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Synthesis and structural characterisation of $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$, an example of a palladium(I)–palladium(I) dimer

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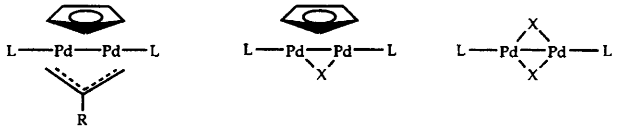
The syntheses, spectroscopic characterisation and in one case (X = Br) the single-crystal structure of the novel Pd^I–Pd^I dimers $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ (X = Br or I) have been determined; preliminary results on their reactions with CO, H_2, $CNC_6H_3Me_2$ and C_2H_2 have also been obtained.

Zero oxidation state palladium compounds are efficient catalysts in several organic syntheses[1] and an important step in the catalytic cycle is the oxidative addition of organic halides to the metal centre.[2] Recently considerable interest has been shown in palladium(I) dimers such as **I** and **II** (see Scheme 1) as possible intermediates in these organic transformations.[3,4] Interestingly the corresponding simple halogen bridged dimers **III** have not previously been reported. We have recently established[5,6] that the reaction between $[Pd_2(dba)_3]$ [dba = PhCHCHC(O)CHCHPh], PBu^t_3 and the halocarbons $CRCl_3$ (R = H or F) leads to the formation of the methylidyne clusters $[Pd_4(\mu_3\text{-}CR)(\mu\text{-}Cl)_3(PBu^t_3)_4]$ in which all the atoms of the organic halides are incorporated as ligands in the final cluster. When this reaction was repeated using $CHBr_3$ and CHI_3 the novel dimers $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ (X = Br **1**, X = I **2**) were obtained. Here we report their syntheses, spectroscopic characterisation and in one case (X = Br) the single-crystal X-ray structural characterisation.

When $[Pd_2(dba)_3]\cdot C_6H_6$ (0.28 g, 0.28 mmol) in toluene (25 cm^3) was treated with 2 mol equivalents of PBu^t_3 (0.11 g, 0.56 mmol) the solution changed to dark orange after 1 h. On addition of 0.5 mol equivalent of $CHBr_3$ (0.05 g, 0.14 mmol) the reaction mixture became green after 4 h. After the solvent had been removed dark green crystals of $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ were obtained from a toluene–acetone mixture at 4 °C (0.04 g, 18% yield).† When this reaction was repeated with $[Pd_2(dba)_3]\cdot C_6H_6$ (0.15 g, 0.14 mmol), $2PBu^t_3$ (0.06 g, 0.28 mmol) and CHI_3 (0.03 g, 0.07 mmol), purple crystals of $[Pd_2(\mu\text{-}I)_2(PBu^t_3)_2]$ were obtained from a toluene–diethyl ether mixture at 4 °C overnight (0.028 g, 23% yield).‡ A single-crystal X-ray analysis§ of compound **1** confirmed that it is a dimer with two bridging bromide ligands and a terminal PBu^t_3 group bonded to each palladium atom. The molecular structure (Fig. 1) demonstrates that this compound has a crystallographically imposed C_2 axis and the asymmetric unit consists of two half molecules. The dimer skeleton has an approximately C_{2h} symmetry. The Pd–Pd bond distances associated with the crystallographically independent molecules are 2.621(2) and 2.628(2) Å which are in the range 2.531–2.699 Å previously reported[3,4,10] for Pd^I–Pd^I dimers. An acute Pd–Br–Pd angle of 63.79(12)° is observed. This is due primarily to the short Pd–Pd bond which closes up the Pd–Br–Pd angle. The majority of Pd^I dimers are derived from the condensation of square-planar fragments, whereas these compounds and those previously reported by Kurosawa and co-



I **II** **III**

Scheme 1 Examples of Pd^I–Pd^I dimers with: two organic bridging groups (**I**), one organic bridge and one halogen (**II**) and two bridging halogens (**III**) (L = phosphine; R = H or alkyl; X = Cl, Br or I)

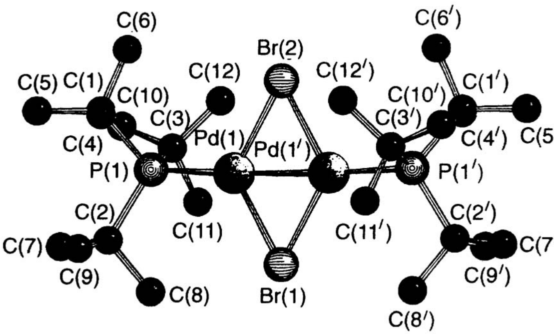


Fig. 1 Molecular structure of $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$. Important bond lengths (Å) include: Pd(1)–Pd(1′) 2.628(2), Pd(1)–Br(2) 2.460(4), Pd(1)–P(1) 2.296(4) [distances for the second half molecule: Pd(2)–Pd(2′) 2.621(2), Pd(2)–Br(3) 2.454(4), Pd(2)–P(2) 2.303(4)]

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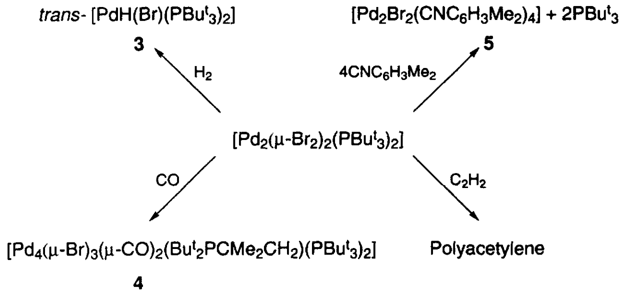
† Selected data for compound **1**. Yield 18% (Found: C, 37.3; H, 6.9; Br, 20.2. $C_{24}H_{54}Br_2P_2Pd_2$ requires C, 37.1; H, 7.0; Br, 20.6%), $^{31}P\text{-}\{^1H\}$ NMR ($[^2H_8]$toluene): δ 87.0 (s).

‡ Selected data for compound **2**. Yield 23% (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%), $^{31}P\text{-}\{^1H\}$ NMR ($[^2H_8]$toluene): δ 102.9 (s).

§ Crystal data. Compound **1** of formula $C_{24}H_{54}Br_2P_2Pd_2$, $M = 777.23$, crystal dimensions 0.2 × 0.2 × 0.1 mm, monoclinic, space group C_2, $a = 13.098$, $b = 14.610$, $c = 16.146$ Å, $\beta = 92.97°$, $U = 3085.6$ Å^3, $Z = 4$, $D_c = 1.673$ Mg m^{-3}, $\mu = 3.870$ mm^{-1}, $F(000) = 1560$. The data were collected on a small Mar Research image plate system using 3 kW sealed tube molybdenum radiation ($T = 293$ K). Exposure time was 4 min per frame, and 95 2° frames were collected. No correction for absorption was applied. Data were processed with the Mar Research versions of Wolfgang Kabsch's program XDS and XSCALE[7] giving an R_{merg} of 0.0571 for the complete dataset in XSCALE. Cell constants were determined using the GLOREF routine in XDS. The errors calculated by this program were unrealistically small, so values extrapolated from comparison with CAD4 data have been used. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities to give $R1 = 0.0549$, $wR2 = 0.1655$ for 1803 unique observed reflections, $w = [q/\sigma^2(F_o^2) + (0.1057P)^2 + (9.252P) + d + e \sin\theta]$ where $P = [f^*_{max}$ of (0 or F_o^2) + $(1 - f)F_c^2]$. The refinement was based on F^2. The structure could not be satisfactorily refined in space group $C2/c$. The programs SHELXS 86 and SHELXL 93[8] were used for all calculations. Hydrogen atoms were placed geometrically using the riding model with the thermal parameters set to 1.5 times that for the atom to which the hydrogen atom is attached. The picture was drawn with SCHAKAL.[9] Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/303.



Scheme 2 Reactions of $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ studied to date; satisfactory elemental analyses were obtained for **3**–**6**.

workers[3] and Felkin and Turner[4a] have trigonal co-ordination geometries if the metal–metal bond is excluded or very distorted square-planar geometries if it is included. Theoretical calculations on compound **1** have indicated that the bridged structure is 131.6 kJ mol^{-1} more stable than the open structure.[11]

When these reactions were repeated using different halogen-containing compounds (*i.e.* *N*-bromosuccinimide, *N*-iodosuccinimide, CBr_4 or CI_4) the dimers **1** and **2** were obtained in similar yields implying that the reactions may proceed by a free radical pathway. The $^{31}P\text{-}\{^1H\}$ NMR spectrum has identified $[Pd(PBu^t_3)_2]$ as an intermediate species. This complex has also been implicated in the syntheses of $[Pd_4(\mu_3\text{-}CR)(\mu\text{-}Cl)_3(PBu^t_3)_4]$ (R = H or F).[6] When $[Pd_2(dba)_3]$ was reacted with 2 equivalents of PBu^t_3 and 0.5 equivalent of *N*-chlorosuccinimide, the expected dimer was not formed. In the reactions between $[Pd_2(dba)_3]$, PBu^t_3 and all of these organic halides cyclometallated species similar to those previously reported[12] are formed in competing reactions which limit the observed yields of compounds **1** and **2**.

The reactions of $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ which have been investigated to date are summarised in Scheme 2. When H_2 was bubbled through a solution of compound **1** in toluene the dimer fragmented giving $[PdH(Br)(PBu^t_3)_2]$ **3**, as a pale yellow compound, and palladium metal. The hydride complex was identified by $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectroscopy. When the reaction was repeated in the presence of 2 equivalents of PBu^t_3 palladium metal was no longer formed and $[Pd(PBu^t_3)_2]$ and the hydride compound were formed in approximately equal yields.

When CO was bubbled through a solution of compound **1** in toluene, an immediate change of colour to dark orange was observed. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed the presence of two products. One of them was identified through $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopy, elemental analyses and positive-ion FAB mass spectrometry as the compound $[Pd_4(\mu\text{-}Br)_3(\mu\text{-}CO)_2(Bu^t_2PCMe_2CH_2)(PBu^t_3)_2]$ **4**. This compound has been recently synthesised[13] from $[Pd_4(O_2CMe)_4(CO)_4]$, PBu^t_3 and CBr_4 and will be fully discussed in a subsequent publication. It has a characteristic $^{31}P\text{-}\{^1H\}$ NMR spectrum with two singlets in a ratio 2 : 1. The smallest signal is observed at δ −10.0 which corresponds to a cyclometallated PBu^t_3 group. The other signal is observed in the *normal* region for Pd–PBu^t_3 (at δ 88.0). When the same reaction was carried out with compound **2**, a dark red compound was formed reversibly. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet at δ 102 and the IR spectrum suggested that there are bridging CO groups in the product. However, this compound readily lost the CO giving back the original Pd^I–Pd^I dimer.

The reaction between compound **1** and 4 equivalents of $CNC_6H_3Me_2$ displaced the two phosphines of the original compound giving $[Pd_2Br_2(CNC_6H_3Me_2)_4]$ **5**. When this reaction was carried out with compound **2**, the analogous compound $[Pd_2I_2(CNC_6H_3Me_2)_4]$ **6** was formed. These compounds were identified through IR, positive-ion FAB mass spectrometry and elemental analyses. The IR spectrum of these compounds showed bands at 2155 and 2151 cm^{-1} for the Br and I compounds suggesting that the $CNC_6H_3Me_2$ groups are all terminal. Similar compounds with comparable spectroscopic properties have been previously reported.[14]

When dissolved in toluene compounds **1** or **2** are good initiators for the polymerisation of acetylene. Compound **1** undergoes some decomposition in the process, whereas **2** is a catalyst.

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