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FULL PAPER

Synthesis and chemistry of diphenyl-2-pyridylphosphine complexes of palladium(0). X-Ray characterisation of $Pd(Ph_2Ppy)_2$-(η^2-DMAD) and *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$

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The zerovalent complexes $Pd(Ph_2Ppy)_3$ **1** and $Pd(Ph_2Ppy)_2$(dba) **2**, where Ph_2Ppy is diphenyl-2-pyridylphosphine and dba = *trans,trans*-dibenzylideneacetone, have been synthesized and characterised. Reactions of **1** with alkynes have been studied and the dimethyl acetylenedicarboxylate complex $Pd(Ph_2Ppy)_2(\eta^2$-DMAD) **3**, where DMAD is dimethyl acetylenedicarboxylate, isolated and structurally characterised. The complexes *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)X$, X = $CF_3CO_2^-$ **4** or Cl^- **5**, and *trans*-$Pd(Ph_2Ppy)_2\{CO(CH_3)C{=}CH_2\}Cl$ **6** result from oxidative addition of phenylacetylene/CF_3CO_2H, phenylacetylene/Et_3NHCl and methacryloyl chloride respectively to **1**, and the crystal structure of **4** is presented. The alkenyl ligand is bound to palladium through the α carbon in **4**. Insertions into the M–C bond of the vinyl complexes have been studied. No isolable insertion product is obtained with carbon monoxide although the complex is active for the catalytic alkoxycarbonylation of phenylacetylene to 2-phenylpropenoate. Propadiene inserts into the Pd–C bond in **4** to give the cationic π-allyl complex $[Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(Ph){=}CH_2\}][CF_3CO_2]$ **7**. The complex $Pd(Ph_2Ppy)_3$ is found to catalyse the vinylation of Ph_2Ppy to the corresponding 2-propenylphosphonium trifluoromethanesulfonate.

Introduction

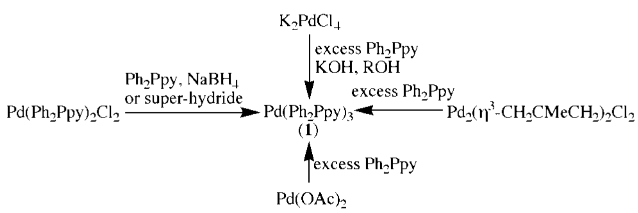
The insertion of unsaturated molecules like CO, alkenes, alkynes and allenes into metal–carbon bonds is a very important step in many transition metal-catalysed processes.[1] A recently developed example, in which a palladium-based catalyst is used, is the alkoxycarbonylation of alkynes.[2] We and others have recently prepared alkoxycarbonyl complexes and commented on their likely role as intermediates in such catalytic reactions where insertion of an unsaturated hydrocarbon into the M–C(O)OR bond and subsequent protonolysis give a vinyl ester.[3] An alternative pathway involves the oxidative addition of HX to a palladium(0) complex to give a metal hydride which inserts the alkyne to produce a palladium alkenyl intermediate. Subsequent insertion of carbon monoxide generates a palladium acyl species which is released by alcohol to give the desired ester. The validity of this mechanism is further demonstrated by the isolation of novel vinylic palladium complexes from mixtures of $Pd(Ph_2Ppy)_3$ (Ph_2Ppy = diphenyl-2-pyridylphosphine), protic acids and phenylacetylene as presented in this paper. The reactivity of these complexes towards insertion of CO and propadiene has also been studied. A 2-propenyl palladium intermediate was too unstable to be isolated, although 2-propenylphosphonium salts have been characterised from these reactions as decomposition products.

Results and discussion

Zerovalent palladium complexes

A common synthetic route to zerovalent platinum and palladium complexes with tertiary aromatic phosphines is by reduction of a metal(II) phosphine species with hydrazine, alcoholic KOH or an excess of phosphine. The zerovalent complexes are, in general, less readily obtained as the σ basicity of the phosphine increases.[4] Syntheses using preformed metal(0) species have since proved to be more versatile.[5]

The complex $Pd(Ph_2Ppy)_3$, **1**, is obtained by a number of synthetic methods as outlined in Scheme 1. In our hands, the



Scheme 1

synthesis from K_2PdCl_4 proved to be the most convenient.[6] When K_2PdCl_4 was treated with 3.5 equivalents of Ph_2Ppy in basic ethanol **1** was obtained as a yellow solid which is moderately stable in air. In addition, $Pd(Ph_2Ppy)_3$ was obtained from $Pd_2(\eta^3\text{-}CH_2CMeCH_2)_2Cl_2$ and a six-fold excess of ligand following a modified literature procedure for the preparation of $Pd(PCy_3)_2$,[7] or from palladium acetate and an excess of Ph_2Ppy. In all cases, an excess of ligand was required in order to isolate the desired complex in good yield. Unlike the smaller nickel(0) centre[8] and the related $Pd(PPh_3)_4$, no tetrakis complex, $Pd(Ph_2Ppy)_4$, was detected by NMR even when Ph_2Ppy : Pd ratios of >4 : 1 were employed. Although published spectroscopic data for **1** are absent, its crystal structure has been reported recently.[9]

The observation of a singlet (δ 21.7) in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of $Pd(Ph_2Ppy)_3$ over the temperature range −80 to +27 °C suggests that either no ligand dissociation occurs or that it takes place rapidly even at low temperature. The complex $Pd(PPh_3)_4$ has been shown to dissociate readily to the tris complex, and there has been much debate as to whether there is further dissociation to the bis(phosphine)palladium(0) complex; $Pd(L)_2$ species are well established for very bulky, electron rich phosphines, *e.g.* $Pd(P^tBu_3)_2$.[10] The extent of ligand dissoci-

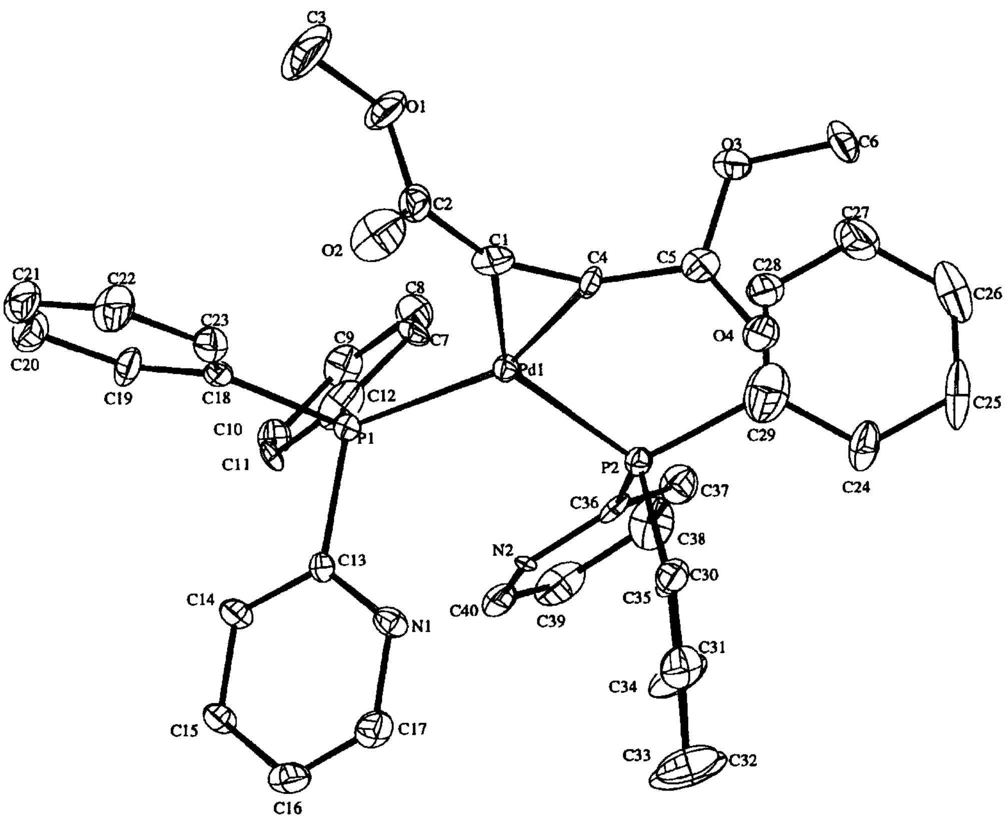


Fig. 1 Structure of $Pd(Ph_2Ppy)_2(\eta^2\text{-DMAD})$ **3**.

ation is believed to be dependent on the steric bulk and basicity of the co-ordinated phosphine. The cone angle of Ph_2Ppy is very similar to that of PPh_3 and, on a purely steric basis, a tetrakis complex would be expected. Since $Pd(Ph_2Ppy)_4$ is not detected, it appears that inherent electronic differences and/or transient chelate formation through the ancillary nitrogen donor(s) may stabilise the sixteen-electron tris complex to the extent that no tetrakis species is observed. Some authors have attributed the stability of co-ordinatively unsaturated species such as **1** to the formation of stronger π bonds in trigonal or linear metal complexes than in corresponding tetrahedral forms.[11]

The complex $Pd(Ph_2Ppy)_2(dba)$, **2**, is prepared by treating $Pd(dba)_2$ (dba = dibenzylideneacetone) with two equivalents of Ph_2Ppy. Replacement of one Ph_2Ppy ligand in $Pd(Ph_2Ppy)_3$ by dimethyl acetylenedicarboxylate (DMAD) gives the complex $Pd(Ph_2Ppy)_2(\eta^2\text{-DMAD})$, **3**. Attempts to isolate $Pd(Ph_2Ppy)_3(CO)$ or $Pd(Ph_2Ppy)_2(\eta^2\text{-}C_2H_4)$ by procedures known to be successful for the PPh_3 analogues failed, $Pd(Ph_2Ppy)_3$ being recovered intact.

Both methoxycarbonyl groups are equivalent in the ^1H NMR spectrum of $Pd(Ph_2Ppy)_2(\eta^2\text{-DMAD})$ **3** giving rise to a singlet at δ 3.21. The infrared spectrum shows a strong band at 1848 cm^{-1} assignable to $\nu(C{\equiv}C)$. This value is very close to that reported for $Pd(PPh_3)_2(\eta^2\text{-DMAD})$ (1845, 1830 cm^{-1} shoulder), and is only slightly higher than the typical value for an unco-ordinated double bond indicating a bonding mode intermediate between that of an alkyne and an alkene. Complexes $M(PR_3)_2(RCCR)$ are stabilised by metals in low oxidation states bearing electron donating ligands especially when the alkynes have electron withdrawing substituents; such is the case in **3**. Only starting material is recovered in similar reactions with the electron rich alkynes butyne, propyne and phenylacetylene.

Available crystallographic data for d^{10} metal complexes of the type $M(PR_3)_2(RCCR)$ show two common characteristics: (i) the co-ordination around the metal is planar and (ii) the substituents on the alkyne ligand adopt a *cis* orientation projecting away from the metal so as to resemble the shape of the excited state of free alkyne. This mode of alkyne co-ordination has been rationalised in terms of electronic arguments where a redistribution of the valence electrons occurs upon bonding to the metal.[12] Both these characteristics are evident in the crystal structure of $Pd(Ph_2Ppy)_2(\eta^2\text{-DMAD})$ as shown in Fig. 1. The complex has monodentate phosphorus bonded Ph_2Ppy ligands and a propeller-like conformation of aromatic rings as does the triphenylphosphine analogue.[13] The M–C bond distances of 2.072(5) and 2.023(5) Å (Table 1) are similar to those reported for the PPh_3 complex. As expected, the shorter Pd–C(4) bond is *trans* to the longer Pd–P(1) bond and *vice versa*. The methoxycarbonyl groups are mutually *cis* and point away from the metal (C–C≡C bond angles of 146°). The alkyne C–C bond length of 1.263(6) Å lies between the typical values for unco-ordinated alkynes and alkenes, and is comparable with data reported for other alkyne complexes which range from 1.279(2) to 1.32(9) Å.[14,15] The co-ordination around the metal is distorted square planar with a P(1)–Pd(1)–P(2) bond angle of 103.98(5)° and a C(1)–Pd–C(4) angle of 35.9(2)°. The dihedral angle between the planes P(1)–Pd(1)–P(2) and C(1)–Pd–C(4) is smaller at 2.9(1)° than that for the PPh_3 analogue (9.7°). The planes of the carboxylates are approximately 33° from collinearity with the alkynic carbons with the plane of the methoxycarbonyl sub-

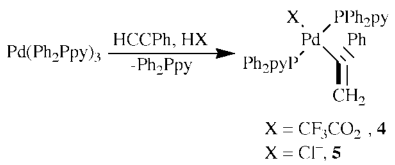
Table 1 Selected bond lengths (Å) and angles (°) in $Pd(Ph_2Ppy)_2(\eta^2\text{-DMAD})$, **3**

Pd(1)–P(1)	2.333(1)	C(2)–O(2)	1.221(5)
Pd(1)–P(2)	2.305(1)	O(1)–C(3)	1.444(6)
Pd(1)–C(1)	2.072(5)	C(4)–C(5)	1.440(6)
Pd(1)–C(4)	2.023(5)	C(5)–O(3)	1.348(5)
C(1)–C(4)	1.263(6)	C(5)–O(4)	1.220(6)
C(1)–C(2)	1.462(7)	O(3)–C(6)	1.450(6)
C(2)–O(1)	1.331(6)		
P(2)–Pd(1)–P(1)	103.98(5)	C(2)–C(1)–C(4)	146.5(5)
C(4)–Pd(1)–C(1)	35.9(2)	C(1)–C(4)–C(5)	146.7(5)

stituent on C(1) being nearly normal to the C(1)–Pd–C(4) plane whereas that on C(4) is not; the two dihedral angles are 86.9(8) and 64.2(2)° respectively. For the triphenylphosphine analogue, $Pd(PPh_3)_2(\eta^2\text{-DMAD})$, the corresponding values are 89.5(3) and 41.6(3)°. As expected on the basis of the rationale proposed by McGinetty,[13] the shorter Pd–C bond is to the carbon of the alkyne [C(1)] that has its substituent carboxylate plane perpendicular to the co-ordination plane.

Oxidative additions to $Pd(Ph_2Ppy)_3$

Although no stable hydride complexes could be isolated from the reactions of $Pd(Ph_2Ppy)_3$ with protic acids, σ-vinyl-palladium derivatives were obtained from the reaction of phenylacetylene with $Pd(Ph_2Ppy)_3$ in the presence of a proton source (Scheme 2). When **1** was treated with equimolar amounts of phenylacetylene and trifluoroacetic acid *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$, **4**, was isolated. Replacing CF_3CO_2H with Et_3NHCl gave *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)$-Cl, **5**. Possible polymerisation and/or phosphonium salt formation were suppressed by adding the acid slowly at 0 °C. Hydrochloric acid was less suitable for the synthesis of **5** as a mixture of products was obtained. No σ-vinyl complex was isolated with propyne, the main product in this case being the phosphonium salt $[Ph_2pyP\{(CH_3)C{=}CH_2\}][CF_3CO_2]$. Similarly, efforts to form such palladium(II) vinyl species from the oxidative addition of vinyl triflate to **1** or **2** gave $[Ph_2pyP\{(CH_3)$-$C{=}CH_2\}][CF_3SO_3]$ as the only isolable product. In the absence of a palladium species, no reaction is observed between Ph_2Ppy and vinyl triflate. It was found that the triflate salt is formed in the presence of catalytic amounts of **1** or **2**. The above observations suggest formation of an unstable palladium(II) vinyl triflate that reductively eliminates to generate the phosphonium triflate and a palladium(0) complex. A similar palladium catalysed formation of $[Ph_3P\{(CH_3)C{=}CH_2\}]^+$ has been reported by Stang and co-workers.[15] Although stable palladium 2-propenyl complexes have not been isolated so far from addition of propenyl triflate to a palladium(0) species, the analogous reaction has been reported for $Pt(PPh_3)_4$ to give the more kinetically robust platinum(II) propenyl complex.[16]



Scheme 2

Literature examples of monosubstituted vinyl ligands σ-bound to palladium through the α carbon (*i.e.* both vinylic protons are on the unco-ordinated β carbon) are rare. Very recently, Scrivanti *et al.*[17] observed σ-alkenyl complexes of this type by solution NMR of $Pd(OAc)_2$–Ph_2Ppy–CH_3SO_3H (1:3:3) and phenylacetylene in C_6D_6 containing methanol. However, they were unable to isolate and characterise fully any 'stable' σ-vinyl complexes. Intimate details of the mechanism of formation of **4** and **5** remain obscure, although displacement of one Ph_2Ppy ligand by phenylacetylene prior to oxidative addition of HX seems unlikely as **1** has been shown to be unreactive toward the alkyne alone.

Sharp singlets at δ 17.1 and 16.5 are observed in the $^{31}P\text{-}\{^1H\}$ NMR spectra of complexes **4** and **5**, respectively. The ^{13}C spectra show pertinent Ph_2Ppy resonances (*ipso* carbons) to be split into triplets, thus a *trans* conformation is assigned, in accord with the crystal structure of **4** (see below). The α vinylic carbon appears at δ 153.6 for complex **4** (δ 159.9, **5**) and the β carbon at δ 117.2 (116.5, **5**); neither vinylic carbon is coupled to phosphorus. In the ^1H NMR the vinylic proton *trans* to the palladium atom couples with the two *trans* phosphorus atoms to give a triplet, whereas the *cis* vinylic proton appears as a singlet. The δ values differ appreciably from those reported for the putative palladium alkenyl complex of Scrivanti *et al.*[17] who saw no $^4J_{PH}$ coupling even at low temperature. In the IR spectra of **4** and **5** the carbon–carbon bond stretch is not observed. The antisymmetric ν(CO) stretch of the carboxylate ligand in **4** appears at 1684.4 cm^{-1}.

Table 2 Selected bond lengths (Å) and angles (°) for *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$, **4**

Pd(1)–P(1)	2.334(2)	Pd(1)–P(2)	2.346(2)
Pd(1)–C(20)	1.998(6)	Pd(1)–O(1)	2.136(5)
C(2)–C(21)	1.328(8)	C(20)–C(22)	1.488(9)
P(1)–C(6)	1.824(8)	P(1)–C(12)	1.829(7)
P(1)–C(1)	1.837(7)	P(2)–C(34)	1.820(8)
P(2)–C(39)	1.820(7)	P(2)–C(28)	1.825(7)
N(1)–C(5)	1.432(8)	N(1)–C(1)	1.437(9)
N(2)–C(34)	1.360(9)	N(2)–C(35)	1.39(1)
C(20)–Pd(1)–O(1)	171.2(3)	C(20)–Pd(1)–P(1)	86.8(2)
O(1)–Pd(1)–P(1)	92.3(2)	C(20)–Pd(1)–P(2)	85.9(2)
O(1)–Pd(1)–P(2)	96.9(2)	P(1)–Pd(1)–P(2)	164.56(8)
C(21)–C(20)–Pd(1)	121.8(6)	C(22)–C(20)–Pd(1)	115.4(5)

Colourless crystals of complex **4** suitable for structural determination were obtained by slow diffusion of light petroleum into a solution of it in toluene. The molecular structure of **4** with the adopted numbering scheme is shown in Fig. 2. Selected bond lengths and angles are summarised in Table 2. Although a few σ-alkenyl palladium complexes have been structurally characterised, **4** is a rare example containing a vinyl group; a similarly co-ordinated vinylamine derivative has been reported recently.[18] In the complex each Ph_2Ppy is co-ordinated to the metal through the phosphorus atom and mutually *trans*. The M–C distance of 1.998(6) Å is close to those of 2.051(2) and 2.004(12) Å reported for $Pd(PMe_3)_2[(CO_2CH_3)C{=}CH(CO_2$-$CH_3)][CCPh]$[19] and $Pd(PMe_3)_2[(^tBuCC)C{=}C(^tBu)(CC^tBu)]Br$,[20] respectively. The average M–P distance is typical for palladium(II) complexes (2.340(2) Å). The phosphine ligands are compressed towards the vinyl group with P–Pd–C angles of 86.8(2) and 85.9(2)° respectively, the O–Pd–P angles being 92.3(2) and 96.9(2)°. The alkenyl group in square planar complexes is generally perpendicular to the co-ordination plane of the molecule; there is no exception in **4** where the dihedral angle between the planes defined by the vinyl group and the co-ordination plane is 85.99(19)°. The C=C bond lengths are somewhat shorter than in the more conjugated derivatives above.

The oxidative addition of methacryloyl chloride $ClCO(CH_3)$-$C{=}CH_2$ to complex **1** gave a compound tentatively assigned as *trans*-$Pd(Ph_2Ppy)_2\{CO(CH_3)C{=}CH_2\}Cl$, **6**. The complex showed two vinylic resonances at δ 6.79 (broad) and 6.44 (t, $^5J_{H,P}$ = 5.5 Hz) in the ^1H NMR with the methyl singlet at δ 1.93. The antisymmetric ν(CO) stretch was observed at 1643.5 cm^{-1} in the infrared spectrum. However, reproducible analytical data for the complex could not be obtained as it decomposed prior to combustion, presumably by loss of the acyl ligand.

Although attempts to isolate an acyl complex by treating $Pd(Ph_2Ppy)(PhC{=}CH_2)(CF_3CO_2)$ **4** with carbon monoxide failed, the reactivity of the vinyl group towards CO suggested the complex may be useful in catalytic applications. Therefore methanol and phenylacetylene were introduced in order to test whether complex **4** would catalyse the alkoxycarbonylation of terminal alkynes in the presence of carbon monoxide. Complex **4**, methanol and phenylacetylene in a 1:10:6 ratio were combined in a glass pressure vessel and carbon monoxide introduced at 30 psi and the mixture left for one day. A ^1H NMR spectrum of the solution showed complete conversion of phenylacetylene into methyl 2-phenylpropenoate, as evidenced by signals at δ 5.65 (s), 6.35 (s) and 3.45 (s) (C_6D_6). In the

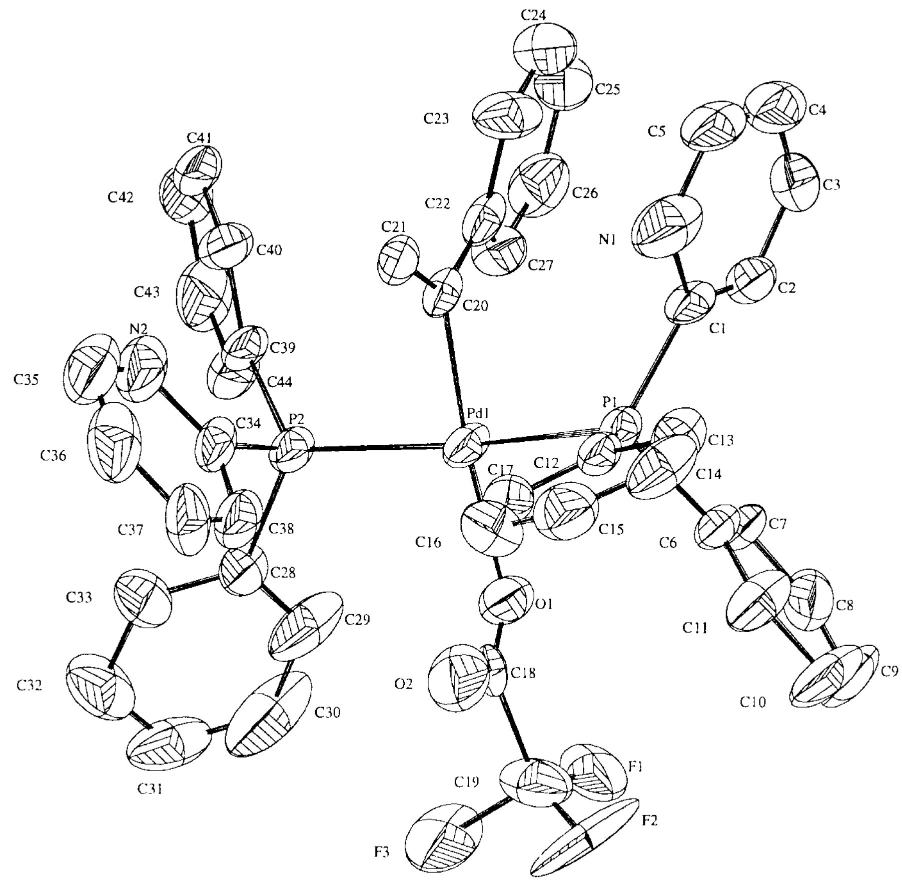
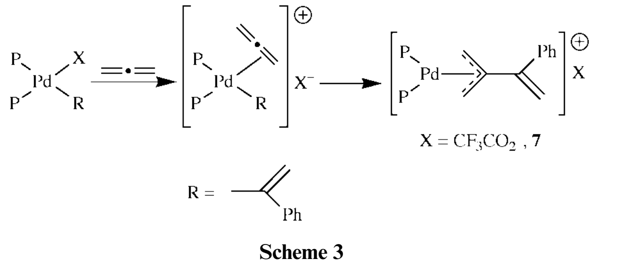


Fig. 2 Structure of *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$ **4**.

^{31}P-{^1H} spectrum two main signals were observed at δ 17.6 and 0.5 assignable to oxidised ligand $Ph_2P(O)py$ and a palladium(I) Ph_2Ppy dimer.[21] An orange solid was precipitated from the reaction solution on addition of light petroleum. GC-MS and NMR analysis of the supernatant solution confirmed formation of methyl 2-phenylpropenoate (*m*/*z* 162) and phosphine oxide (*m*/*z* 280). The isolated solid gave two broad vinylic resonances at δ 6.45 and 5.67 in the ^1H NMR spectrum, shifted downfield in comparison with the vinylic resonances of complex **4** {δ 5.11 (t, 5.5 Hz), δ 4.74 (s)}, indicating introduction of an electron withdrawing group. Acquisition of further spectroscopic data for the complex was not possible since decomposition occurred during its purification.

Insertions into the palladium–carbon bond of the vinyl complexes were further investigated by treating complex **4** with propadiene. The cationic π-allyl complex $[Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(Ph){=}CH_2\}][CF_3CO_2]$, **7**, was formed from insertion of allene into the metal–carbon bond. In accord with similar reported reactions, insertion takes place *via* migration of the R group to the central most electrophilic carbon atom of allene[22] (Scheme 3). Known reactions of this type involve insertion of



Scheme 3

allene into a metal–halide, –alkyl or –acyl bond. This is the first example of insertion into a palladium–vinylic bond. The ^{31}P spectrum of **7** reveals a singlet at ambient temperature. In the ^1H NMR spectrum the *syn* and *anti* protons (with respect to the palladium centre) give two broad signals and the vinylic protons two separate singlets. The NMR data compare well with those of the structurally characterised analogue $[Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(CH_3){=}CH_2\}][CF_3CO_2]$ (ref. 3) confirming the assignment of **7**.

Conclusion

The zerovalent palladium complex $Pd(Ph_2Ppy)_3$ has been shown to undergo oxidative addition of phenylacetylene–HX mixtures to give stable σ-vinyl complexes of the type *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)X$ where the alkenyl ligand is bound through the α-carbon. This chemistry does not extend to propyne–HX mixtures where only phosphonium salts of the type $[Ph_2Ppy\{(CH_3)C{=}CH_2\}]X$ are isolated. The Pd–vinyl bond is not stable to CO, but simple insertion (acyl) products are not isolated from these reactions only ill characterised decomposition products. Oxidative addition of methacryloyl chloride to *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)X$ does give a thermally unstable acyl species. The Pd-vinyl complexes act as catalysts for the selective formation of methyl 2-phenylpropenoate from methanol and phenylacetylene.

Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled from sodium–benzophenone under nitrogen, except for toluene (sodium), methanol (calcium hydride) and dichloromethane (calcium hydride). Light petroleum had bp 40–60 °C. All other chemicals were used as supplied (Aldrich) without further purification. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX400 spectrometer operating at 400.13 and 100 MHz, respectively, ^{31}P NMR spectra using a JEOL FX90Q spectrometer at 36.2 MHz and referenced to

85% H_3PO_4 (δ 0). Infrared spectra were recorded as KBr discs on a Nicolet 510 FT-IR spectrophotometer. Microanalyses were obtained within the department. The compounds $[Pd(\eta^3\text{-}CH_2CMeCH_2)Cl]_2$,[23] $Pd_2(dba)_3$,[24] 2-propenyl triflate[25] and propadiene[26] were prepared by literature procedures.

Preparations

$Pd(Ph_2Ppy)_3$ 1. To a suspension of $[Pd(\eta^3\text{-}CH_2CMeCH_2)Cl]_2$ (0.2 g, 0.51 mmol) in methanol (8 ml) at −5 °C was added a cooled solution of Ph_2Ppy (0.8 g, 3.04 mmol) in methanol (7 ml) over 2 min. A bright yellow solid was formed quickly after completion of the addition. The mixture was stirred for two hours and Et_2O (15 ml) added to complete the precipitation. The yellow solid was washed twice with diethyl ether and dried *in vacuo*. Yield = 0.75 g (82%). Calc. for $C_{51}H_{42}N_3P_3Pd$: C, 68.4; H, 4.7; N, 4.7. Found: C, 68.3; H, 4.9; N, 4.8%. $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): δ 21.7. ^1H NMR (C_6D_6): δ (d, py), 7.60 (dd, py), 6.88 (t, py), 7.75 (m, 4 H, Ph), 7.10 (m, 6 H, Ph), 6.55 (dd, py). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6): δ 164.68 (d, *J* 26, py, *ipso*-C), 149.60 (d, *J* 11, C), 138.65 (d, *J* 14, CH), 134.71 (d, *J* 18, CH), 134.01 (d, *J* 18, CH), 132.22 (d, *J* 9, CH), 131.30 (s, CH), 128.90 (d, *J* 24 Hz, CH) and 125.40 (s, CH). The complex was also prepared by adapting the known procedure for the formation of $Pt(Ph_2Ppy)_3$.

$Pd(Ph_2Ppy)_2(dba)$ 2. To a solution of $Pd(dba)_2$ (0.5 g, 0.54 mmol) in toluene (40 ml) was added, over 3 min, a solution of Ph_2Ppy (0.57 g, 2.16 mmol) in toluene (20 ml). After stirring (3 h) the dark solution was filtered through Celite and reduced to half volume. Light petroleum (60 ml) was added to precipitate the compound as a yellow solid. The product was recrystallised by diffusion of light petroleum into a solution of **2** in toluene. Yield 0.8 g (85%). Calc. for $C_{51}H_{42}N_2OP_2Pd$: C, 70.6; H, 4.9; N, 3.2. Found: C, 70.2; H, 4.8; N, 3.6%. $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): δ 24.7. ^1H NMR (C_6D_6): δ 8.36 (m, 2 H, py), 7.75–7.50 (br, 10 H, dba), 7.25–7.04 (m, 20 H, Ph), 6.88 (t, 4 H, py) and 6.49 (m, 2 H, py).

$Pd(Ph_2Ppy)_2(\eta^2\text{-}DMAD)$ 3. Dimethyl acetylenedicarboxylate (0.2 ml) in Et_2O (1 : 10 v/v) was added dropwise to a suspension of $Pd(Ph_2Ppy)_3$ (0.2 g, 0.22 mmol) in Et_2O (40 ml) to give an immediate white precipitate. After a few minutes of stirring the supernatant was decanted and the compound dried under a stream of nitrogen. Yield 0.13 g (76%). Calc. for $C_{40}H_{34}N_2O_4P_2Pd$: C, 62.0; H, 4.4; N, 3.6. Found: C, 61.7; H, 4.6; N, 3.4%. IR (KBr disks, cm^{-1}): ν(DMAD) ν(C≡C) 1848.0s, 1728.7s, ν_{asym}(CO) 1689.0vs, 1218.4vs, 1040.35s, $\nu(Ph_2Ppy)$ 1571.3s, 1434.6vs, 1097.5s, 747.76s, 695.3vs and 514.05vs. $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): δ 29.6. ^1H NMR (C_6D_6): δ 8.28 (d, 2 H, py), 7.83 (m, 4 H, Ph), 7.76 (t, 2 H, py), 7.04 (m, 6 H, Ph), 6.90 (dt, 2 H, py), 6.46 (dt, 2 H, py) and 3.21 (s, 3 H, DMAD). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6): δ 187.0 (s, CO_2CH_3), 162.78 (t, *J* 49 Hz, py, *ipso*-C), 148.27 (t, *J* 25, C), 134.38 (d, *J* 24, CH), 133.38 (d, *J* 31, CH), 124.27 (s, CH), 111.9 (d, $^2J_{C,P}$ = 263.3 Hz, C≡C), 49.92 (s, CO_2CH_3).

***trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$ 4.** The complex $Pd(Ph_2Ppy)_3$ (0.14 g, 0.16 mmol) was dissolved in toluene (25 ml) and CF_3CO_2H (0.3 ml) added causing an immediate change from yellow to red. Phenylacetylene (0.1 ml) was introduced and the solution stirred for 3 h, then filtered through Celite and the solvent removed to afford a red oil. Addition of CH_2Cl_2 (6 ml) gave a red solution and white precipitate. The precipitate was collected and washed with light petroleum (20 ml). The product was obtained as colourless crystals by diffusion of light petroleum into a solution of the complex in a 1 : 1 mixture of toluene and acetonitrile. Yield 0.11 g (85%). Calc. for $C_{44}H_{35}F_3N_2O_2P_2Pd$: C, 63.3; H ,4.0; N 3.2. Found: C, 62.9; H, 4.0; N, 3.2%. IR (KBr disks, cm^{-1}): $\nu(CF_3CO_2)$ 1684.4vs, 1200.0, 1131.2s, $\nu(Ph_2Ppy)$ 1437.5, 693.8, 521.9. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 17.1. ^1H NMR (C_6D_6): δ 8.25 (d, 2 H, py), 7.74 (br, 8 H), 7.43 (d, 2 H, py), 7.21 (d, 2 H, py), 6.88 (m, 12 H), 6.58 (m, 3 H), 6.50 (t, 2 H), 5.11 (t, $^4J_{H,P}$ = 5.5 Hz, H_2C=CPh) and 4.74 (s, H_2C=CPh). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6–CD_3CN): δ 153.6 (s, C_α) and 117.2 (s, C_β).

***trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)Cl$ 5.** To a solution of $Pd(Ph_2Ppy)_3$ (0.4 g, 0.45 mmol) and phenylacetylene (0.1 ml, 0.90 mmol) in toluene (45 ml) was added a solution of triethylammonium chloride (0.06 g, 0.45 mmol) in methanol (8 ml) over 5 min. An immediate change from yellow to red occurred on addition of the Et_3NHCl. After stirring (3 h) the solvent was evaporated to afford a yellow solid. Yield = 0.22 g (64%). Calc. for $C_{42}H_{35}ClN_2P_2Pd$: C, 65.4; H, 4.6; N, 3.6. Found: C, 64.9; H, 4.6; N, 3.3%. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 16.5. ^1H NMR ($CDCl_3$): δ 8.57 (d, 2 H, py), 7.84 (d, 2 H, py), 7.63 (br, 8 H, Ph), 7.45 (t, 2 H, py), 7.2–6.9 (m, 10 H, Ph), 6.73 (m, 2 H, *Ph*CCH_2), 6.68 (m, 3 H, *Ph*CCH_2), 5.06 (t, $^4J_{H,P}$ = 6.1 Hz, *trans-H*C=CPh) and 4.72 (s, *cis-H*C=CPh); (C_6D_6) 5.59 (t, $^4J_{H,P}$ = 5.9 Hz, *trans-H*C=CPh) and 5.32 (s, *cis-H*C=CPh). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 159.9 (s, C_α) and 116.5 (s, C_β).

$[Ph_2pyP\{(CH_3)C{=}CH_2\}][CF_3CO_2]$. To a cooled solution of $Pd(Ph_2Ppy)_3$ (0.33 g, 0.37 mmol) in THF (30 ml) was added slowly CF_3CO_2H (0.25 ml, 0.33 mmol). Propyne (≈1 g) was then bubbled through the solution. The resultant red solution was allowed to warm slowly to room temperature and stirred for five hours. The solvent was removed *in vacuo* to afford an oily residue that was triturated with Et_2O to give a yellow solid. Yield = 0.10 g (72%). Calc. for $C_{22}H_{19}F_3NO_2P$: C, 63.3; H, 4.6; N, 3.4. Found: C, 63.2; H, 4.7; N, 3.3%. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 15.2. ^1H NMR ($CDCl_3$): δ 8.93 (d, 1 H, py), 8.13 (m, 1 H, py), 7.88 (t, 1 H, py), 7.8–7.6 (m, 11 H), 6.59 (d, $^3J_{H,P}$ = 47.7, $CH_3C{=}CH_2$), 5.84 (d, $^3J_{H,P}$ = 22.5, $CH_3C{=}CH_2$) and 2.12 (d, $^3J_{H,P}$ = 13.9 Hz, $CH_3C{=}CH_2$). Attempts to isolate a σ-vinyl palladium(II) species from the oxidative addition of $Cl(CH_3)C{=}CH_2$ to either complex **1** or **2** failed.

$[Ph_2pyP\{(CH_3)C{=}CH_2\}][CF_3SO_3]$. To a solution of Ph_2Ppy (1.03 g, 3.91 mmol) in Et_2O (60 ml) was added vinyl triflate (0.70 g, 3.66 mmol) and $Pd(Ph_2Ppy)_2(dba)$ (0.33 g, 0.37 mmol). The resultant red solution was stirred overnight. The precipitated white solid was collected and recrystallised from THF–light petroleum. Yield = 1.16 g (70%). Calc. for $C_{21}H_{19}F_3NO_3PS$: C, 52.0; H, 4.0; N, 2.9. Found: C, 51.8; H, 4.1; N, 2.9%. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 17.1. ^1H NMR ($CDCl_3$): δ 6.65 (dd, $^3J_{H,P}$ = 47.7, $^2J_{H,H}$ = 1.2, $CH_3C{=}CH_2$), 5.89 (d, $^3J_{H,P}$ = 22.5, $CH_3C{=}CH_2$) and 2.17 (d, $^3J_{H,P}$ = 13.9 Hz, $CH_3C{=}CH_2$). This reaction can also be performed catalytically with complex **1** (10%) to give 70% yield.

***trans*-$Pd(Ph_2Ppy)_2\{CO(CH_3)C{=}CH_2\}Cl$ 6.** The complex $Pd(Ph_2Ppy)_3$ (0.20 g, 0.22 mmol) was dissolved in toluene (25 ml) and a solution of methacryloyl chloride (30 μl, 0.4 mmol) in toluene (2 ml) added *via* syringe. The flask was sealed and the yellow solution left to stir overnight with heating at 75 °C. The precipitation of a white solid that occurred during the reaction was completed by addition of light petroleum (25 ml). Recrystallisation from CH_2Cl_2–toluene–light petroleum gave 110 mg (67%) of **6** as yellow microcrystals. No microanalysis was possible as the complex decomposed prior to combustion. IR (KBr disks, cm^{-1}): ν(CO) 1643.5m, 1200.0s, $\nu(Ph_2Ppy)$ 1435.1, 693.4, 521.2. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 19.2. ^1H NMR ($CDCl_3$): δ 6.79 (br, $C{=}CH_2$), 6.44 (t, $^5J_{H,P}$ = 5.5 Hz, $H_2C{=}C$) and 1.93 (s, $C{=}CCH_3$). It is noteworthy that no acyl complexes could be isolated from CO insertion reactions into the Pd–vinyl bond; only decomposition to unidentified species was observed when such reactions were attempted.

Table 3 Crystal data for $Pd(Ph_2Ppy)_2(\eta^2\text{-DMAD})$ **3** and *trans*-$Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$ **4**

	3	**4**
Empirical formula	$C_{40}H_{34}N_2O_4P_2Pd$	$C_{44}H_{35}F_3N_2O_2P_2Pd$
Formula weight	777.05	849.08
T/K	150(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	12.8446(6)	11.837(2)
b/Å	14.596(4)	13.342(7)
c/Å	18.6187(14)	13.729(3)
α/°		95.32(7)
β/°	97.777(13)	103.28(2)
γ/°		110.28(3)
V/Å^3	3458.5(11)	1943.8(12)
Z	4	2
μ/mm^{-1}	0.674	0.614
Reflections collected	12630	7136
Independent reflections	5163	5014
R_{int}	0.0906	0.0827
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0413, 0.0814	0.0397, 0.0587
(all data)	0.0726, 0.1071	0.0740, 0.1120

[$Pd(Ph_2Ppy)_2\{\eta^3\text{-}C_3H_4C(Ph){=}CH_2\}$][$CF_3CO_2$] 7. The complex $Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$ (0.2 g, 0.24 mmol) was dissolved in toluene (30 ml) and propadiene (0.5 g, 12.5 mmol) passed through the solution. After 18 h the solvent was evaporated and the red solid washed with hexane. Yield = 0.17 g (68%). Calc. for $C_{47}H_{38}F_3N_2O_2P_2Pd$: C, 63.5; H, 4.3; N, 3.2. Found: C, 63.6; H, 4.3; N, 3.3%. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 22.8. ^1H NMR ($CDCl_3$): δ 5.39 (br s, 1 H, C=CH_2), 5.32 (br s, 1 H, C=CH_2), 3.83 (br s, 2 H, allyl H_{syn}) and 3.45 (br s, 2 H, allyl H_{anti}).

Methoxycarbonylation of phenylacetylene

The complex $Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$ (30 mg, 0.03 mmol), methanol (12 µl, 0.3 mmol) and phenylacetylene (20 µl, 0.2 mmol) were combined in C_6D_6 (2 ml) and 30 psi of CO pressure applied. The solution was stirred for one day and ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra recorded. Light petroleum was added for precipitation of solid products and a sample from the supernatant solution was analysed by GC-MS (m/z 162, methyl 2-phenylpropenoate) and NMR; the ^1H and ^{13}C spectra were in agreement with those reported.[27]

Crystallography

Single crystals of complexes **3** and **4** suitable for X-ray diffraction analysis were mounted on glass fibres and data were recorded on a Delft Instruments FAST TV area detector at the window of a rotating anode generator with a molybdenum target [λ(Mo-Kα) = 0.71069 Å], driven by MADNES[28] software using a procedure previously described.[29] Data reduction was performed using the program ABSMAD.[30]

The structures were solved by heavy atom methods (SHELXS)[31] and then subjected to full-matrix least squares refinement based on F_o^2 (SHELXL 93).[32] Non-hydrogen atoms were refined anisotropically with all hydrogens fixed in idealised positions and isotropic thermal parameters tied to the value of the parent atom. The nitrogen atoms in the pyridyl rings were distinguished from the carbons by inspection of peak heights in the difference map, bond lengths and consideration of thermal ellipsoids. Data were corrected for absorption effects using the program DIFABS.[33] Diagrams were drawn with SNOOPI.[34] The crystal data are summarised in Table 3.

CCDC reference number 186/1776.

See http://www.rsc.org/suppdata/dt/a9/a908050c/ for crystallographic files in .cif format.

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