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Palladium diphenyl-2-pyridylphosphine complexes

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Received 2nd July 1998, Accepted 30th September 1998

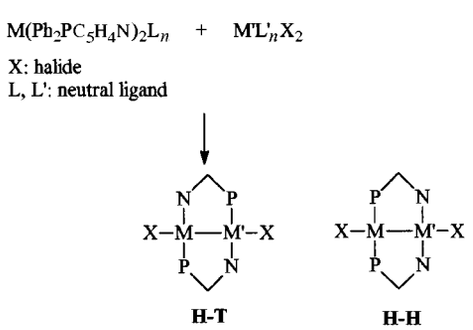
The stoichiometric reaction of diphenyl-2-pyridylphosphine ($Ph_2PC_5H_4N$-2) and palladium(II) acetate afforded the palladium(I) dimer $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(OAc)_2]$ **1**. Attempts to isolate the monomer, $[Pd(\mu\text{-}Ph_2PC_5H_4N)_2(OAc)_2]$, from 2:1 stoichiometry reactions ($Ph_2PC_5H_4N$:Pd), resulted only in the isolation of **1**. When >3 mole equivalents of $Ph_2PC_5H_4N$ were used the zerovalent palladium complex $[Pd(Ph_2PC_5H_4N)_3]$ was isolated. Other palladium(I) dimers with carboxylic or sulfonic anionic ligands have been prepared by a metathesis reaction of the co-ordinated acetates. The complexes **1** and $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$ **2** have been structurally characterised as head-to-tail dimers. The mononuclear complex $[Pd(Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$ has been obtained by reaction of $Ph_2C_5H_4N$ with $[Pd(CH_3CN)_2(O_2CCF_3)_2]$. Complex **1** reacts with dimethyl acetylenedicarboxylate to give $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(OAc)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)]$, while attempts to isolate an A-frame carbonyl complex were unsuccessful.

Introduction

Both in terms of their high activity and superior selectivity attained under mild conditions, complexes generated *in situ* from mixtures of palladium acetate, diphenyl-2-pyridylphosphine ($Ph_2PC_5H_4N$-2) and sulfonic acids are highly efficient catalysts for the methoxycarbonylation of propyne to methyl methacrylate (MMA).[1] With this in mind we have undertaken a study on the co-ordination and reaction chemistry of this catalyst system. Broadly speaking two catalytic mechanisms may be in operation, namely the hydride and the methoxycarbonyl cycles. Drent *et al.*[2] have presented a compelling argument for the operation of the latter based on selectivity improvements obtained on increasing the steric bulk of the phosphine ligand. More recently others have provided evidence for the existence of the hydride cycle.[3]

Palladium complexes of arylphosphines show enhanced catalytic performance in carbonylation reactions when the well established triphenylphosphine ligand is replaced by $Ph_2PC_5H_4N$-2.[1] Optimum rates and selectivities are realised when a protic acid co-catalyst whose conjugate base is weakly co-ordinating, *e.g.* trifluoromethanesulfonic acid, is present.[4] However, much of the co-ordination chemistry of $Ph_2PC_5H_4N$ dimers has been established with halides as terminal donors and the possible non-innocent involvement of the secondary ligands has been largely ignored. The disposition of nitrogen and phosphorus donors in ($Ph_2PC_5H_4N$) render it an excellent bridging ligand for late-transition metals, such that a host of homo- and hetero-binuclear dimers have been reported.[5] The usual synthetic approach to the dimers is through the coupling of two preformed mononuclear complexes (Scheme 1). A change in the formal oxidation state of the metals is implicit in such a reaction. The resulting dimers exist in two geometric forms: the more stable head-to-tail (H-T) isomer has the two like donors bound to different metals, whereas the head to head (H-H) isomer has the nitrogen and phosphorus donors at the same metal (Scheme 1). Several examples of the less stable H-H isomers have been isolated.[5a,f,6]

Prompted by the above observations, we report here aspects of the co-ordination chemistry of $Ph_2PC_5H_4N$ with palladium in the presence of oxygen-bearing secondary ligands, including acetate. Unlike the known systems with halides, the oxyligands promote the formation of palladium(I) dimers from solely palladium(II) precursors.



Scheme 1

Results and discussion

Palladium(I) dimers

Phosphorus NMR data for the compounds discussed below are collected in Table 1. The dimer $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(OAc)_2]$ **1** is obtained in high yield from the reaction of palladium(II) acetate and $Ph_2PC_5H_4N$ in a 1:1 molar ratio. This contrasts with analogous compounds containing halides as terminal donors; dimers are only obtained when two preformed mononuclear species are combined (Scheme 1). In the present case, the redox chemistry is not solely metal-based, rather two acetate groups undergo a reductive elimination to generate a palladium(0) species which reacts with a palladium(II) complex to give the palladium(I) dimer and the elimination product, diacetyl peroxide (Scheme 2).

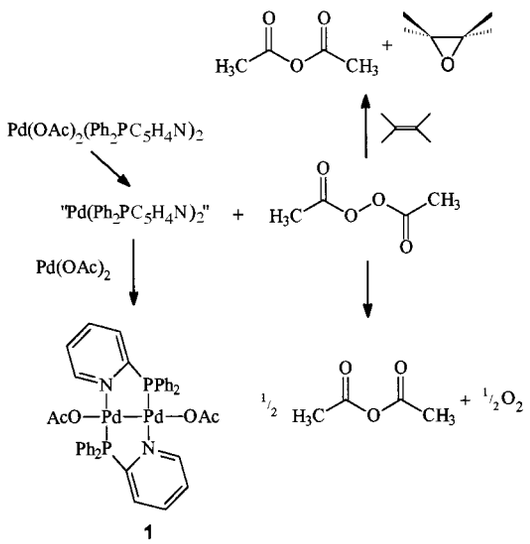
The inability to synthesize $Pd(Ph_2PC_5H_4N)_2X_2$ ($X = CH_3CO_2^-$, $CF_3CO_2^-$, $CH_3SO_3^-$, $p\text{-}H_3CC_6H_4SO_3^-$ or $CF_3SO_3^-$) compounds by simple mixing (see below) is indicative of their inherent instability toward reductive elimination. It is well established that triphenylphosphine can reduce palladium(II) to palladium(0) when oxygen-bearing anions are present,[7] *e.g.* $[Pd(PPh_3)_2(OAc)_2]$ is reduced spontaneously (but slowly) to a palladium(0) species with concomitant production of phosphine oxide.[8]

When a 1:1 mixture of $Pd(OAc)_2$ and $Ph_2PC_5H_4N$ is monitored by ^{31}P NMR spectroscopy the initial spectrum reveals a number of signals between δ 10 and 20. Complex **1** (δ 4.5) is present as a minor product 20 min after mixing, with a species giving a signal at δ 9.4 predominating. The peak at δ 9.4 is

Table 1 The ^{31}P NMR data for the $Ph_2PC_5H_4N$ complexes

Compound	^{31}P-{^1H} (δ)[a]
1 $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(OAc)_2]$	+4.5
2 $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$	+0.1
3 $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_3SCH_3)_2]$	−3.3
4 $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_3SCF_3)_2]$	−2.4
5 $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_3SC_6H_4CH_3\text{-}p)_2]$	−3.1
6 $[Pd(Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$	+14.8
7 $[Pd(Ph_2PC_5H_4N)_2(C{\equiv}CPh)_2]$	+23.7
8 $[Pd(Ph_2PC_5H_4N)_2(C{\equiv}CMe)_2]$	+23.4
9 $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(OAc)_2(\mu\text{-DMAD})]$	+31.6
10 $[Pd(Ph_2PC_5H_4N)_3]$[b]	+21.7
$Ph_2PC_5H_4N$	−6.7

[a] In $CDCl_3$, unless otherwise mentioned. [b] In d^6-benzene.



Scheme 2

assigned to $[Pd(Ph_2PC_5H_4N)_2(OAc)_2]$ which could not be isolated; the remaining peaks are presumably due to other intermediates. As the reaction proceeds the signals due to $[Pd(Ph_2PC_5H_4N)_2(OAc)_2]$ and other intermediates decay while that for **1** grows until it is the major component after 24 h following which **1** can be isolated in good yield (*ca.* 80%). Our failure to isolate the bis(acetate) complex is due to the spontaneous elimination of both acetates to form a zerovalent complex of lower co-ordination number (akin to the PPh_3 analogue); evidence for the formation of the unstable diacyl peroxide species (Scheme 2) appears to account for the fate of the acetate groups (see below). The unassigned signals are likely to arise from different isomers of this palladium(0) intermediate where diphenyl-2-pyridylphosphine may act as a chelating, bridging or mono co-ordinated ligand and which then reacts with $Pd(OAc)_2$ or $[Pd(Ph_2PC_5H_4N)_2(OAc)_2]$ to form the dimer **1**. The unstable diacyl peroxide species is likely to decompose to acetic anhydride and oxygen as indicated in the ^{13}C-{^1H} NMR spectrum of the mixture after the reaction is complete; signals at δ 21.13 and 165.40 being assigned to acetic anhydride. Acetic anhydride is also observed in the ^1H NMR spectrum of this mixture along with a trace of acetic acid, presumably arising from trace hydrolysis due to adventitious water; these resonances account for approximately half of the total acetate CH_3 resonance intensities. Their identity is confirmed by further addition of an acetic anhydride–acetic acid mixture to the NMR sample. Loss of oxygen from the elimination by-product was further established by the addition of 2,3-dimethylbut-2-ene to the reaction mixture. Formation of the corresponding epoxide was observed by GCMS analysis.

When iodomethane was added to a 1:2 mixture of $Pd(OAc)_2$ and $Ph_2PC_5H_4N$, monomeric $[Pd(Ph_2PC_5H_4N)_2I_2$ and dimeric $[Pd_2(Ph_2PC_5H_4N)_2I_2]$ were obtained. The methyl iodo complex, $[Pd(Ph_2PC_5H_4N)_2(CH_3)I]$, which might be expected from oxidative addition to a palladium(0) intermediate, was not observed. The mononuclear diodo complex could arise from successive additions of MeI to a palladium intermediate with the liberation of ethane. It is noteworthy that Amatore *et al.*[8] reported the formation of the oxidative addition product $[Pd(PPh_3)_2(Ph)I]$ from the reaction of $[Pd(PPh_3)_2]$ with iodobenzene.

The ^{31}P NMR spectrum of a 1:2 $Pd(OAc)_2$–$Ph_2PC_5H_4N$ mixture is substantially different from that of the 1:1 mixture. A very broad signal appears at δ 26.2 (in CH_2Cl_2) with a second at δ 16.2 but neither could be assigned. At the end of the reaction several phosphorus containing species were observed, but only the dimer **1** was isolated upon crystallisation. Ratios of pyridyl phosphine to $Pd(OAc)_2$ greater than 3:1 afford the zerovalent complex $[Pd(Ph_2PC_5H_4N)_3]$ which has been isolated and characterised as detailed in the Experimental section.

In contrast to previous observations with triphenylphosphine,[9] formation of $Ph_2PC_5H_4N$ oxide is not taking place in the stoichiometric mixture of $Ph_2PC_5H_4N$–$Pd(OAc)_2$, as evidenced by the absence of a resonance at δ 20 in the final spectrum of the reaction mixture. The possible formation of the *N*-oxide is also excluded as all the phosphine ligand in the 1:1 mixture is utilised to form the palladium complex **1**. The operation of an alternative reaction pathway for $Ph_2PC_5H_4N$ with respect to PPh_3 is likely to be a result of the second available (pyridine) donor in $Ph_2PC_5H_4N$. Thus, stable dimeric complexes such as **1** form readily when the palladium(0) intermediate species is generated *in situ* in the presence of unchanged $Pd(OAc)_2$; the bridging configuration of the phosphine in the palladium(I) dimeric product would no doubt render the ligand less labile and hence less available for subsequent oxidation than in related PPh_3 systems. In the case of PPh_3 such an intermediate is likely to decompose in the absence of any other substrate along with (in the presence of an appropriate oxygen donor) formation of the phosphine oxide. The detection of acetic anhydride in the final solution suggests an electron transfer directly from the acetate to the metal centre without $Ph_2PC_5H_4N$ involvement and is probably best described as a reductive elimination in the classical sense.

The dimers **2**–**5** are conveniently prepared by the addition of one mol equivalent of the protic acid of the appropriate oxyanion to the 1:1 mixture of $Pd(OAc)_2$ and $Ph_2PC_5H_4N$. Anion exchange proceeds readily as the sulfonic and trifluoroacetic acids employed herein are appreciably stronger protic acids than is acetic.

X-Ray quality crystals of $[Pd_2(Ph_2PC_5H_4N)_2(OAc)_2]\cdot CH_2Cl_2$ **1** and $[Pd_2(Ph_2PC_5H_4N)_2(O_2CCF_3)_2]\cdot 0.5CH_2Cl_2$ **2** were obtained by slow diffusion of light petroleum into solutions of the appropriate complex in dichloromethane. There are two independent molecules of **2** in the asymmetric unit which, although crystallographically distinct, are structurally similar. The molecular structures of **1** and one of the independent molecules of **2** with the adopted numbering scheme are shown in Figs. 1 and 2. Selected bond lengths and angles are summarised in Table 2.

Although several structures of complexes with bridging $Ph_2C_5H_4N$ ligands have been reported,[5a,f,6b,10] the structures of **1** and **2** are the first to contain an unsupported palladium–oxygen bond. The Pd–Pd bond lengths of 2.579(1) and 2.561(1) Å, respectively, are the shortest reported for the palladium(I)–$Ph_2PC_5H_4N$ dimeric series {*cf.* 2.597 Å for $[Pd_2(Ph_2PC_5H_4N)_2I_2]$ and 2.594 Å for $[Pd_2(Ph_2PC_5H_4N)_2Cl_2]$[5a,11]} reflecting the weaker interaction of oxygen donors with the metal. In both **1** and **2** the two Pd–O bond lengths are quite distinct being 2.189(3), 2.139(4) and 2.183(6), 2.307(8) Å, respectively. There appears to be a correlation between the Pd–O bond length and the accompanying P–Pd–O bond angle: the longer terminal Pd–O bonds in both complexes are associated with the tighter P–Pd–O angle (Table 2) and it would appear that the steric bulk

Table 2 Selected bond lengths (Å) and angles (°) for $[Pd_2(Ph_2PC_5H_4N)_2(OAc)_2]$ **1** and $[Pd_2(Ph_2PC_5C_4N)_2(O_2CCF_3)_2]$ **2**

1

Pd(1)–N(2)	2.117(5)	Pd(2)–O(3)	2.139(4)
Pd(1)–P(1)	2.197(2)	Pd(2)–N(1)	2.114(4)
Pd(1)–Pd(2)	2.5795(7)	Pd(2)–P(2)	2.201(2)
Pd(1)–O(1)	2.189(3)		
N(2)–Pd(1)–P(1)	174.2(1)	N(2)–Pd(1)–O(1)	92.1(2)
P(2)–Pd(2)–Pd(1)	80.7(2)	P(2)–Pd(2)–O(3)	98.0(1)
N(2)–Pd(1)–Pd(2)	93.7(1)	P(1)–Pd(1)–Pd(2)	80.61(4)
O(3)–Pd(2)–Pd(1)	170.3(1)	N(1)–Pd(2)–O(3)	86.9(2)
N(1)–Pd(2)–P(2)	173.9(1)	O(1)–Pd(1)–P(1)	93.5(1)
N(2)–Pd(1)–Pd(2)	93.7(1)	O(1)–Pd(1)–Pd(2)	173.0(1)

2

Pd(1)–N(2)	2.110(7)	P(1)–C(5)	1.817(8)
Pd(1)–P(1)	2.197(3)	Pd(1)–O(3)	2.307(8)
Pd(1)–Pd(2)	2.561(1)	Pd(2)–N(1)	2.114(7)
Pd(2)–O(1)	2.183(6)	Pd(2)–P(2)	2.216(2)
N(2)–Pd(1)–P(1)	174.7(2)	P(2)–Pd(2)–Pd(1)	80.62(8)
N(2)–Pd(1)–O(3)	92.2(3)	P(1)–Pd(1)–O(3)	92.9(2)
N(2)–Pd(1)–Pd(2)	93.6(2)	P(1)–Pd(1)–Pd(2)	81.11(9)
O(3)–Pd(1)–Pd(2)	168.4(2)	N(1)–Pd(2)–O(1)	87.9(2)
N(1)–Pd(2)–P(2)	173.6(2)	O(1)–Pd(2)–P(2)	97.6(2)
N(1)–Pd(2)–Pd(1)	94.4(2)	O(1)–Pd(2)–Pd(1)	171.9(2)

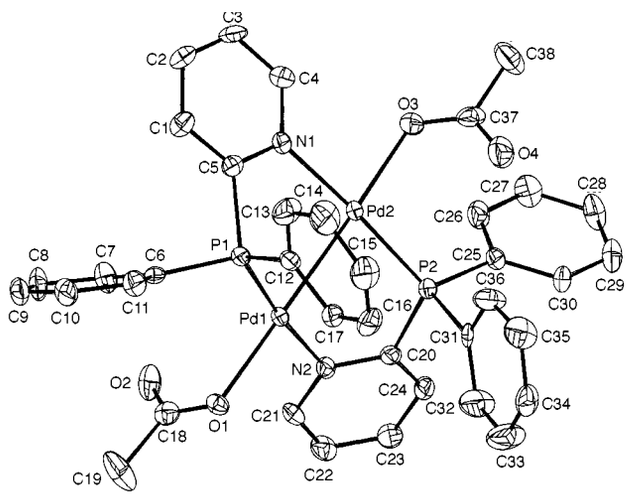


Fig. 1 Molecular structure and atom labelling scheme of $[Pd_2(Ph_2PC_5H_4N)_2(OAc)_2]$. Hydrogen atoms are omitted for clarity.

of the two phenyl substituents on the phosphorus atoms causes a lengthening of the Pd–O bond as the P–Pd–O angle contracts. The Pd–O distances of 2.18 ± 1 Å in **1** and **2** compare well with those observed in $[Pd_2(dppm)_2(O_2CCF_3)_2]$.[12] The mean of the Pd–O lengths is considerably shorter for the acetate ligand reflecting its better donor ability with respect to the more weakly co-ordinating trifluoro analogue. However, due to the *trans* influence of the metal–metal bond[13] and the larger radius of Pd^{I}, both are longer than equivalent Pd–O bonds in mononuclear palladium(II) compounds.

The Pd–P (**1**, average 2.199; **2**, 2.207 and 2.209 Å for the second independent molecule) and Pd–N (**1**, average 2.116; **2**, 2.112 and 2.128 Å for the second independent molecule) distances are similar to those for the iodo- (Pd–P, average 2.212 and Pd–N, 2.112 Å) and chloro- (Pd–P, average 2.205 and Pd–N, 2.114 Å) analogues. The Pd–P distances are shorter than those found in complexes of bridging diphosphines and this is attributed to the relative *trans* influences of the P and N atoms. The Pd–Pd–O angles deviate from linearity by 9.66/7.1° for **1** and 11.6/8.1° for **2** and are *transoid* with respect to the M–M axis in both complexes as opposed to the dimers $[Pd_2(dppm)_2(O_2CCF_3)_2]$ and $[Pd_2(Ph_2PC_5H_4N)_2I_2]$ where the terminal

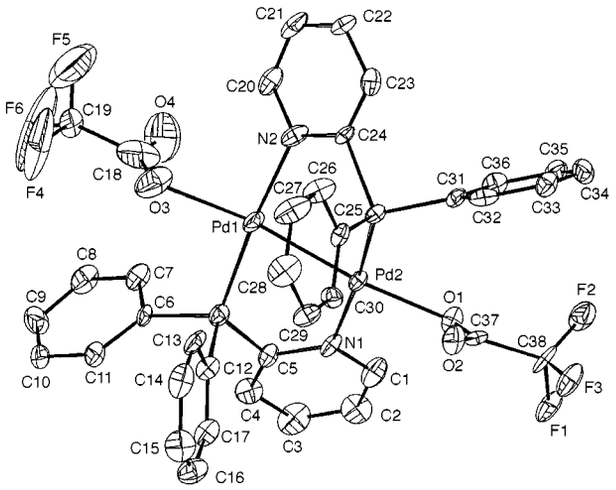


Fig. 2 Molecular structure and atom labelling scheme of $[Pd_2(Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$. Hydrogen atoms are omitted for clarity.

ligands are *cisoid*.[5a,12] The palladium centres have planar co-ordination geometries with the angles between the palladium–ligand bonds varying from 80.6(4) to 98.0(1)° in both complexes. Unlike $[Pd_2(Ph_2PC_5H_4N)_2I_2]$, the two halves of the dimer are quite distinct with respect to their L–Pd–L′ bond angles. The Pd–N–C–P–Pd five-membered rings are non-planar, and the eight–membered framework adopts a twisted boat conformation.

The phosphorus atoms in the binuclear complexes **1**–**5** are equivalent giving a sharp singlet in their ^{31}P-$\{^1H\}$ NMR spectra. It is reasonable to assign the solution species as H-T isomers in accord with the solid-state structures presented above and the established thermodynamic stability of such a geometry. Palladium dimers of $Ph_2PC_5H_4N$ preferentially adopt a H-T arrangement as the labile nature of the Pd–P bond allows this thermodynamically more stable isomer to predominate. Variable temperature ^{31}P-$\{^1H\}$ NMR studies show no evidence of fluxionality of the $Ph_2PC_5H_4N$ ligand, precluding the possibility of H-T ↔ H-H isomerisation. The ^{31}P-$\{^1H\}$ NMR data show that there is a tend in $\delta(^{31}P)$ as a function of the anionic ligand, with the dimers **2**–**5** containing the less basic trifluoroacetate and especially sulfonate groups showing ^{31}P shifts to high field of those of the parental acetate dimer.

The ^1H NMR spectra of the complexes closely resemble that of uncomplexed $Ph_2PC_5H_4N$. At least three of the pyridyl protons give discrete signals, whereas two unresolved multiplets appear for the phenyl groups. The only significant co-ordination shift is for the proton *ortho* to the phosphorus centre, H(6), which resonates between 0.4 and 0.7 ppm upfield of its position in the spectrum of free $Ph_2PC_5H_4N$.

Changes in the electronic framework of the aromatic rings on co-ordination are inferred from the ^{13}C NMR spectra, where low-field shifts of up to 5 ppm are observed for all carbons in the pyridine ring with respect to those of $Ph_2PC_5H_4N$. The phenyl carbons are largely unaltered except for the *ipso*-carbons, C(1), which shift 8 ppm upfield upon co-ordination.

In the solid state IR spectrum of complex **1** the acetates have ν(C=O) and ν(C–O) at 1581 and 1366 cm^{-1}, respectively; these frequencies suggest that inferred structural information should be treated with caution in these systems since the former is lower than that reported for monodentate palladium acetates and compares to anticipated values for bridging or anionic acetates, whereas the latter is within the range expected for monodentate co-ordination.[14] The symmetric carbonyl stretch is assigned at 1681 cm^{-1} for **2**, again within the expected range (1680–1720 cm^{-1}) for monodentate binding.[12] For the complexes **3**–**5** broad, strong $\nu(SO_3)$ stretches are seen between 1260

and 1006 cm^{-1} which are split implying bound (monodentate) sulfonates.[15]

Palladium(II) complexes

The only complex of the type $[PdX_2(Ph_2PC_5H_4N)_2]$, where X is an oxyanion, isolated during the present study was *cis*-$[Pd(Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$ **6**. Although as already detailed for the parent acetate system, such species are believed to be present during the early stages of reaction, they are unstable with respect to reductive elimination and give palladium(I) dimers as the only isolable compounds. The bis(ligand)bis(trifluoroacetate) complex was synthesized by the reaction of $[Pd(CH_3CN)_2(O_2CCF_3)_2]$ with 2 moles of $Ph_2PC_5H_4N$. Both *cis* and *trans* isomers of $[Pd(Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$ are possible, although the formation of only one is indicated by ^{31}P NMR spectroscopy where a single phosphorus resonance is observed (δ 14.8). Inspection of the ^{13}C NMR spectrum confirms the geometry as *cis*, where pertinent ligand resonances occur as doublets showing coupling to only one phosphorus atom. It is known that $^3J_{CP}$ is usually of equivalent magnitude to $^1J_{CP}$ in *trans* isomers giving virtual triplets for carbons directly bound to phosphorus:[16] this is clearly not the case here, and the isolated complex is assigned a *cis*-$[Pd(Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$ stereochemistry.

Only palladium(I) dimers were isolated when the same procedure was applied for the attempted preparation of $[Pd(Ph_2PC_5H_4N)_2X_2]$ (where $X = CH_3SO_3^-$, $CF_3SO_3^-$ or p-$H_3CC_6H_4SO_3^-$). Efforts to procure palladium(II) complexes from other starting materials were also unsuccessful: the reaction of $[Pd(Ph_2PC_5H_4N)_2Cl_2]$ with two equivalents of CF_3SO_3Ag afforded only the dimer **4**, re-emphasising the inherent stability of these dimers.

The alkynyl complexes $[Pd(Ph_2PC_5H_4N)_2(C{\equiv}CPh)_2]$ **7** and $[Pd(Ph_2PC_5H_4N)_2(C{\equiv}CMe)_2]$ **8** were obtained from the reaction of palladium acetate with diphenyl-2-pyridylphosphine and a ten-fold excess of the appropriate acetylene. Both white solids reveal an infrared band of medium intensity characteristic of ν(C≡C) stretches (2105 cm^{-1} for **7** and 2110 cm^{-1} for **8**). Alkynylpalladium(II) complexes can be obtained by oxidative addition of alkynyl halides to palladium(0) complexes or *via* metathesis reactions of halogenopalladium(II) complexes with Li(C≡CR).[17] It has been reported recently that alkynylpalladium(II) complexes can be prepared by the direct reaction of a palladium(II) complex with a terminal alkyne.[18]

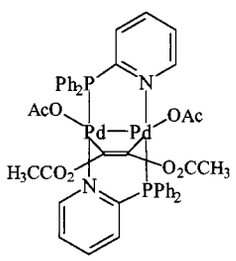
When complex **10** is dissolved in acetonitrile $Ph_2PC_5H_4N$ remains chelated to the palladium centre without a solvent molecule replacing the co-ordinated pyridyl nitrogen. Additionally, variable temperature ^{31}P-{^1H} NMR spectroscopy ($CDCl_3$, ≤60 °C) showed a lack of exchange between the mono co-ordinated and chelated ligand. These results suggest formation of a kinetically rigid four-membered chelate.

Balch and co-workers[19] have shown that $[Pd_2(Ph_2PC_5H_4N)_2Cl_2]$ reacts with CO to give an unbridged Pd–Pd complex with terminal carbonyl ligands, as indicated by the presence of new bands at 2019 and 1994 cm^{-1} in the solution infrared spectrum. Attempts to isolate the carbonyl complex resulted only in the recovery of $[Pd_2(Ph_2PC_5H_4N)_2Cl_2]$.

Exposure of a $CDCl_3$ solution of complex **1** to 1 atm of carbon monoxide causes no change in the ^1H or ^{31}P-{^1H} NMR spectra, although new infrared bands appear in solution. A very strong sharp absorbance arises at 2253 cm^{-1} and although not assigned is very close to the value of 2248 cm^{-1} reported for $[Pd(CO)_4]^{2+}$,[20] while others at 1820.9, 1793.4 and 1712.9 cm^{-1} may indicate the presence of bridging carbonyls. The solid that precipitates from solution was isolated and its IR spectrum recorded as a KBr disc. A medium intensity band at 1873 cm^{-1} was observed while the rest of the spectrum remains unchanged. The available data show an interaction of **1** with carbon monoxide in solution although the nature of the species is not clear since the NMR and IR spectra of the adduct are otherwise very similar to those of **1**.

Despite the reluctance of the dimers to insert carbon monoxide into the Pd–Pd bond, $[Pd_2(Ph_2PC_5H_4N)_2(OAc)_2]$ **1** reacts readily with DMAD ($MeO_2C{\equiv}CO_2Me$) to give the expected dimetallated alkene product **9**, in accord with the previously reported chloride analogue. Other unactivated alkynes such as butyne and terminal alkynes did not afford the corresponding insertion products.

The two phenyl rings attached to each phosphorus atom in the co-ordinated $Ph_2PC_5H_4N$ ligands are no longer equivalent in complex **9**. Consequently, two sets of resonances appear in the ^1H and ^{13}C-{^1H} NMR spectra, one for the phenyl ring facing the acetate group and one for the ring facing the alkene group. In the IR spectrum a strong doublet appears due to the carbonyl groups of DMAD at 1726.4 and 1697.5 cm^{-1} [ν(C=O)]. An absorption due to the C=C bond could not be assigned.



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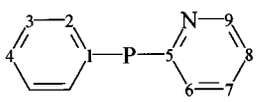
Conclusion

Equimolar solutions of palladium(II) acetate and $Ph_2PC_5H_4N$ are unstable with respect to reductive elimination to give initially palladium(0) species which appear to conproportionate with Pd^{II} to give ultimately palladium(I) dimers. No external reductant is required for this reaction which occurs more readily than with Ph_3P in place of $Ph_2PC_5H_4N$ or than for palladium halides. These observations may be relevant to the alkoxycarbonylation of alkynes where palladium diphenyl-2-pyridylphosphine complexes with oxyanions are known to be far more effective catalysts than triphenylphosphine analoges or than with palladium halides.

Experimental

Reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, solid complexes being stored in a desiccator under air. All solvents were refluxed under nitrogen over sodium–benzophenone and were distilled immediately prior to use with the exception of dichloromethane which was dried over CaH_2 and toluene which was refluxed over sodium. Light petroleum had boiling point 40–60°. The ^{31}P-{^1H} NMR spectra (referenced to 85% H_3PO_4) were collected on a JEOL FX90Q spectrometer operating at 36.2 MHz, ^1H (400.13) and ^{13}C-{^1H} (100 MHz) spectra on a Bruker DPX400 unless stated otherwise and referenced to $SiMe_4$. The NMR assignments are with respect to the labelling scheme shown below. Infrared spectra were recorded as KBr discs on a Nicolet 510 FT-IR spectrophotometer. The compounds $[PdCl_2(PhCN)_2]$, $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone)[21] and $[PdCl_2(Ph_2PC_5H_4N)_2]$[5a,c] were prepared by literature procedures. The $[Pd(CH_3CN)_nX_2]$ (X = O_2CCF_3, O_3SCH_3, O_3SCF_3, or $O_3SC_6H_4CH_3$-p) complexes were prepared by a procedure similar to that reported for $[Pd(CH_3CN)_4(O_3SCF_3)_2]$.[22]



Preparation

$Ph_2PC_5H_4N$. A modified literature procedure[23] was followed for the synthesis of $Ph_2PC_5H_4N$. Sodium metal (1.06 g, 46 mmol) was dissolved in liquid ammonia (100 ml) at −80 °C and triphenylphosphine (6.00 g, 23 mmol) added as a solid. The resultant mixture was stirred for 30 min. A diethyl ether solution of *tert*-butyl chloride (10 ml, 23 mmol) was then added to destroy the phenylsodium formed, followed by a diethyl ether solution (10 ml) of 2-bromopyridine (2.2 ml, 23 mmol). The temperature was allowed to rise slowly (8 h) to room temperature during which time the ammonia evaporated to leave a yellow solid. Saturated aqueous ammonium chloride was added to the solid, and the aqueous phase extracted with CH_2Cl_2 (3 × 50 ml). The organic extracts were combined and the solvent removed under reduced pressure. The product was obtained as white crystals after recrystallisation from hot light petroleum. Yield 5.0 g, 83%. (Found: C, 77.3; H, 5.4; N, 5.3. Calc. for $C_{17}H_{14}NP$: C, 77.56; H, 5.57; N, 5.32%). ^{1}H NMR ($CDCl_3$, δ): 7.30 (H^6, d), 7.76 (H^7, t), 7.36 (H^8, t) and 8.86 (H^9, d). ^{13}C NMR/DEPT ($CDCl_3$, δ): 136.2 (C^1, d, J 11.6), 134.2 (C^2, d, J 20.0), 128.7 (C^3, d, J 7.4), 129.1 (C^4, s), 164.0 (C^5, d, J 3), 135.8 (C^6, d, J 2.1), 127.9 (C^7, d, J 15.2), 122.2 (C^8, s), and 150.4 (C^9, d, J 13 Hz).

$[Pd_2(Ph_2PC_5H_4N)_2X_2]$ 1–5. A solution of $Ph_2PC_5H_4N$ (0.24 g, 0.9 mmol) in dichloromethane (10 ml) was added slowly to a suspension of palladium(II) acetate (0.2 g, 0.9 mmol) in dichloromethane (20 ml). For complexes **2**–**5**, one equivalent of the corresponding acid, HX, was subsequently added and the mixture stirred (3 h). The red solution was filtered through Celite and evaporated to dryness. The resultant red solid was washed with Et_2O (2 × 30 ml) and dried *in vacuo*. Red crystals were obtained by slow diffusion of light petroleum into a dichloromethane solution. Typical yields >80%. Infrared as KBr discs, and NMR data in $CDCl_3$.

$[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(OAc)_2]$ **1** (Found: C, 53.7; H, 4.4; N, 3.7. Calc. for $C_{38}H_{34}N_2O_4P_2Pd_2$: C, 53.23; H, 4.00; N, 3.27%): IR ν(C=O) 1581.0s, ν(C–O) 1365.6vs, 1318.7m cm^{-1}; ^{1}H NMR δ 6.90 (H^6, br s), 7.70 (H^7, t, 7.8 J Hz), 8.94 (H^9, br s) and 1.44 (OAc); ^{13}C NMR/DEPT δ 133.6 (C^2, t, J 5.6), 128.4 (C^3, t, J 4.9), 130.1 (C^4, s), 169.4 (C^5, dd, J 70.1/5.3), 137.6 (C^6, s), 129.4 (C^7, d, J 24.1), 125.6 (C^8, s), 152.4 (C^9, t, J 5.6 Hz), 23.4 (CH_3) and 176.1 (CO_2^-).

$[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$ **2** (Found: C, 47.2; H, 2.9; N, 3.0. Calc. for $C_{38}H_{28}F_6N_2O_4P_2Pd_2$: C, 47.28; H, 2.92; N, 3.08%): ν(C=O) 1681.2vs, ν(C–O) 1409.4m, ν(CF_3) 1193.7/1131.2 cm^{-1}; ^{1}H NMR δ 6.88 (H^6, br s), 7.76 (H^7, t, J 7.8 Hz) and 8.77 (H^9, br s); ^{13}C NMR/DEPT δ 128.5 (C^1, t, J 27.9), 133.5 (C^2, t, J 6.0), 129.0 (C^3, t, J 5.3), 130.9 (C^4, s), 167.7 (C^5, dd, J 70.9/6.6), 138.5 (C^6, s), 129.8 (C^7, d, J 4.9), 126.2 (C^8, s), 151.6 (C^9, t, J 6.0), 116.0 (CF_3, q, 292.5 Hz) and 160.3 (CO_2^-, q, J 35 Hz).

$[Pd_2(Ph_2PC_5H_4N)_2(O_3SCH_3)_2]$ **3** (Found: C, 46.4; H, 3.7; N, 3.0. Calc. for $C_{36}H_{34}N_2O_6P_2Pd_2S_2$: C, 46.52; H, 3.69; N, 3.01%): ν(SO_3) 1249.7vs, 1142.4s, 1097.6s, 1006.3vs ($Ph_2PC_5H_4N$), 535.55s cm^{-1}; ^{1} H NMR δ 6.70 (H^6, br s), 7.70 (H^7, t, J 7.8), 7.48 (H^8, t, J 7.8 Hz), 8.97 (H^9, br s), 2.06 (CH_3SO_3), 7.2–7.4 (Ph, m); ^{13}C NMR/DEPT δ 128.6 (C^1, dd, J 58.3/4.9), 134.3 (C^2, t), 129.6 (C^3, t), 131.4 (C^4, t), 167.9 (C^5, dd, J 79/6.3), 139.2 (C^6, s), 126.7 (C^8, s), 153.4 (C^9, t, J 6.3 Hz) and 39.1 (CH_3, s).

$[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_3SCF_3)_2]$ 4 (Found: C, 41.5; H, 3.5; N, 3.3. Calc. for $C_{36}H_{28}F_6N_2O_6P_2Pd_2S_2$: C, 41.68; H, 2.72; N, 2.70%): ν(SO_3) 1257.8vs, 1180s, 1032.0/1004.7s cm^{-1}; ^{1}H NMR δ 6.80 (H^6, br s), 7.80 (H^7, t, 7.8 Hz), 8.76 (H^9, br s), 7.30–7.75 (Ph, m).

$[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_3SC_6H_4CH_3\text{-}p)_2]$ **5** (Found: C, 52.4; H, 3.9; N, 2.5. Calc. for $C_{48}H_{42}N_2O_6P_2Pd_2S_2$: C, 53.29; H, 3.91; N, 2.59%): ν(SO_3) 1193.7, 1031.2/1009.0vs cm^{-1}; ^{1}H NMR δ 6.64 (H^6, br s), 7.69 (H^7, t, J 7.6 Hz), 8.92 (H^9, br s), 7.34 (Ph, m), 6.93 (tosyl, d, 8 Hz), 6.75 (tosyl, d, 8 Hz) and 2.22 (tosyl, s); ^{13}C NMR/DEPT δ 134.0 (C^2, t, J 5.8), 129.0 (C^3, t, J 5.8), 130.9 (C^4, s), 167.9 (C^5, d, J 71.9), 138.9 (C^6, s), 125.9 (C^8, s), 153.3 (C^9, t, J 5.8 Hz), 141.7/139.3/128.2/26.1 (tosylate).

***cis*-$[Pd_2(Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$ 6.** A solution of $Ph_2PC_5H_4N$ (0.25 g, 0.96 mmol) in acetonitrile (10 ml) was added slowly to a solution of $[Pd(CH_3CN)_2(O_2CCF_3)_2]$ (0.2 g, 0.48 mmol) in acetonitrile (20 ml) to give a pale yellow solution. After stirring for 2 h the solvent was evaporated and the resultant yellow oil stirred overnight with light petroleum to afford a yellow powder (Found: C, 53.1; H, 3.2; N, 3.1. Calc. for $C_{38}H_{28}F_6N_2O_4P_2Pd$: C, 53.13; H, 3.29; N, 3.26%). ^{1}H NMR ($CDCl_3$, δ): 7.29 (H^6, br), 7.78 (H^7, br), 7.69 (H^8, br) and 8.27 (H^9, br). ^{13}C NMR/DEPT ($CDCl_3$, δ): 125.2 (C^1, d, J 17.4 Hz), 134.2 (C^2, d, J 10.9), 128.8 (C^3, d, J 11.8), 132.1 (C^4, s), 156 (C^5, d), 149.5 (C^6, d, J 16.2), 130.8 (C^7, d, 20.7 J Hz), 124.8 (C^8, s), 137.8 (C^9), 116.1 (CF_3, q, J 292) and 160.3 (CO_2, q, J 36 Hz).

***cis*-$[Pd_2(Ph_2PC_5H_4N)_2(C{\equiv}CR)_2]$ (R = Ph 7 or Me 8).** To the red solution formed on addition of $Ph_2PC_5H_4N$ (0.48 g, 1.9 mmol) to a suspension of $Pd(OAc)_2$ (0.2 g, 0.9 mmol) in CH_2Cl_2 (40 ml) was added phenylacetylene (1 ml) or propyne (1 ml) as appropriate. The complexes $[Pd(Ph_2PC_5H_4N)_2(C{\equiv}CR)_2]$ precipitated as white solids.

$[Pd(Ph_2PC_5H_4N)_2(C{\equiv}CPh)_2]$ **7** (Found: C, 71.9; H, 4.4; N, 3.2. Calc. for $C_{50}H_{38}N_2P_2Pd$: C, 71.90; H, 4.59; N, 3.35%): ^{1}H NMR ($CDCl_3$, δ 8.7 (d, 2H), 8.23 (br, 2H), 8.03 (br, 6H), 7.5 (t, 2H), 7.3 (m, 12H), 7.19 (m, 4H), 6.9 (m, 6H) and 6.34 (d, 4H).

$[Pd(Ph_2PC_5H_4N)_2(C{\equiv}CMe)_2]$ **8** (Found: C, 68.2; H, 4.9; N, 4.0. Calc. for $C_{40}H_{34}N_2P_2Pd$: C, 67.56; H, 4.82; N, 3.94%).

$[Pd_2(Ph_2PC_5H_4N)_2(OAc)_2(\mu\text{-DMAD})]$ 9. Dimethyl acetylenedicarboxylate (0.3 ml) was added to a solution of $[Pd_2(Ph_2PC_5H_4N)_2(OAc)_2]$ (0.09 g, 0.4 mmol) in toluene (30 ml) and the red solution stirred for 3 h. Addition of light petroleum (100 ml) precipitated a yellow solid (Found: C, 44.7; H, 3.2; N, 3.2. Calc. for $C_{40}H_{42}N_2O_8P_2Pd_2$: C, 46.44; H, 3.03; N 3.01%). IR (KBr disk, cm^{-1}): ν(DMAD) 1726.4s, 1697.5s, 1263.5s, 1217.5s, (OAc) 1583.7s, 1386.9m, 1327.1m, ($Ph_2PC_5H_4N$) 1435.1s, 1096.6s, 696.35m and 534.32s. ^{1}H NMR ($CDCl_3$, δ): 7.58 (H^6, m), 9.40 (H^9, br), 7.98 (m, 4H), 7.76 (m, 4H), 7.45 (m, 4H), 7.25 (m, 4H), 2.86 (s, 3H, DMAD) and 1.35 (s, OAc). ^{13}C-{^{1}H} NMR ($CDCl_3$, δ): 133.1 (*o*-C of Ph, d, J 50), 132.0 (*o*-C of Ph, d, J 46), 129.6 (*p*-C of Ph, s), 129.2 (*p*-C of Ph, s), 127.5 (*m*-C of Ph, d, J 43), (*m*-CPh, d, J 43 Hz), 161.2 (s, O_2CCH_3), 14.27 (s, O_2CCH_3), 176.46 (s, CO_2CH_3) and 49.88 (s, CO_2CH_3).

$[Pd_2(Ph_2PC_5H_4N)_3]$ 10. A solution of $Ph_2PC_5H_4N$ (1.66 g, 6.3 mmol) in methanol (5 ml) was added to a suspension of $Pd(OAc)_2$ (0.2 g, 0.9 mmol) in methanol (20 ml). The mixture was stirred for 5 h during which time a bright yellow solid precipitated. Diethyl ether (50 ml) was added to complete precipitation and the resultant yellow solid filtered off, washed with Et_2O (2 × 30 ml) and dried *in vacuo*. Yellow crystals of complex **10** were obtained by slow diffusion of light petroleum into a toluene solution of the complex (Found: C, 71.0; H, 4.6; N, 4.7. Calc. for $C_{51}H_{42}N_2P_2Pd$: C, 68.35; H, 4.72; N, 4.69%). ^{1}H NMR (C_6D_6, δ): 8.46 (d, 2H), 7.78 (m, 12H), 7.42 (m, 3H), 7.12 (m, 18H), 6.86 (t, 3H) and 6.52 (dd, 3H).

Crystallography

Data for compounds **1** and **2** were recorded on a FAST TV Area detector diffractometer, with a molybdenum target [λ(Mo-Kα) = 0.71069 Å], equipped with an Oxford Cryosystems cryostat and driven by MADNES software operating on a MicroVax 3200 computer, following previously described procedures.[24] Crystals of **1** and **2** were mounted on glass fibres using the oil drop technique and collected at 150 and 120 K respectively. The structures were solved *via* heavy atom methods

Table 3 Crystal data for $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(OAc)_2]$ **1** and $[Pd_2(\mu\text{-}Ph_2PC_5H_4N)_2(O_2CCF_3)_2]$ **2**

	1	**2**
Empirical formula	$C_{38}H_{34}N_2O_4P_2Pd_2 \cdot CH_2Cl_2$	$C_{38}H_{28}F_6N_2O_4P_2Pd_2$
Formula weight	940.06	965.08
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1$
a/Å	12.532(2)	12.413(9)
b/Å	20.159(4)	20.703(10)
c/Å	14.7610(6)	15.580(9)
β/°	104.24(3)	108.53(10)
U/Å^3	3614.7(10)	3796(4)
Z	4	4
D_c/Mg m^{-3}	1.663	1.762
θ/mm^{-1}	1.201	1.176
$F(000)$	1812	1992
Crystal size/mm	0.18 × 0.07 × 0.145	0.2 × 0.11 × 0.2
θ range/°	1.75 to 25.01	1.84 to 25.03
Index ranges	$-10 \leqslant h \leqslant 14$, $-23 \leqslant k \leqslant 23$, $-17 \leqslant l \leqslant 16$	$-13 \leqslant h \leqslant 13$, $22 \leqslant k \leqslant 21$, $18 \leqslant l \leqslant 18$
Reflections collected	14885	16331
Independent reflections	5391	9636
R_{int}	0.0959	0.0689
Data/restraints/parameters	5383/0/455	9628/1/1000
Goodness of fit on F^2	1.027	1.059
Final R, $wR2$ $[I > 2\sigma(I)]$	0.0478, 0.1067	0.0438. 0.1078
(all data)	0.0630, 0.1143	0.0472, 0.1112
Largest difference peak and hole/e Å^{-3}	1.956 and −0.992	1.436 and −0.874
Absolute structure parameter		0.02(3)

(SHELXS),[25] and then subjected to full matrix least-squares refinement on F_o^2 (SHELXL 93).[26] Non-hydrogen atoms were made anisotropic, with hydrogens in calculated positions (C–H 0.96 Å, with U_{iso} tied to U_{eq} of the parent atoms). The weighting scheme used was $w = 1/[(2F_o^2)]$. The disordered solvent molecule present in **1** was freely refined as two components, with the major part having 75% occupancy. Absorption corrections were applied using DIFABS[27] and diagrams drawn with SNOOPI.[28] Further details are given in Table 3.

CCDC reference number 186/1182.

See http://www.rsc.org/suppdata/dt/1998/3771/ for crystallographic files in .cif format.

Acknowledgements

We are grateful to ICI Acrylics for financial support for this study (A. D. and P. D. N.) and to EPSRC for support for the crystallography unit at Cardiff.

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