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The surprisingly facile formation of Pd(I)-phosphido complexes from *ortho*-biphenylphosphines and palladium acetate†

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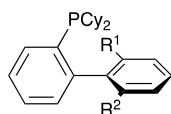
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The widely-used *ortho*-biphenylphosphine ligands SPhos and RuPhos not only undergo facile orthometallation with palladium acetate, yielding strained, four-membered dimeric palladacycles but more surprisingly, in the presence of alcoholic solvents, along with the less encumbered analogue MePhos, yield unusual dinuclear Pd(I) complexes, in which the Pd-centers are bridged by both a phosphido ligand and by the arene of a coordinated phosphine donor.

SPhos was one of the first of a class of highly successful *ortho*-biphenylphosphines, *o*-BPPs, introduced by Buchwald and co-workers.¹ To date, over 1100 publications include the use of SPhos as a ligand, while Buchwald's original report on the preparation and use of SPhos in palladium-catalysed Suzuki cross-coupling has been cited nearly 700 times. Simple mixtures of SPhos-ligated palladium pre-catalysts have been exploited in a wide range of catalytic transformations, including the Suzuki reaction,^{2,3} Kumada-Corriu cross-coupling,⁴ Negishi coupling,⁵ Buchwald-Hartwig amination,⁶ the borylation of aryl chlorides,⁷ and (hetero)aromatic C-H arylation reactions.⁸

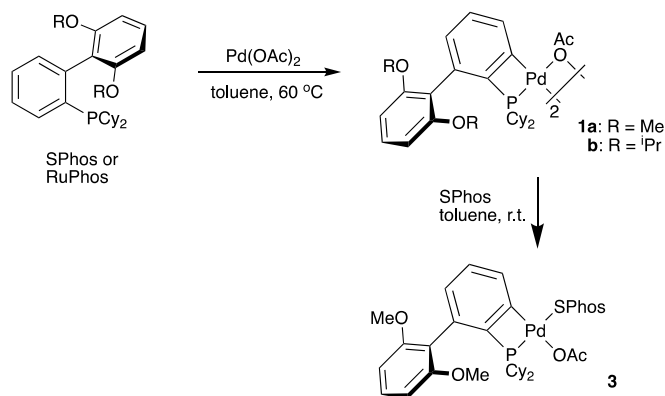


SPhos, R¹ = R² = OMe
RuPhos, R¹ = R² = OⁱPr
MePhos, R¹ = Me; R² = H

Given the very high utility of palladium-SPhos mixtures as pre-catalysts in a wide variety of transformations it is important to understand the precise roles and reactivities of the ligand. Herein we report that not only do SPhos and the related ligand RuPhos give strained, four-membered palladacycles under mild

conditions, but that in the presence of alcoholic solvents these ligands, and the related but less encumbered *o*-BPP ligand MePhos, undergo facile and unexpected P-C cleavage to generate dimeric palladium(I) phosphido-bridged complexes.

Warming Pd(OAc)₂ with 1 equivalent of SPhos or RuPhos in toluene at 60 °C for two hours gave the palladacyclic complexes, **1a** and **b** (Scheme 1);⁹ the single crystal X-ray structure of complex **1a** is shown in Figure 1(a). The ³¹P NMR spectrum of complex **1a** shows a singlet at δ -47.7 ppm, consistent with the formation of a strained, 4-membered palladacycle. To the best of our knowledge, no 4-membered palladacycles of SPhos has been structurally characterised, although structures with other *o*-BPP ligands with bulkier *tert*-butyl residues on the phosphorus are known.¹⁰ Interestingly, when a 1:1 mixture of Pd(OAc)₂ and SPhos in a mixture of dichloromethane and methanol (2:1) was left standing at room temperature for several weeks a small number of crystals of the chloride-bridged analogue **2** were obtained, the crystal structure of which is shown in Figure 1(b) suggesting reasonably facile halide abstraction from the solvent. This reaction proved highly capricious and as yet we have been unable to produce **2** in useful amounts.



Scheme 1. Syntheses of palladacycles.

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† Dedicated to Professor Geoff Cloke on occasion of his 65th birthday, many happy returns Geoff.

Electronic Supplementary Information (ESI) available: Crystallographic data for compounds **1a**, **2**, **4a** and **4b**, CCDC 1884584-1884587. Experimental details, spectroscopic data, crystallographic data and CIF files, see DOI: 10.1039/x0xx00000x

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Reaction of the palladacycle **1a** with SPhos in toluene yielded the mononuclear adduct **3**. The ^{31}P NMR spectrum of the complex **3** revealed an AB system with a high-field doublet for the orthometallated SPhos ligand at δ -49.2 and a low field doublet at 49.7 for the non-orthometallated SPhos ligand. The large (394.7 Hz) mutual coupling indicates a *trans*-disposition of the two inequivalent P-donors.

(a)

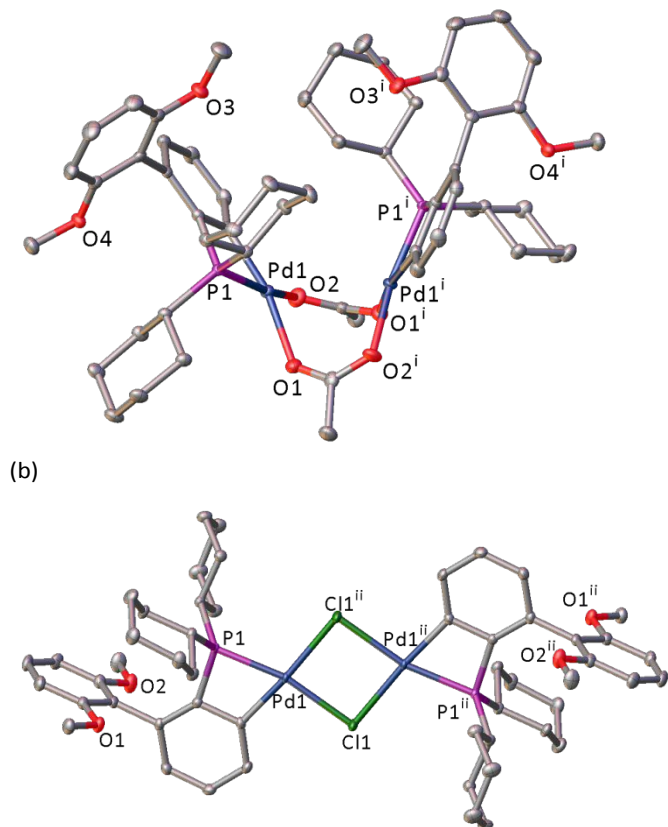
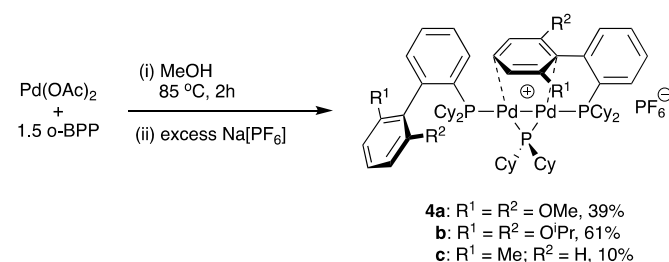


Figure 1. Crystal structures of the palladacycles of SPhos. (a) Complex **1a** with hydrogen atoms and toluene solvent omitted for clarity. Symmetry code *i* $\frac{1}{2}$ -*x*, +*y*, $\frac{1}{2}$ -*z*. (b) Complex **2** Crystal structure of **2**, with hydrogen atoms omitted for clarity. Symmetry code *ii* 1-*x*, -*y*, -*z*.

In contrast with the reactions in toluene, heating palladium acetate with SPhos, RuPhos or the smaller analogue MePhos in methanol followed by salt metathesis with $\text{Na}[\text{PF}_6]$ ¹¹ and purification by column chromatography on silica, yielded the unusual dinuclear phosphido- and arene-bridged Pd(I) cationic complexes **4a** – **c** respectively (Scheme 2) and the crystal structures of the cations **4a** and **b** are shown in Figure 2. The yields of the products suggest that the formation of the phosphido-bridged products is favoured by increased steric bulk in the ortho-position of the substituted arene of the ligands. Clearly, these dinuclear palladium (I) complexes are related to the previously reported species **5** and **6**,¹² with the exception that they contain a phosphido-bridge, formed by P-C bond scission.¹³ Similarly, phosphide-bridged Pd(I) dimers such as **7** are known,¹⁴ but the phosphide-bridged, arene-bridged motif displayed by the complexes **4** is very rare with, to the best of our knowledge, only one structurally-characterised example (**8**) reported previously.¹⁵ The Pd-Pd bond-lengths in **4a** and **b**

(2.6246(9) and 2.6076(4) Å respectively) fall in the range of those reported for one-atom bridged Pd(I) dimers,^{16,17}



Scheme 2. Synthesis of Pd(I)-phosphido dimers.

(a)

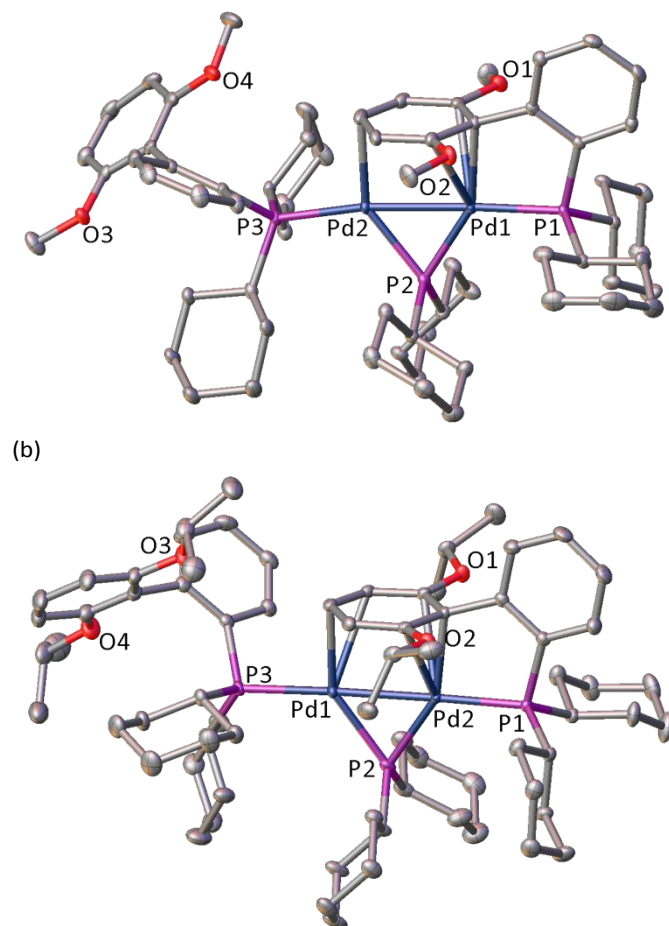
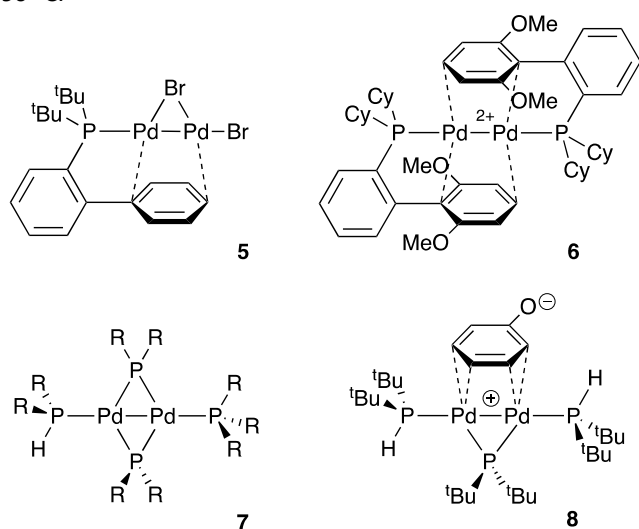


Figure 2. X-ray crystal structures of the cationic complexes **4a** and **b**, $[\text{PF}_6]^-$ and H-atoms omitted for clarity.

The ^{31}P NMR spectra of the complexes **4a** and **b** recorded at room temperature show distinct environments for the terminal and arene-bridging SPhos donors, along with a low-field doublet of doublets for the phosphide (280.1 and 276.9 respectively for **4a** and **b**) with mutual couplings between all of the P-donors.⁹ By contrast, while a doublet of doublets is apparent at 290.9 ppm for the phosphide ligand in **4c** at room temperature, a single, very broad peak for the phosphine environments centered at 43 ppm is suggestive of a fluxional process, most likely the interchange of coordinating and non-coordinating

arene groups on the two phosphines. Variable temperature ^{31}P NMR spectroscopy of complexes **4a** and **b** indicate that coalescence occurs in the former above 90 °C, whereas in the latter the two phosphine environments coalesce to a doublet by 90 °C.⁹

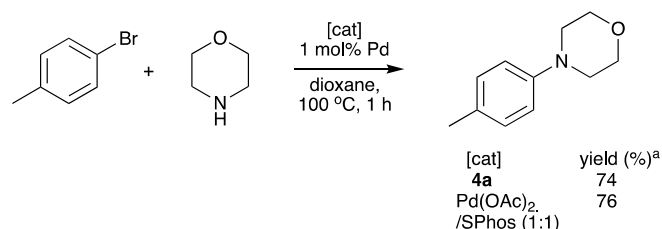


In order to briefly probe the mechanism of formation of **4a**, we recorded the ^{31}P NMR spectra of crude reaction mixtures obtained on heating SPhos with palladium acetate in a variety of alcohols (85 °C, 2 h)⁹ or 5% water in 1,4-dioxane. From this it was established that the formation of **4a** fell in the order MeOH > EtOH > MeOCH₂CH₂OH > *n*-butanol while no product was observed with *t*-amyl alcohol or water. We have recently shown that palladium acetate reacts very readily with water or alcohols to give palladium trimers with a μ^2 -OR or -OH ligand or a hexametallic complex with a μ^4 -oxo,¹⁸ but it seems we can rule out such species acting simply as intramolecular bases here, due to the lack of reactivity in water or *t*-amyl alcohol. Simple protonation of an intermediate by the alcohol can also be excluded, again due to the lack of formation of **4a** in either *t*-amyl alcohol or water. It seems likely, therefore, that the function of the alcohol is to act as a β -hydride donor via the formation of a palladium alkoxide.

All the ^{31}P NMR spectra recorded for the crude reaction mixtures obtained in ethanol, *n*-butanol, 2-methoxyethanol and *t*-amyl alcohol also showed the presence of the palladacyclic SPhos-adduct **3**.⁹ However, heating solutions of the palladacycle **1a** or the adduct **3** in methanol did not give any of the phosphide complex **4a**, as determined by ^{31}P NMR spectroscopy of crude reaction mixtures. This suggests that while palladacycles can form on heating in alcohols, they do not appear to be intermediates in the formation of the phosphide-bridged dimers **4**. Indeed, we have previously shown that the arene motif in a palladacycle can itself act as a bridging group in a Pd(I) dimer.¹⁹

Finally, we very briefly examined the application of one of the Pd(I)-dimers, complex **4a**, in a representative catalytic reaction. Pd(I) dimers have been exploited as pre-catalysts in a range of catalytic reactions, including Suzuki coupling, the Heck

reaction, Kumada coupling, Negishi coupling and Buchwald-Hartwig amination.²⁰⁻²⁷ Accordingly, we briefly examined the amination of 4-bromotoluene with morpholine, under conditions reported recently using complex **6** as a pre-catalyst²⁷ and the results are summarised in Scheme 3. As can be seen, complex **4a** is a viable pre-catalyst for the reaction, rather than a decomposition product, giving similar performance to a 1:1 mixture of palladium acetate and SPhos.



Scheme 3. Buchwald-Hartwig amination. ^a Yield determined by GC, dodecane internal standard.

In conclusion, the *o*-BPP ligands SPhos, RuPhos and MePhos do not simply behave as innocent P-donor ligands on reaction with palladium acetate in either toluene or alcohols at elevated temperatures. In the former solvent, SPhos and RuPhos give strained 4-membered palladacycles, while in alcoholic solvents that possess β -hydrogens all three ligands give Pd(I) dimers bridged by an arene from one of the coordinated phosphines and a phosphide derived by P-C bond-cleavage. We are currently fully exploring the implications of this non-innocent behaviour to catalysis and these results will be published in due course.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- S. D. Walker, T. E. Barder, J. R. Martinelli and S. L. Buchwald, *Angew. Chem. Int. Ed.* 2004, **43**, 1871.
- T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.* 2005, **127**, 4685.
- Overview: R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461.
- R. Martin and S. L. Buchwald, *J. Am. Chem. Soc.* 2007, **129**, 3844.
- Selected examples: (a) J. E. Milne and S. L. Buchwald, *J. Am. Chem. Soc.* 2004, **126**, 13028; (b) A. J. Ross, H. L. Lang and R. F. W. Jackson, *J. Org. Chem.* 2010, **75**, 245; (c) S. Seel, T.

COMMUNICATION

Journal Name

- Thaler, K. Takatsu, C. Zhang, H. Zipse, B. F. Straub, P. Mayer, and P. Knochel, *J. Am. Chem. Soc.* 2011, **133**, 4774.
- 6 Overview: D. S. Surry and S. L. Buchwald, *Chem. Sci.*, 2011, **2**, 27.
- 7 K. L. Billingsley, T. E. Barder and S. L. Buchwald, *Angew. Chem. Int. Ed.* 2007, **46**, 5359
- 8 Selected examples: (a) M. Lafrance, D. Shore and K. Fagnou, *Org. Lett.* 2006, **8**, 5097; (b) R. B. Bedford, S. J. Durrant and M. Montgomery, *Angew. Chem. Int. Ed.* 2015, **127**, 8911; (c) F. Ichiokaa Y. Itaia, Y. Nishiib and M. Miura, *Synlett* 2017, **28**, 2812.
- 9 See supplementary information for details.
- 10 (a) U. Christmann, D. A. Pantazis, J. Benet-Buchholz, J. E. McGrady, F. Maseras and R. Vilar, *J. Am. Chem. Soc.* 2006, **128**, 6376; (b) A. M. Allgeier, B. J. Shaw, T.-L. Hwang, J. E. Milne, J. S. Tedrow and C. N. Wilde *Organometallics*, 2012, **31**, 519; (c) C. Jimeno, U. Christmann, E. C. Escudero-Adán, Ramon Vilar and M. A. Pericàs, *Chem. Eur. J.* 2012, **18**, 16510; (d) C. W. Holzappel and B. Omondi, *Acta Cryst.* 2013, **E69**, m86.
- 11 Without this metathesis step, the nature of the counter-anion proved capricious; on separate occasions crystal structures containing nitrite or acetate were obtained.
- 12 (a) U. Christmann, R. Vilar, A. J. P. White and D. J. Williams, *Chem. Commun.* 2004, 1294; (b) T. E. Barder, *J. Am. Chem. Soc.* 2006, **128**, 898.
- 13 For an overview of related P-C bond cleavage processes, see: A. W. Parkins, *Coord. Chem. Rev.* 2006, **250**, 449.
- 14 A. M. Arif, D. E. Heaton, R. A. Jones and C. M. Nunn *Inorg. Chem.* 1987, **26**, 4228.
- 15 M. Sommovigo, M. Pasquali, P. Leoni, D. Braga and P. Sabatino *Chem. Ber.* 1991, **124**, 97.
- 16 S. Lin, D. E. Herbert, A. Velian, M. W. Day and T. Agapie, *J. Am. Chem. Soc.* 2013, **135**, 15830.
- 17 (a) T. Murahashi, N. Kanehisa, Y. Kai, T. Otani and H. Kurosawa, *Chem. Commun.* 1996, 825; (b) T. Murahashi and H. Kurosawa, *J. Organomet. Chem.* 1999, **574**, 142.
- 18 R. B. Bedford, J. G. Bowen, R. B. Davidson, M. F. Haddow, A. E. Seymour-Julen, H. A. Sparkes and R. L. Webster *Angew. Chem. Int. Ed.* 2015, **54**, 6591.
- 19 R. B. Bedford, M. F. Haddow, C. J. Mitchell and R. L. Webster, *Angew. Chem. Int. Ed.* 2011, **50**, 5524.
- 20 R. K. Das, B. Saha, S. M. W. Rahaman and J. K. Bera, *Chem. Eur. J.*, 2010, **16**, 14459.
- 21 M. Aufiero, T. Scattolin, F. Proutière and F. Schoenebeck, *Organometallics*, 2015, **34**, 5191.
- 22 T. Sperger, C. K. Stirner and F. Schoenebeck, *Synthesis*, 2017, 115.
- 23 I. Kalvet, T. Sperger, T. Scattolin, G. Magnin and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2017, **56**, 7078.
- 24 S. T. Keaveney, G. Kunda and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2018, **57**, 12573.
- 25 I. Kalvet, G. Magnin and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2017, **56**, 1581.
- 26 J. P. Stambuli, R. Kuwano and J. F. Hartwig, *Angew. Chem. Int. Ed.* 2002, **41**, 4746.
- 27 K. O. Kirlikovali, E. Cho, T. J. Downard, L. Grigoryan, Z. Han, S. Hong, D. Jung, J. C. Quintana, V. Reynoso, S. Ro, Y. Shen, K. Swartz, E. T. Sahakyan, A. I. Wixtrom, B. Yoshida, A. L. Rheingold and A. M. Spokoyny, *Dalton Trans.*, 2018, **47**, 3684.

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Heating palladium acetate with *ortho*-biphenylphosphine ligands in alcoholic solvents gives facile P-C bond-cleavage, yielding Pd(I)-dimers bridged by phosphide ligands.