(5)	0.204
Cl6	0.1411(4)	0.2380(3)	0.6049(4)	0.140
Cl7	0.3386(5)	0.3531(3)	0.5965(5)	0.160
Cl8	0.3941(6)	0.1764(4)	0.6152(5)	0.208
Cl9	−0.0685(3)	−0.1089(3)	0.6302(3)	0.128
Cl10	0.0806(4)	0.0416(2)	0.6953(2)	0.105
Cl11	0.1777(4)	−0.1216(3)	0.7703(3)	0.116
P1	0.9879(2)	1.0611(2)	0.2679(2)	0.042
P2	1.0399(2)	1.1196(2)	0.0586(2)	0.042
C1	0.8600(8)	0.8951(6)	0.1667(6)	0.049
C2	1.0398(8)	1.1721(6)	0.2586(7)	0.053
C3	1.1089(8)	1.1863(5)	0.1713(6)	0.049
C4	0.612(1)	0.898(1)	0.790(1)	0.125
C5	0.306(1)	0.2574(9)	0.642(1)	0.101
C6	0.037(1)	−0.0596(9)	0.7310(8)	0.085
C11	1.1199(7)	1.0131(6)	0.3670(6)	0.048
C12	1.2476(8)	1.0123(9)	0.3379(8)	0.077
C13	1.3571(9)	0.9754(7)	0.4241(9)	0.083
C14	1.326(1)	0.8876(8)	0.4515(9)	0.081
C15	1.200(1)	0.8863(8)	0.4799(9)	0.090
C16	1.0890(9)	0.9230(7)	0.3957(8)	0.068
C21	0.8477(8)	1.0696(6)	0.3252(6)	0.053
C22	0.7290(8)	1.1061(6)	0.2517(7)	0.054
C23	0.6108(9)	1.1051(7)	0.2969(8)	0.072
C24	0.641(1)	1.1483(9)	0.399(1)	0.085
C25	0.759(1)	1.1141(9)	0.4752(8)	0.086
C26	0.878(1)	1.1164(7)	0.4294(7)	0.067
C31	1.1749(7)	1.0991(6)	−0.0003(6)	0.048
C32	1.2416(9)	1.1793(6)	−0.0276(8)	0.064
C33	1.3533(9)	1.1566(7)	−0.0757(8)	0.071
C34	1.4495(8)	1.0974(8)	−0.0083(8)	0.069
C35	1.3839(9)	1.0188(7)	0.0177(8)	0.071
C36	1.2733(8)	1.0391(6)	0.0668(7)	0.059
C41	0.9283(8)	1.1915(5)	−0.0290(7)	0.049
C42	0.879(1)	1.1558(8)	−0.1357(7)	0.074
C43	0.791(1)	1.218(1)	−0.2070(8)	0.097
C44	0.678(1)	1.2432(8)	−0.1644(9)	0.083
C45	0.727(1)	1.2796(7)	−0.0556(9)	0.078
C46	0.8147(9)	1.2160(7)	0.0142(7)	0.065

[a] $U_{eq} = \frac{1}{3} \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

Catalytic reactions of 1,3-butadiene with ethyl methylacetoacetate

In a typical experiment, a thick walled Schlenk vessel fitted with a Young tap was charged with ethyl methylacetoacetate (2.9 g, 20.0 mmol), the catalyst (0.2 mmol) and a solvent (10 ml). 1.3-Butadiene (5 ml, 60.4 mmol) and a weighed amount of dodecane (*c.* 2 g; as an internal standard) were added and the reaction mixture was stirred at 20 °C. Samples were removed after cooling the reaction mixture to −10 °C and the reaction was terminated by adding elemental sulfur (*c.* 60 mg). The product and solvent were isolated by vessel-to-vessel vacuum distillation and analysed quantitatively by gas chromatography using a 30 m × 0.32 mm CW 20 m FS 476 capillary column heated from 60 to 220 °C at 6 °C/min.



Pd–P1 2.225(2), Pd–P2 2.317(2), Pd–Cl1 2.398(2), Pd–C1 2.101(9), C1–Cl2 1.752(9), P1–C2 1.839(9), P2–C3 1.839(9), C2–C3 1.55(1), P1–Pd–P2 87.2(1), P2–Pd–Cl1 93.1(1), Cl1–Pd–C1 88.7(2), P1–Pd–C1 91.2(2), Pd–C1–Cl2 109.3(4), Pd–P1–C2 109.6(3), Pd–P2–C3 108.0(3).

Fig. 7. The molecular structure of $ClCH_2Pd(Cy_2PC_2H_4PCy_2)Cl$ with selected bond distances (Å) and angles (°). The compound crystallises with three molecules of $CDCl_3$.

Crystal structure analysis

Computer programmes used: data reduction: DATAP, ref. 29a; structure solution: SHELXS-86, ref. 29b; structure refinement: GFMLX, a modified version of ORFLS, ref. 29c. Molecular diagram (50% thermal ellipsoids): ORTEP, ref. 30. Computer: VAX 4000-3000. Scattering factors: ref. 31.

Supplementary material

Further details of the crystal structure investigations (listings of hydrogen atom positional parameters, anisotropic thermal parameters, distances and angles) may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-57995, the names of the authors and the journal citation.

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