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Synthesis of two novel dinuclear palladium(I) complexes and studies of their catalytic activity in amination reactions†

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Two novel palladium(I) dinuclear complexes have been prepared and their structural characterization has revealed an unprecedented μ^2-η^3:η^3 coordination between a phenyl ring from P^tBu_2Bph (Bph = Biphenyl) and the Pd^I–Pd^I unit present in the complexes.

Dinuclear Pd^I–Pd^I complexes tend to react readily with small molecules, being potential catalysts for a wide range of transformations.[1] Consequently, there is considerable interest in developing novel synthetic routes to prepare this type of dinuclear compound. We have previously reported the synthesis of the dinuclear species $[Pd_2(\mu\text{-}X)_2(P^tBu_3)_2]$ (X = Br, I).[2,3] These compounds have a strained $Pd_2(\mu\text{-}X)_2$ core which is probably the reason for their high reactivity towards a wide range of small molecules (namely CO, CNR, O_2 and C_2R_2). More recently Hartwig[4] and Prashad[5] have demonstrated that $[Pd_2(\mu\text{-}Br)_2(P^tBu_3)_2]$ is a precatalyst for the amination of various aryl halides. Since the reactivity of Pd^I–Pd^I complexes is highly dependent on the nature of the phosphine it is of interest to synthesise dinuclear complexes with a wide range of phosphines.

As part of our systematic efforts to prepare novel Pd^I–Pd^I compounds we have recently turned our attention to some of the sterically demanding phosphines reported by Buchwald.[6] Herein we report the formation of the new mono-phosphine palladium complex $[Pd(dba)(P^tBu_2Bph)]$ (**1**) (where Bph = biphenyl) which upon addition of $[Pd(COD)X_2]$ (X = Br, Cl) reacts to form the novel dinuclear palladium(I) complexes $[Pd_2X(\mu\text{-}X)(\mu\text{-}P^tBu_2Bph)]$ (**2**, X = Br; **3**, X = Cl).

Using the same conproportionation approach previously reported to prepare $[Pd_2(\mu\text{-}Br)_2(P^tBu_3)_2]$,[3] one equivalent of $[Pd_2(dba)_3]$ and four of P^tBu_2Bph were mixed and reacted for 48 hours. Upon addition of one equivalent of $[Pd(COD)Br_2]$ to the reaction mixture, an immediate color change from orange to brown was observed followed by the precipitation of a dark brown solid which was isolated and, on the basis of structural, spectroscopic and analytical techniques, characterized as the novel palladium complex **2** (see Fig. 1 and structural discussion below).‡ As expected, **2** is a Pd^I–Pd^I dinuclear complex with a bridging bromide, but with only one phosphine retained in the dinuclear core—in spite of having used the appropriate stoichiometry to form a complex with formulation $[Pd_2(\mu\text{-}Br)_2(P^tBu_2Bph)_2]$. Carrying out the reaction in a 2 : 1 palladium : phosphine ratio led to the formation of **2** in higher yields. When a similar conproportionation reaction was carried out using $[Pd(COD)Cl_2]$ as the palladium(II) source, the dinuclear species **3** was obtained (see Scheme 1).§ Crystals of **2** suitable for X-ray analysis were obtained by layering a THF solution of **2** with hexane. The single crystal analysis revealed the molecular structure shown in Fig. 1.¶

The structure of the related chloride complex **3** was also determined† and shown to be isostructural with **2**. The two rings of the biphenyl group are rotated substantially with respect to each other (by 73 and 79° respectively in **2** and **3**) thereby facilitating π-bonding between the terminal ring and the metal centers. In both **2** and **3** there is a significant pyramidalization at C(1), [0.14, 0.15 Å respectively] coupled with a contraction of the P–C(12)–C(7) angle [115.2(5) and 115.2(7)°], allowing a symmetric approach of C(1) and C(4) to Pd(1) and Pd(2) respectively. It is interesting to note that in both these complexes the plane of the phenyl ring is not orthogonal to the Pd_2X plane. Thus the distances from the metal centers to each of the *ortho* and *meta*-carbon atoms are asymmetric, although all of them short enough to be considered bonding (see Fig. 1 and ESI†). These differences in the Pd–C distances are accentuated by an additional slight skewing of the C(1)···(4) vector with respect to the Pd(1)–Pd(2) bond direction. Complexes where an arene is π-coordinated to a Pd^I–Pd^I unit are rare.[7–11] In contrast to the previously reported examples, to the best of our knowledge, **2** and **3** are the first structurally characterised compounds where an arene is coordinated to a Pd^I–Pd^I unit in a μ^2-η^3:η^3 fashion.[12]

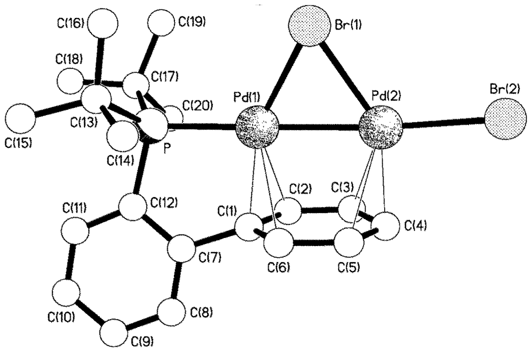
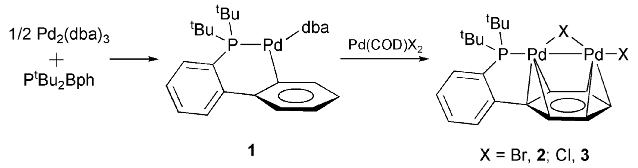


Fig. 1 The molecular structure of **2**. Selected bond lengths (Å); Pd(1)–Pd(2) 2.5627(8), Pd(1)–Br(1) 2.4615(9), Pd(1)–P 2.2841(17), Pd(1)–C(1) 2.140(6), Pd(1)–C(2) 2.340(7), Pd(1)–C(6) 2.637(7), Pd(2)–Br(1) 2.5633(10), Pd(2)–Br(2) 2.4931(10), Pd(2)–C(3) 2.443(8), Pd(2)–C(4) 2.113(8), Pd(2)–C(5) 2.545(9).

The solid state structures of **2** and **3** are consistent with the spectroscopic and analytical characterization of the bulk materials. The $^{31}P\{^1H\}$ NMR spectra of both dinuclear compounds show singlets (at 67.7 and 62.0 ppm for **2** and **3** respectively) while the FAB(+) mass spectra indicate the presence of peaks for [**2** − Br] and [**3** − Cl] respectively. The ^1H and ^{13}C NMR data are consistent with a μ^2-η^3:η^3 coordinated phenyl group (the resonances of which are shifted to higher field). Elemental analyses of the bulk materials were also consistent with the formulations found in the solid state.

These results indicate that the reaction between a Pd^0 complex—generated from the reaction of $[Pd_2(dba)_3]$ with P^tBu_2Bph—and $[Pd(COD)X_2]$ leads to the formation of the dinuclear species **2** and **3**. Consequently it was of interest to determine the exact nature of the palladium(0) compound formed *in situ* prior to the conproportionation reactions. One equivalent of $[Pd_2(dba)_3]$ and two of P^tBu_2Bph were reacted for 48 hours. After this time $^{31}P\{^1H\}$ NMR



Scheme 1

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† Electronic supplementary information (ESI) available: experimental details and X-ray data for compounds **1–3**. See http://www.rsc.org/suppdata/cc/b4/b402283a/

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spectroscopy indicated that most of the free phosphine had been consumed and only one new phosphine-containing species [δ = 59.5 ppm (s)] had formed. The solvent was evaporated under reduced pressure and the remaining oily material was recrystallized from a diethyl ether–hexane mixture to yield [Pd(dba)(P^{t}Bu$_2$Bph)] (**1**). The crystal structure of **1** shows it to be very similar to the closely related PCy$_2$(phenanthrene) and PCy$_2$(dimethoxybiphenyl) analogues previously reported by Buchwald.[13,14] The palladium is π-bonded to one of the olefinic units of the dba and σ-bonded to the phosphorus atom, the third coordination site on the metal being occupied by a "linkage" to one of the *ortho* carbon atoms of the terminal phenyl ring of the biphenyl unit (Fig. 2).§ The coordination geometry in **1** is analogous to that observed in the recently reported[14] Pd(dba){PCy$_2$(dimethoxybiphenyl)} complex where the "bond" between the palladium centre and the aromatic ring involves only a single carbon atom. As was observed in **2** and **3** the two rings of the biphenyl group in **1** are rotated substantially with respect to each other (66°) thereby facilitating π-bonding between the terminal ring and the metal centre. The solid state structure of **1** is consistent with the spectroscopic and analytical characterization of the bulk material. The ^{31}P{^{1}H} spectrum of the complex shows a singlet at 59.5 ppm while the molecular peak (*m*/*z* = 638 amu) in the FAB(+) mass spectrum corresponds to the proposed formulation.

Buchwald has established that different palladium sources in combination with biaryl-based phosphines catalyse cross coupling reactions.[15] It was thus of interest to evaluate the catalytic properties of **2** and **3**. Four amination reactions were studied and the preliminary results are summarized in Table 1.

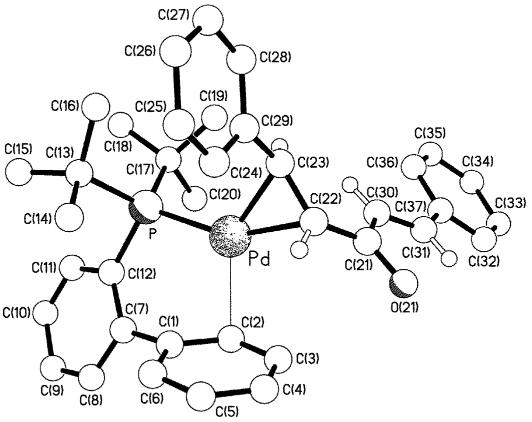
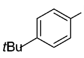
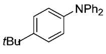
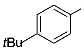
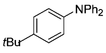
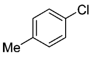
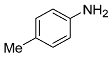
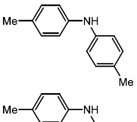
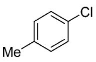
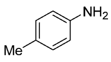
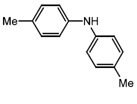


Fig. 2 Molecular structure of **1**. Selected bond lengths (Å); Pd–P 2.3269(18), Pd–C(2) 2.401(6), Pd–C(22) 2.165(6), Pd–C(23) 2.124(6).

Table 1 Amination of aryl halides[a]

Cat.	Aryl halide	Amine	Product	Time/h	Yield (%)[b]
2		Ph$_2$NH		19	86
3		Ph$_2$NH		19	76
2				3	78
3				3	81

[a] The reactions were carried out at RT, in THF (1 mL) using either 1 mol% of either **2** or **3** and on a 1 mmol scale (see ESI for details). [b] Isolated yields.

The expected coupling products were obtained in good yields indicating that **2** and **3** catalyse the amination of aryl halides. It is worth noting that the coupling reaction that yields di-*p*-tolylamine has been previously reported by Buchwald[16] using [Pd$_2$(dba)$_3$] and P^{t}Bu$_2$Bph (reported yield of 90% at 80 °C). As can be seen in Table 1, **2** and **3** catalyse this reaction at room temperature, in a comparable timescale and in reasonably good yields. We are currently studying a wider range of substrates and experimental conditions to optimise the cross-coupling reactions and elucidate the mechanism of the catalytic process. In summary, two novel dinuclear palladium(I) compounds have been prepared and demonstrated to have an unusual structure with a μ^2-η^3:η^3 coordinated phenyl ring bound to the Pd^{I}–Pd^{I} unit of the complexes. Furthermore, these compounds have been shown to catalyse the amination of aryl halides in good yields at room temperature.

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Notes and references

‡ *Selected data for* **2**: Yield: 45%. Anal. Calcd for C$_{20}$H$_{27}$Br$_2$PPd$_2$: C, 35.80, H, 4.06. Found: C, 35.89, H, 4.01. ^{31}P{^{1}H} NMR (THF-d$_8$) δ 67.7 (s); FAB(+) MS: *m*/*z* 591 (M − Br)

§ *Selected data for* **3**: Yield: 71%. Anal. Calcd for C$_{20}$H$_{27}$Cl$_2$PPd$_2$: C, 41.26, H, 4.60. Found: C 40.99, H 4.42. ^{31}P{^{1}H} NMR (DCM–d$_2$): δ 62.0 (s); FAB(+) MS: *m*/*z* 549 (M–Cl)

¶ *Crystal data for* **1**: C$_{37}$H$_{41}$OPPd·0.5C$_6$H$_{14}$, M = 682.15, $P2_1/c$ (no. 14), a = 18.999(3), b = 9.9530(18), c = 19.111(6) Å, β = 102.658(16)°, V = 3526.0(13) Å^3, Z = 4, D_c = 1.285 g cm^{-3}, μ(Mo–Kα) = 0.600 mm^{-1}, T = 203 K; 6208 independent measured reflections, R_1 = 0.063, wR_2 = 0.119, 3922 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 50°], 386 parameters. CCDC 224107. *For* **2**: C$_{20}$H$_{27}$Br$_2$PPd$_2$, M = 671.01, $I2/a$ (no. 15), a = 16.195(3), b = 8.037(2), c = 34.199(9) Å, β = 98.901(11)°, V = 4397.8(18) Å^3, Z = 8, D_c = 2.027 g cm^{-3}, μ(Mo–Kα) = 5.344 mm^{-1}, T = 203 K; 6418 independent measured reflections, R_1 = 0.054, wR_2 = 0.091, 3989 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 60°], 226 parameters. CCDC 224108. See http://www.rsc.org/suppdata/cc/b4/b402283a/ for crystallographic data in .cif format.

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