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Reactivity studies of $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ ($X = Br, I$) with CNR (R = 2,6-dimethylphenyl), H_2 and alkynes

Víctor Durà-Vilà, D. Michael P. Mingos [1], Ramón Vilar *, Andrew J.P. White, David J. Williams

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, SW7 2AY, UK

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Abstract

Improved syntheses for the dimeric compounds $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ ($X = Br, I$) have been developed and the X-ray crystal structure for the dimer with $X = I$ is reported. The reactions of these dimers with CNR (R = 2,6-dimethylphenyl), H_2 and a series of terminal and substituted alkynes are also reported. The dimer with $X = Br$ is an initiator for the catalytic polymerisation of phenylacetylene. The product of the dimers with disubstituted alkynes results in the synthesis of trimeric species with formula $[Pd_3(\mu\text{-}X)_4\{\eta^2\text{-}C_4(CO_2R)_4\}_2][PBu^t_3Me]_2$ ($X = Br, I$; $R = Me, Et$). The X-ray crystal structure of one of these compounds (when $R = Et$ and $X = I$) is presented, demonstrating that the palladium dimers assist the C–C coupling of the alkynes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Dimer; Isocyanides; Dihydrogen; Alkynes; Trimer

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1. Introduction

The catalytic properties of palladium complexes are well established and have been extensively exploited in a wide variety of processes [1]. Due to this, there is a continuing interest in finding new palladium compounds with improved catalytic properties or which show novel reactivity patterns. Our group and others have concentrated on the study of palladium dimers (and clusters) as potential catalysts. The presence of more than one metal centre might have a cooperative effect and improve the catalytic properties of these species. Several Pd(I)–Pd(I) dimers are known and there is current interest in understanding their reactivities and possible use in catalysis [2].

In spite of the extensive studies on Pd(I) dimers, it is surprising that the simple halogen-bridged compounds $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ ($X = Br$, **1**; $X = I$, **2**) were not reported until recently [3]. In a previous communication we reported that **1** and **2** can be obtained, albeit in low yields, by reacting $[Pd_2(dba)_3]\cdot C_6H_6$ (dba = dibenzylideneacetone) with PBu^t_3 and CHX_3. The palladium atoms in **1** and **2** have a formal oxidation state of one and a strained geometry due to a very acute Pd–X–Pd angle. They readily react with small molecules such as CO, C_2H_2 and O_2 giving a wide range of products [4]. Particularly interesting is the reaction between **1** and ethyne, which yields polyacetylene and partial decomposition of the dimer. This suggests that **1** is either acting as a catalyst or as an initiator for the polymerisation of ethyne. These results encouraged us to study more extensively the reactivity of dimers **1** and **2** with a range of alkynes. Herein we report an improved synthetic route to $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ ($X = Br, I$) and the structural characterisation of the dimer when $X = I$. The reactions of these dimers with isocyanide, H_2 and alkynes are also presented.

2. Results and discussion

2.1. Synthesis and characterisation of $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ ($X = Br, I$)

In a previous communication [3], we reported that

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* Corresponding author.

E-mail address: r.vilar@ic.ac.uk (R. Vilar)

[1] Present address: St. Edmund Hall, Queens Lane, Oxford OX1 4AR, UK.

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the reaction between $[Pd_2(dba)_3]{\cdot}C_6H_6$, PBu^t_3, and CHX_3 (X = Br, I) gave the novel dimers $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ (X = Br, **1** and X = I, **2**) in 18 and 23% yields, respectively. Stimulated by their novel properties and reactions, studies were undertaken to improve the yields associated with their syntheses. Several other halogenating agents such as CBr_4, *N*-bromosuccinimide, CI_4 and *N*-iodosuccinimide were used for their syntheses, but unfortunately the yields were not improved. Therefore, the following alternative reaction was studied:

$$[Pd_2(dba)_3] + 4PBu^t_3 + 2[Pd(COD)Br_2] \xrightarrow[-3\ \text{dba}]{-2\ \text{COD}} 2[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$$

The Pd(0) compound $[Pd_2(dba)_3]{\cdot}C_6H_6$ in the presence of four equivalents of PBu^t_3 generates $[Pd(PBu^t_3)_2]$ in situ, which conproportionates with the Pd(II) complex $[PdBr_2(COD)]$ (COD = 1,5-cyclooctadiene) to give $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ in higher yield than the previous synthesis (60% based on palladium). A similar approach was taken for the synthesis of $[Pd_2(\mu\text{-}I)_2(PBu^t_3)_2]$ but, unfortunately, an analogous high-yield route for this dimer was not observed. In spite of this the yield of this compound was improved by modifications on the crystallisation process.

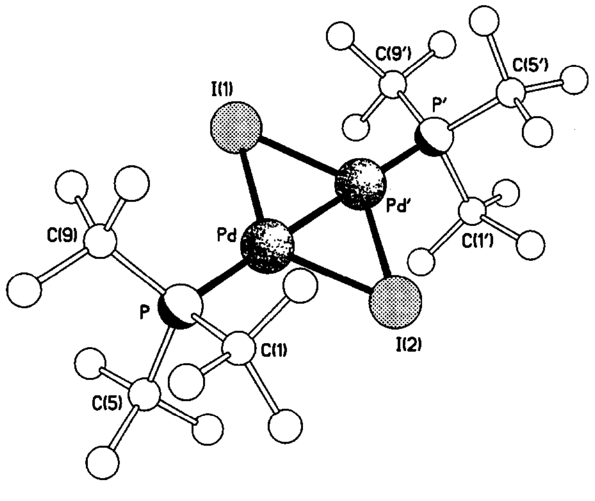


Fig. 1. Molecular structure of $[Pd_2(\mu\text{-}I)_2(PBu^t_3)_2]$.

Table 1
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Pd–I(1)	2.604(3)	Pd–I(2)	2.591(4)
Pd–P	2.318(3)	Pd–Pd'	2.697(1)
Bond angles			
P–Pd–I(1)	122.1(4)	P–Pd–I(2)	120.5(4)
I(1)–Pd–I(2)	117.45(3)	P–Pd–Pd'	179.0(3)
Pd'–Pd–I(2)	58.64(5)	Pd'–Pd–I(1)	58.82(5)
Pd–I(1)–Pd'	62.4(1)	Pd–I(2)–Pd'	62.7(1)

Both synthetic routes to dimer **1** produced a competing side product, which was characterised as $[PBu^t_3Br]^+$ on the basis of $^{31}P\{^1H\}$-NMR spectroscopy [5] and accurate positive-ion FAB mass spectroscopy. The formation of this product might be an important reason for the low yield obtained originally in this synthesis.

The $^{31}P\{^1H\}$-NMR spectra of **1** and **2** showed singlets at 87.0 and 102.9 ppm, respectively, which are consistent with previously reported data. The dimers were studied by Raman spectroscopy. Dimer **1** showed peaks at 200 and 152 cm^{-1}, which can be assigned to the bridging bromides stretching vibration modes A_g and B_g that involve a combination of metal–metal and metal–bromide stretches. Unfortunately, the dimer **2** was too dark to obtain a meaningful Raman spectrum.

We have previously reported the X-ray crystal structure of compound **1** [3]. In order to compare the structural features of dimers **1** and **2**, the X-ray crystal structure of **2** was completed (see Fig. 1). This compound crystallised by cooling down a warm and saturated solution of **2** in acetone.

The X-ray analysis of **2** shows the molecule to have the expected dimeric structure with a metal–metal bond between the two palladium(I) centres. The structure has crystallographic C_2 symmetry about an axis passing through the two iodine atoms, and as such is essentially isostructural with the bromine analogue [3]. The Pd–Pd distance in **2** [2.697(1) Å] is significantly longer than that in the bromine analogue **1** [2.628(2) Å], though still within the range reported previously for Pd–Pd dimers [2]. The two Pd–I distances do not differ significantly and are, as expected longer than those of the bromines in **1**. The Pd–I–Pd angles are slightly contracted at 62.4(1)° [I(1)] and 62.7(1)° [I(2)] than their counterparts in **1** [63.8(1)°]; the Pd–P distance occurs in the normal range. There are no intermolecular interactions of note (Table 1).

2.2. Reactions of $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ (X = Br, I) with CNXyl (CNXyl = 2,6-dimethylphenyl isocyanide)

It has been previously established that in the presence of CO dimers **1** and **2** are good starting materials for the syntheses of hexa- and tetrapalladium cluster compounds [4]. This encouraged us to study analogous reactions with isocyanides.

When a solution of **1** in toluene was treated with two equivalents of CNXyl, an immediate change in colour from green to dark orange was observed. The reaction was stirred for 2 h and the $^{31}P\{^1H\}$-NMR spectrum was recorded. It showed two singlets, one at 87.0 ppm (chemical shift of the starting material **1**) and a second one at 63.1 ppm (which corresponds to free PBu^t_3). This suggested that the reaction had not gone to completion.

Table 2
Details for the positive-ion FAB mass spectrum of **3**

m/z	Intensity (%)	Assignment
896	10	$[M]^+$
819	25	$[M-Br]^+$
688	50	$[M-Br-CNXyl]^+$
580	32	$[M-Br-CNXyl-Pd]^+$
449	15	$[M-Br-2CNXyl-Pd]^+$
368	80	$[M-2Br-2CNXyl-Pd]^+$
236	95	$[M-2Br-3CNXyl-Pd]^+$

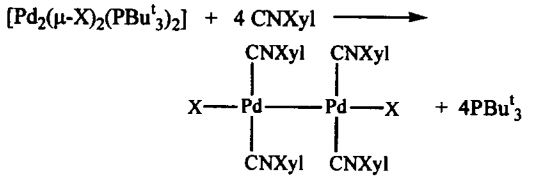
The reaction was then repeated using four equivalents of the isocyanide. The $^{31}P\{^1H\}$-NMR spectrum showed only one signal at 63.0 ppm, suggesting that all the phosphine ligands had been replaced by the CNXyl groups. Hexane was added to the reaction mixture and a dark yellow crystalline solid precipitated. On the basis of IR, FAB-MS and elemental analyses, this product was formulated as $[Pd_2Br_2(CNXyl)_4]$ (**3**).

In palladium compounds, terminal isocyanides show IR bands ν(CN) between 2221 and 2080 cm^{-1} [6]. The IR spectrum of **3** showed a very strong and sharp band at 2157 cm^{-1}, suggesting that the CNXyl groups are all equivalent and terminal. The FAB mass spectrum showed a very clear fragmentation pattern for the proposed formulation of **3** (see Table 2). Elemental analyses were also consistent with this formulation.

These compounds have previously been prepared by reacting CNR with $[Pd(dba)_2]$ and $[PdCl_2(C_6H_5CN)_2]$ [7]. The X-ray crystal structures for $[Pd_2I_2(CNMe)_4]$ and $[Pd_2Cl_2(CNBu^t)_4]$ have been described [8,9].

Analogous results to the reaction of **1** with the isocyanide were obtained when **2** was reacted with four equivalents of CNXyl. The product obtained was formulated on the basis of IR, FAB-MS and elemental analyses as $[Pd_2I_2(CNXyl)_4]$ (**4**).

In contrast to the reaction between these dimers and CO, which yield tetra and hexa-palladium cluster compounds, **1** and **2** react with CNXyl retaining their original dimeric skeleton. The general reaction can then be written as follows:

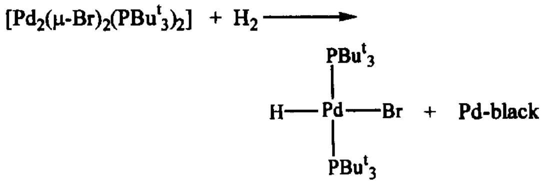


$$[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2] + 4\,CNXyl \longrightarrow [X(CNXyl)_2Pd\text{-}Pd(CNXyl)_2X] + 4PBu^t_3$$

2.3. Reactions of $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ (X = Br, I) with H_2

Palladium hydrido complexes have been implicated in several catalytic reactions. Thus, the synthesis of palladium-hydrido compounds is of continuing interest. Very few palladium dimers or clusters with hydrido ligands have been reported. With this in mind, the reactions of **1** and **2** with H_2 were studied.

When H_2 was bubbled through a solution of **1** in toluene for 15 min, the original green colour disappeared giving a pale yellow solution and a black precipitate (palladium metal). The reaction mixture was filtered, the solvent removed under reduced pressure and the crude solid was recrystallised from hexane. The crystals obtained were identified as *trans*-$[Pd(H)Br(PBu^t_3)_2]$ on the basis of $^{31}P\{^1H\}$- and ^1H-NMR spectroscopy. The $^{31}P\{^1H\}$-NMR spectrum of this compound showed a singlet at 84.0 ppm, while the ^1H-NMR spectrum showed a triplet at −15.5 ppm, suggesting the formation of a hydrido complex in which the hydrido group is coupling to two equivalent phosphines. Analogous compounds have been previously synthesised and characterised by NMR (which is consistent with this formulation) [10].



$$[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2] + H_2 \longrightarrow trans\text{-}[Pd(H)Br(PBu^t_3)_2] + \text{Pd-black}$$

In contrast to the highly reactive dimer **1**, when H_2 was bubbled through a solution of **2** in toluene no reaction was observed. Even after several hours the original $^{31}P\{^1H\}$- and ^1H-NMR spectra did not change.

2.4. Reactions of $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ with terminal alkynes

Dimers **1** and **2** readily react with ethyne, which is polymerised to yield polyethyne. This result encouraged us to undertake a more detailed investigation on the reactivity of these dimers with alkynes.

When one equivalent of **1** in toluene was reacted with 50 equivalents of degassed phenylacetylene, formation of polyphenylacetylene was observed. The reaction mixture changed from dark green to dark orange and became more viscous. The ^{31}P-NMR spectrum of the mixture showed that the original dimer (δ = 87.0 ppm) had reacted, yielding products that showed singlets at 99.7 and 93.2 ppm. In spite of various attempts, it has not been possible to isolate these products even when the reaction is repeated using smaller amounts of phenylacetylene, i.e. 1, 2, 5 and 10 equivalents. After 18 h the reaction mixture was poured into hexane and a brown solid precipitated. This solid was identified as polyphenylacetylene on the basis of IR and ^1H-NMR spectroscopy. The polymer obtained has an average molecular weight of 35 900 g mol^{-1} ($M_w = 35\,900$ and $M_n = 11\,400$).

Interestingly, when dimer **2** was reacted with phenylacetylene no polymerisation reaction was observed. Even when phenylacetylene was used as a solvent, no polyphenylacetylene was formed and only partial reaction of **2** was detected. The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture showed two singlets: one at δ 102.9 ppm (which corresponds to **2**) and a second one at 52.0 ppm. As will be discussed in the next section, the peak at 52.0 corresponds to the formation of $[\mathrm{PBu}^t_3\mathrm{Me}]^+$, which in some cases is associated with the formation of tripalladium compounds containing coupled alkynes in the coordination sphere (see compound **5** in the next section). It is worth mentioning that dimer **2** has been shown to be less reactive than **1**, not only in this reaction but also when reacted with O_2 and CO [3,4].

The reactivity of dimer **1** with monosubstituted dialkynes species was also studied. Reaction using $HC{\equiv}C(CH_2)_2C{\equiv}CH$ as a solvent yielded a very dark red sticky polymer. The IR spectrum of this polymer did not show any alkyne groups, but a broad absorption in the 1645–1655 cm^{-1} region for the alkene groups, which suggested a hyperbranched polymer. Unfortunately this polymeric product is very insoluble and to date it has not been fully characterised.

2.5. Reactions of $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ with disubstituted alkynes

In order to gain some information about the organometallic intermediates generated in the polymerisation of phenylacetylene, disubstituted acetylenes were reacted with dimers **1** and **2**. In these reactions polymerisation was not observed (due to the absence of a terminal acidic proton) but interesting organometallic complexes were isolated.

When a solution of **2** in benzene was treated with a 50-fold excess of $EtO_2CC{\equiv}CCO_2Et$ a dark orange solution was obtained. The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture showed two major peaks at 51.4 and 52.2 ppm. Addition of hexane to the reaction mixture precipitated a dark orange sticky solid. This solid showed strong C=O stretches in the IR spectrum and a singlet at 51.4 ppm in the $^{31}P\{^1H\}$-NMR spectrum. In order to confirm the exact formulation of this compound, single crystals were grown from a toluene–hexane mixture. The X-ray structure is seen to be a tripalladium complex (**5**) in which two $[PdI_2\{\eta^2\text{-}C_4(CO_2Et)_4\}]$ units are linked to a central palladium atom via their iodine centres (Fig. 2).

This trimeric arrangement of the palladium centres was unexpected but not unprecedented. There are three complexes with a $[Pd_3(\mu\text{-}X)_4]$ core that have been previously characterised by structural methods [11]. All of them contain chloride as the bridging halide, **5** being the first example with bridging iodines. In these previously reported structures the Pd–Cl bonds are shorter for the central $[PdCl_4]^{2-}$ unit than those for the other two palladium atoms. On this basis (plus some conductivity studies), Maitlis and co-workers have suggested that these trimeric species have an important ionic contribution and could then be postulated as $[PdCl_4]^{2-}[PdL]_2$ [11a]. Analogous structural patterns are observed for **5** (see Table 3), suggesting that an alternative arrangement comprising a central $[PdI_4]^{2-}$ unit linked to two peripheral $[Pd\{\eta^2\text{-}C_4(CO_2Et)_4\}]$ moieties could then be considered.

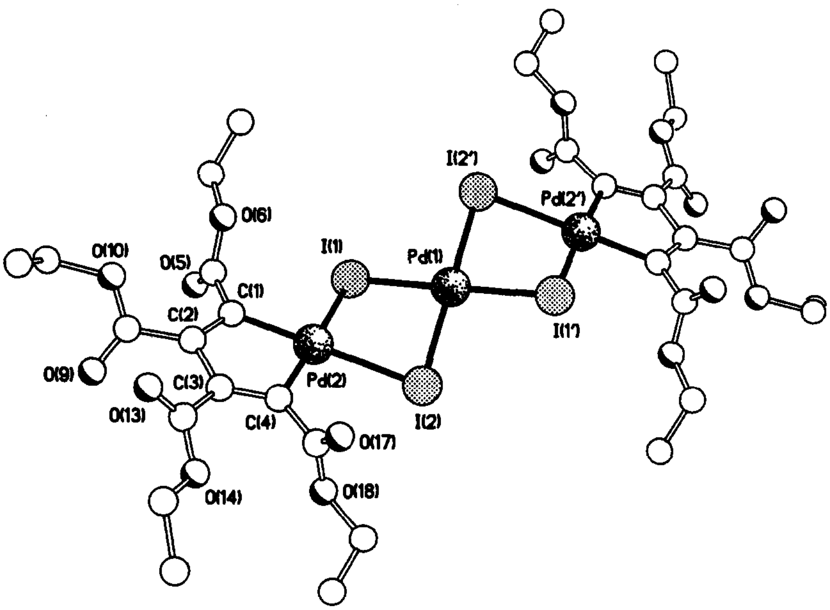


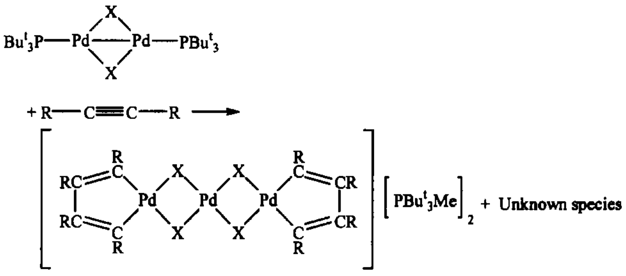
Fig. 2. Molecular structure of the anionic component of **5**.

Table 3
Selected bond lengths (Å) and angles (°) for the two crystallographically independent molecules (**A** and **B**) in the structure of **5**

	A	**B**		**A**	**B**
Bond lengths					
Pd(1)–I(1)	2.600(1)	2.597(1)	Pd(1)–I(2)	2.601(1)	2.607(1)
Pd(2)–I(1)	2.685(1)	2.679(2)	Pd(2)–I(2)	2.686(1)	2.696(2)
Pd(2)–C(1)	2.008(13)	1.98(2)	Pd(2)–C(4)	2.04(2)	1.999(14)
C(1)–C(2)	1.37(2)	1.36(2)	C(2)–C(3)	1.46(2)	1.52(2)
C(3)–C(4)	1.34(2)	1.29(2)			
Bond angles					
I(1)–Pd(1)–I(2)	88.27(3)	87.99(3)	I(1)–Pd(1)–I(1)′	180.0	180.0
I(1)–Pd(1)–I(2)′	91.73(3)	92.01(3)	I(2)′–Pd(1)–I(2)	180.0	180.0
I(1)–Pd(2)–I(2)	84.80(4)	84.50(5)	I(1)–Pd(2)–C(1)	97.0(3)	97.7(4)
I(1)–Pd(2)–C(4)	176.8(4)	177.1(4)	I(2)–Pd(2)–C(1)	177.4(4)	171.5(4)
I(2)–Pd(2)–C(4)	97.9(4)	98.4(4)	C(1)–Pd(2)–C(4)	80.4(5)	79.4(6)
Pd(1)–I(1)–Pd(2)	86.73(4)	80.19(4)	Pd(1)–I(2)–Pd(2)	86.69(3)	80.34(4)

The formal oxidation state of the palladium atoms in **5** is + 2, giving an overall charge to the complex of − 2; to counterbalance this charge there are two phosphonium cations, thus giving the overall formulation $[Pd_3(\mu\text{-}I)_4\{\eta^2\text{-}C_4(CO_2Et)_4\}_2][PBu^t_3Me]_2$ to compound **5**. The crystals contain two crystallographically independent C_i symmetric complexes that differ noticeably in the relative fold angles about the I···I vectors in the Pd_2I_2 four-membered rings; in molecule **A** the ring is folded by ca. 39° out of planarity, whereas in molecule **B** it is folded by ca. 56°, thus the overall lengths of the two molecules are very different, the Pd(2)···Pd(2′) distances being 7.26 and 6.82 Å for molecules **A** and **B**, respectively. Although in both molecules the five-membered chelate rings are essentially planar (maximum deviations from planarity of 0.001 and 0.035 Å for molecules **A** and **B** respectively), the distortions in the associated palladium coordination planes differ markedly. In molecule **A** the coordination plane is planar to within 0.044 Å, whereas in molecule **B** there are departures of up to 0.113 Å [for C(1)]. The geometry at Pd(1) is distorted square planar with *cis* angles in the range 88.3(1)–91.7(1)° for molecule **A** [88.0(1)–92.0(1)° for molecule **B**], the two Pd–I distances not differing appreciably. The geometry at Pd(2) is more distorted, with *cis* angles in the range 80.4(5)–97.9(4)° [79.4(6)–98.4(4)°], the more acute angle reflecting the bite of the chelate ring. The Pd(2)–I(1) and Pd(2)–I(2) distances in the two molecules are comparable, but significantly longer than their counterparts to Pd(1), reflecting the dominance of the central $[PdI_4]^{2-}$ anion and the looser association of the $[Pd\{\eta^2\text{-}C_4(CO_2Et)_4\}]$ units. Probably one of the most interesting features of this structure is the presence of two organic moieties coordinated to the terminal palladium atoms; each of them corresponds to the C–C coupling of two alkynes yielding a coordinated diolefin. Within each five-membered chelate ring there is a distinct pattern of bond localisation, with the C(1)–C(2) and C(3)–C(4) bonds exhibiting distinct double-bond character, whereas C(2)–C(3) is of conventional single-bond length. There are no inter-complex or anion···cation interactions of note. The C–C coupling of alkynes on palladium centres is well known. Similar arrangements to the coupled alkynes in **5** have been previously observed. Ibers and co-workers [12b] and Moseley and Maitlis [12a] have demonstrated the formation of a $[Pd(\eta^2\text{-}C_4R_4)_2]$ unit in the cyclotrimeristaion of acetylenes [12]. Rheingold et al. have reported the formation of $[Pd_2(\mu\text{-}I)_2\{\eta^2\text{-}C_4(CO_2Me)_4\}_2][PPh_3Me]_2$ when reacting $[Pd\{\eta^2\text{-}C_4(CO_2Me)_4\}(PPh_3)_2]_n$ with an excess of methyl iodide [13].

Even though few analogous complexes to **5** have been previously reported, the synthesis of **5** from dimer **2** is not obvious and suggests very interesting questions about the formation mechanism. Overall, the reaction to prepare **5** could be written as



X = Br, I; R = -CO₂Me, -CO₂Et

which implies the oxidation of Pd(I) centres to Pd(II), the reduction of four molecules of acetylene to the coupled olefins and the oxidation of P(III) to P(V) (this in order to form the unexpected $[PBu^t_3Me]^+$ cation). Moreover, a complex rearrangement has to occur to transform the dimer to the trimeric species. To date, a clear mechanism has not been developed but we believe that, in order for this reaction to occur, the dimer **2** has to disproportionate to a Pd(II) and a Pd(0) species. It has previously been demonstrated that Pd(0) species promote the C–C coupling of acetylenes to yield the $[Pd(\eta^2\text{-}C_4R_4)_2]$ fragment [12]. Further reactions with iodine-containing compounds would yield the trimeric species **5**. One of the most puzzling facts in this reaction is the formation of the $[PBu^t_3Me]^+$ counterion. The presence of this counterion has been clearly established by structural analysis, by accurate FAB-MS and by NMR spectroscopy. In order for this cation to form, a methyl has to be extracted from the reaction media. We have discarded the possibility of methyl extraction from the solvent (benzene instead of toluene was used as a reaction solvent) or from the alkyne (which is $EtO_2CC{\equiv}CCO_2Et$). It is possible that in the oxidation of PBu^t_3 to the P(V) species a methyl is extracted from another PBu^t_3. It is well known that this phosphine is prone to cyclometallation in which a methyl from one of the Bu^t groups of the phosphine is somehow activated by coordination to palladium. This is supported by the fact that cyclometallated phosphine was clearly identified (from ^{31}P-NMR spectroscopy) in the reaction mixture of some of these reactions (e.g. when two equivalents of the alkyne were used). If this is correct, other signals should be observed in the ^{31}P-NMR for the fragmented phosphine. As has been indicated above, besides the signal for the trimer, there is a second one in the same region (52.2 ppm). This signal could correspond to the fragmented PBu^t_3 (for example $PBu^t_2Pr^i$ coordinated to palladium shows signals around 50 ppm) [14].

Analogous trimers to **5** were obtained when **2** was reacted with $MeO_2CC{\equiv}CCO_2Me$ and when **1** was reacted with both acetylenes (i.e. $RO_2CC{\equiv}CCO_2R$, R = Me, Et). This demonstrated the general pattern of the reaction between the dimeric species and activated acetylenes. However, further studies will need to be carried out to establish the exact mechanism of this unusual reaction.

3. Conclusions

The dimer $[Pd_2(\mu\text{-}I)_2(PBu^t_3)_2]$ has been structurally characterised, showing an analogous structure to the previously reported dimer with X = Br. An improved route for the synthesis of $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ has been obtained. The reactions of these dimers with CNXyl, H_2 and a series of mono- and disubstituted alkynes have been established. These studies, together with the previously reported reactions with CO, demonstrate the rich and varied chemistry of **1** and **2**. The reactions of the dimers with CNXyl showed that the dimeric structure is kept, while the reaction with H_2 breaks down the dimer **1** into a monometallic hydrido species. Interestingly, the iodo dimer does not react at atmospheric pressure with H_2. Dimer **1** has proved to be a good catalyst for the polymerisation of phenylacetylene, while dimer **2** has not. These results demonstrate that, in general, **1** is more reactive than **2** (this has also been observed when the dimers react with CO and O_2). The reactions between both these dimers and activated disubstituted alkynes have uncovered an interesting chemistry. One of the products resulting from these reactions has been structurally characterised, showing the formation of tripalladium species. The mechanism involved in these reactions seems to be quite complex and will need further studies to be properly understood.

4. Experimental

4.1. General procedures and instrumentation

All the reactions were carried out using standard Schlenk line techniques under an atmosphere of pure N_2. All the solvents used were dry and free of oxygen. Infrared spectra were recorded in a Perkin–Elmer 1720 Infrared Fourier Transform Spectrometer between 4000 and 400 cm^{-1} as KBr pellets. The Raman spectra were recorded in a LabRam Infinity No 3/8 IF, at 532 nm. $^{31}P\{^1H\}$-NMR spectra were recorded on a JEOL JNM-EX270 Fourier Transform NMR spectrometer operating at frequencies of 250.1 MHz (^{1}H) and 101.3 MHz ($^{31}P\{^1H\}$) with chemical shifts reported relative to TMS and H_3PO_4, respectively. FAB mass spectra were recorded by J. Barton at Imperial College. FAB mass spectra simulations were done using the Isotope computer program. $[Pd_2(dba)_3]\cdot C_6H_6$, $[PdBr_2(C_6H_5CN)_2]$ and $[PdBr_2(COD)]$ were prepared according to literature procedures [15–17].

4.2. Preparations

4.2.1. Synthesis of $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ (1) from CBr_4

A solution of PBu^t_3 (0.080 g, 0.4 mmol) in toluene was added to a solution of $[Pd_2(dba)_3]\cdot C_6H_6$ (0.200 g, 0.2 mmol) in toluene (ca. 10 ml). After 1 h, CBr_4 (0.033 g, 0.1 mmol) was added and the reaction mixture was stirred for a further 5 h. The reaction mixture was then filtered and the volume of the filtrate reduced to a half. An equal amount of acetone was added and the resulting solution was left overnight at 4°C to give a green crystalline material (0.028 g, 18%), which was characterised as the previously reported dimer $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$. Anal. Found: C, 37.3; H, 6.9; Br, 20.2. $C_{24}H_{54}Br_2P_2Pd_2$ requires C, 37.1; H, 7.0; Br, 20.6%. $^{31}P\{^1H\}$-NMR in C_6D_6: δ 87.0 (s) ppm.

4.2.2. Synthesis of $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ (1) from $[PdBr_2(COD)]$

$[Pd_2(dba)_3]\cdot C_6H_6$ (0.101 g, 0.1 mmol) was dissolved in toluene (ca. 10 ml) and a solution of PBu^t_3 (0.080 g, 0.4 mmol) in toluene was added with stirring. After 1 h $[PdBr_2(COD)]$ (0.081 g, 0.2 mmol) was added. The reaction was allowed to continue for 4 h with continuous stirring. The solvent was removed under reduced pressure and a dark green solid was obtained. The precipitate was washed with acetone, dried under vacuum and characterised as dimer **1** (0.094 g, 60%). $^{31}P\{^1H\}$-NMR in C_6D_6: δ 86.9 (s) ppm.

4.2.3. Synthesis of [Pd$_2$(μ-I)$_2$(PBu$^t_3$)$_2$] (2) from CHI$_3$

An analogous procedure to the one shown before was carried out to prepare $[Pd_2(\mu\text{-}I)_2(PBu^t_3)_2]$. In this case CHI_3 was used as the halogenating agent and a mixture of toluene–diethyl ether was used to recrystallise the product at −20°C. The purple solid obtained (0.073 g, 40%) was characterised on the basis of $^{31}P\{^1H\}$-NMR as the previously reported dimer $[Pd_2(\mu\text{-}I)_2(PBu^t_3)_2]$. Single crystals of dimer **2** were obtained by slowly cooling down a warm saturated solution of **2** in acetone. Anal. Found: C, 33.4; H, 6.2; I, 29.3. $C_{24}H_{54}I_2P_2Pd_2$ requires C, 33.1; H, 6.2; I, 29.3%. $^{31}P\{^1H\}$-NMR in C_6D_6: δ 102.9 (s) ppm.

4.2.4. Synthesis of [Pd$_2$Br$_2$(CNXyl)$_4$] (3)

Four equivalents of CNXyl (0.045 g, 0.34 mmol) in acetone (15 ml) were added to a solution of **1** (0.065 g, 0.084 mmol) in toluene (15 ml). After the addition an immediate change in colour from dark green to orange was observed. The reaction was left stirring for 2 h. After this time hexane was added (40 ml) and a dark yellow crystalline solid precipitated (0.056 g, 74%). This solid was formulated as $[Pd_2Br_2(CNXyl)_4]$. Anal. Found: C, 48.3; H, 3.8; N, 6.1. $C_{36}H_{36}N_4Br_2Pd_2$ requires C, 48.2; H, 4.0; N, 6.2%. ^1H-NMR in C_6D_6: δ at 6.6 (t), 6.5 (d) and 2.3 (s) ^3J(H–H) 8 Hz. IR ν(CN) 2154 cm^{-1}.

4.2.5. Synthesis of [Pd$_2$I$_2$(CNXyl)$_4$] (4)

This compound was prepared in the same way as **3** using a solution of **2** (0.061 g, 0.07 mmol) in toluene (15 ml) and CNXyl (0.037 g, 0.28 mmol). The final orange product was recrystallised from toluene–hexane at −30°C (0.041 g, 58%). Anal. Found: C, 43.6; H, 4.0; N, 5.2. $C_{36}H_{36}N_4I_2Pd_2$ requires C, 43.6; H, 3.6; N, 5.7%. IR ν(CN) 2151 cm^{-1}.

4.2.6. Reactions of 1 with H$_2$

Dimer **1** (0.078 g, 0.10 mmol) was dissolved in toluene and H_2 was bubbled through this solution for 10 min. The reaction was stirred under an H_2 atmosphere for 4 h. After this time the reaction mixture was filtered (to remove the palladium black generated) and the solvent was removed under reduced pressure. An off-white crystalline material was obtained after recrystallising the crude product from hexane. This solid was formulated as *trans*-$[Pd(Br)H(PBu^t_3)_2]$ based on the previously reported NMR data [10]. $^{31}P\{^1H\}$-NMR in C_6D_6: δ 84.0 ppm (s). ^1H-NMR in C_6D_6: δ −15.5 ppm (t) [^2J(P–H) 7 Hz].

4.2.7. Reactions of 1 with PhC≡CH

Dimer **1** (0.14 g, 0.18 mmol) was dissolved in toluene and 50 equivalents of degassed PhC≡CH (0.92 g, 9 mmol) in toluene were added. The solution became dark red–orange immediately and was left to react for a further 18 h. Addition of hexane precipitated a brown solid (0.074 g, 8%), which was spectroscopically characterised as polyphenylacetylene. IR (KBr) ν(cm^{-1}) 3054 (s), 3021(s), 1596(s), 1490(s), 1442(s), 757(vs), 696(vs). $M_w = 35\,900$, $M_n = 11\,400$. ^1H-NMR ($CDCl_3$), δ(ppm) broad signal between 6.5 and 7.5 ppm.

4.2.8. Synthesis of
[Pd$_3$(μ-I)4(η^2-C$_4${CO$_2$Et}$_4$}$_2$][PBu$^t_3$Me]$_2$ (5)

Dimer **2** (0.050 g, 0.057 mmol) was dissolved in toluene and 50 equivalents of degassed $EtO_2CC\equiv CCO_2Et$ (0.550 g, 3.2 mmol) in toluene were added. An immediate change in colour from green to dark orange was observed. The reaction was left stirring overnight. A sticky, dark orange solid precipitated upon addition of diethyl ether or hexane to the reaction mixture. Single crystals of **5** were obtained by liquid diffusion of the toluene solution with hexane. Anal. Found: C, 35.9; H, 5.2. $[C_{32}H_{40}O_{16}I_4Pd_3][C_{13}H_{30}P]_2$ requires C, 34.9; H, 4.9%; IR (KBr) ν(cm^{-1}) 2977(s), 1723(vs), 1697(vs), 1257(s), 1200(s), 1035(s); $^{31}P\{^1H\}$-NMR in C_6D_6: δ 52.4 (s) ppm. The accurate FAB$^+$ mass spectrum showed the following peaks: 217.2087 (100%), 218.2120 (15%), 219.1259 (5%). The molecular peak corresponds to $[PBu^t_3Me]^+$ (calculated mass: 217.2085).

4.3. Crystallography

Crystal data for **2**: $C_{24}H_{54}P_2I_2Pd_2$, $M = 871.2$, monoclinic, space group *C*2 (no. 5), $a = 13.330(1)$, $b = 14.950(1)$, $c = 8.013(1)$ Å, $\beta = 92.57(1)°$, $V = 1595.3(2)$ Å^3, $Z = 2$ (the molecule has crystallographic C_2 symmetry), $D_{calc.} = 1.814$ g cm^{-3}, $\mu(Cu\text{-}K_\alpha) = 25.29$ mm^{-1}, $F(000) = 852$, $T = 183$ K; dark purple platy needles, 0.14 × 0.09 × 0.03 mm^3, Siemens P4/RA diffractometer, ω-scans, 1324 independent reflections. The structure was solved by the heavy atom method and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.040$, $wR_2 = 0.102$ for 1117 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 128°$] and 138 parameters. The final ΔF map did not contain any residual electron-density peaks in the locations required for the presence of a mirror plane normal to the two-fold axis, and thus the space group *C*2/*m* was precluded. This fact, coupled with a difference in *R* factors for the two enantiomeric structures (vide infra) gave further credence to the choice of $C2$ as the correct space group. The absolute chirality of the structure could not be unambiguously determined; though a significant difference was apparent in an R factor test [$R_1^+ = 0.0408$, $R_1^- = 0.0412$], the Flack parameter [$x^+ = 0.41(7)$, $x^- = 0.59(7)$] and the fact that the use of the TWIN instruction resulted in a lower overall R factor [$R_1^+ = 0.0402$] indicated the presence of racemic twinning. CCDC 141761.

Crystal data for **5**: $[C_{32}H_{40}O_{16}I_4Pd_3][C_{13}H_{30}P]_2$, $M = 1942.1$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.615(1)$, $b = 18.786(2)$, $c = 20.530(1)$ Å, $\alpha = 98.54(1)$, $\beta = 104.32(1)$, $\gamma = 103.67(1)°$, $V = 3759.9(5)$ Å^3, $Z = 2$ (there are two crystallographically independent C_i symmetric molecules in the asymmetric unit), $D_{calc.} = 1.715$ g cm^{-3}, $\mu(\text{Cu-K}_\alpha) = 19.49$ mm^{-1}, $F(000) = 1912$, $T = 203$ K; red rhombic needles, 0.30 × 0.26 × 0.05 mm, Siemens P4/RA diffractometer, ω-scans, 9877 independent reflections. The structure was solved by direct methods and the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.068$, $wR_2 = 0.169$ for 7227 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$] and 854 parameters. CCDC 141762.

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