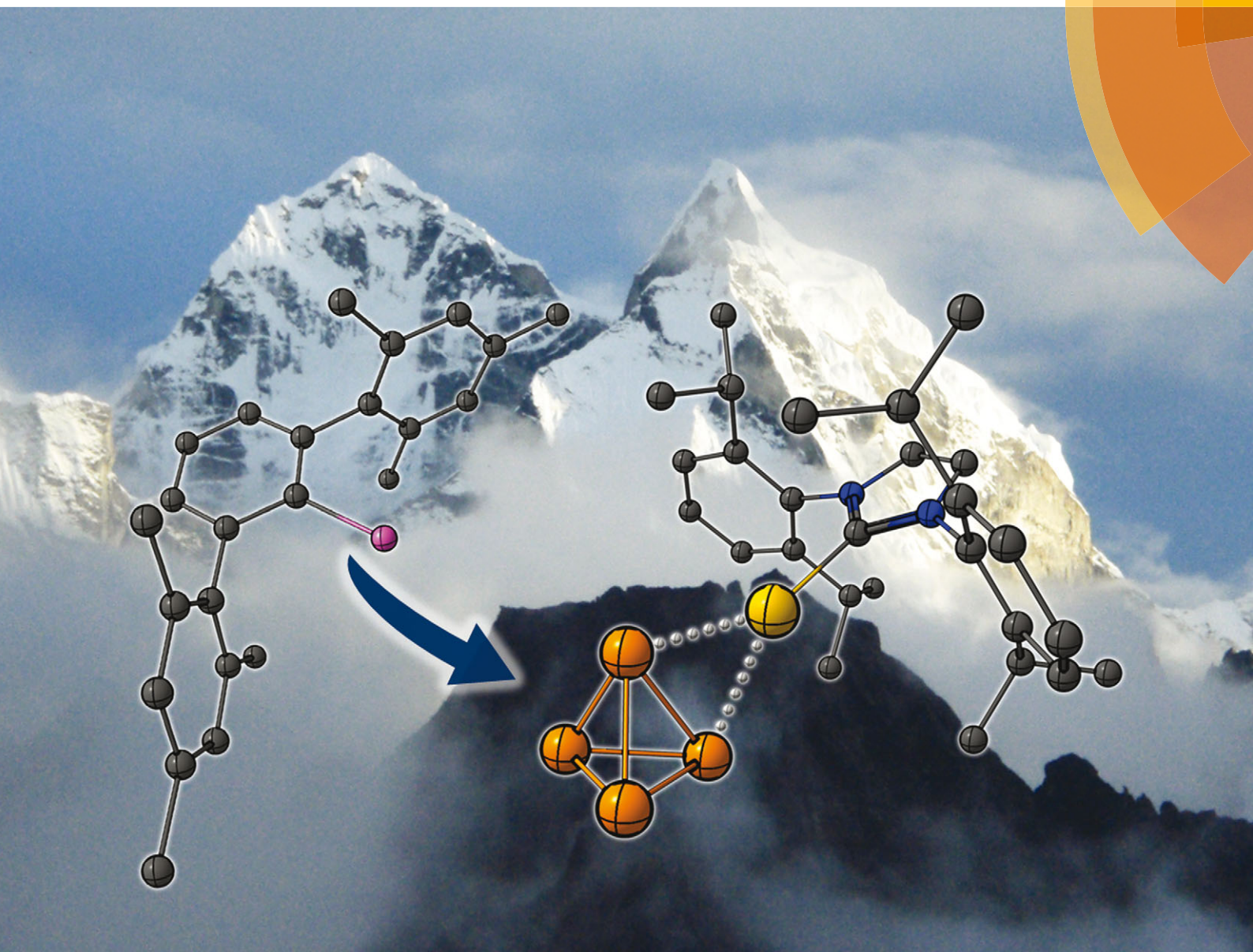


ChemComm

Chemical Communications

www.rsc.org/chemcomm



ISSN 1359-7345



COMMUNICATION

Koop Lammertsma *et al.*
Functionalization of P_4 in the coordination sphere of coinage metal cations

175 YEARS



Cite this: *Chem. Commun.*, 2016, 52, 3284

Received 6th December 2015,
Accepted 30th December 2015

DOI: 10.1039/c5cc10037b

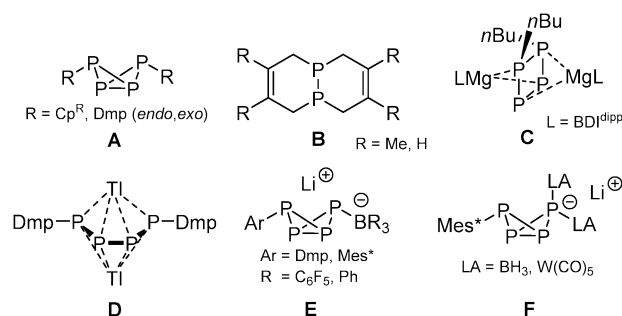
www.rsc.org/chemcomm

Functionalization of P₄ in the coordination sphere of coinage metal cations†

Jaap E. Borger,^a Martijn S. Bakker,^a Andreas W. Ehlers,^a Martin Lutz,^b
J. Chris Slootweg^a and Koop Lammertsma^{a,c}

Selective functionalization of white phosphorus is achieved by addition of ArLi to unique cationic coinage metal η²-P₄ complexes. This novel approach allows controlled P–C bond formation using the bulky DmpLi (Dmp = 2,6-Mes₂C₆H₃) and the unencumbered MesLi, giving sterically diverse doubly complexed RP₄ butterfly derivatives in a single step.

Controlling direct P–C bond formation using P₄ as starting material is of interest in avoiding chlorinated intermediates, such as PCl₃, for the production of organophosphorus compounds. Yet this task is extremely challenging due to the highly reactive nature of the P₄ tetrahedron.¹ Currently, several selective methods have been developed, like the use of ambiphilic carbenes pioneered by the group of Bertrand,² and the metal-mediated radical functionalization of P₄ reported by Scheer *et al.* (A; R = Cp^R, Scheme 1)³ as well as by Cummins and co-workers (R = Dmp),⁴ who also demonstrated facile P-functionalization chemistry by embedding photochemically generated P₂ fragments into organic frameworks (B).⁵ In contrast, conventional methods for the formation of P–C bonds,⁶ such as the use of organolithium and Grignard reagents, have been less fruitful due to the low selectivity and complex product distributions associated with their reactions with P₄.⁷ An intriguing exception was recently described by Hill, who achieved selective activation of P₄ using a β-diketiminato organomagnesium compound, producing the [nBu₂P₄]^{2−} dianion C,⁸ which is related to the thallium tetraphosphabutadienediide [Ar₂P₄]^{2−} salt D reported by Power *et al.*⁹ We showed that the reactivity of bulky ArLi reagents



Scheme 1 Methods allowing selective direct P–C bond formation using P₄. Dmp = 2,6-dimesitylphenyl; BDI^{dipp} = HC(C(Me)N(2,6-iPr₂C₆H₃))₂; Mes* = 2,4,6-tBu₃C₆H₂; Cp^R = Cp^{BIG}, Cp^{'''}, Cp*, Cp^{4iPr}.

toward P₄ can be controlled in the presence of Lewis acids (B(C₆F₅)₃ and BPh₃), giving the LA-stabilized bicyclo[1.1.0]tetraphosphabutanides [ArP₄·LA][−] E that can subsequently be functionalized selectively generating the neutral disubstituted bicyclic phosphanes ArP₄R (type A) and the doubly coordinated tetraphosphides [ArP₄·(LA)₂][−] F.¹⁰ Key in this approach is the irreversible formation of the transient phosphide [RP₄][−] that is directly trapped by the Lewis acid. Note that P₄ does not form an adduct with BPh₃ or even B(C₆F₅)₃,¹⁰ and therefore requires the use of sterically encumbered FLP-type ArLi/LA combinations to avoid quenching. In this work, we present an alternative strategy by using novel cationic coinage metal based Lewis adducts of P₄ as synthon that now tolerate varied bulk on the ArLi reagents, as demonstrated by the selective addition of Dmp (Dmp = 2,6-dimesitylphenyl) and mesityl lithium, resulting in the formation of unique doubly complexed RP₄ butterfly cations.

Commercially available IPrMCl (M = Cu, Au; IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) in combination with Li⁺ [Al(pftb)₄][−] (pftb = perfluoro-*tert*-butoxy)^{11,12} as chloride scavenger were found to be suitable starting materials allowing the isolation of readily available LA–P₄ adducts. The complexation of P₄ was achieved by dropwise addition of a solution of IPrMCl (1 equiv.; M = Cu, Au) in DCM to a suspension of white phosphorus (1.1 equiv.) and Li[Al(pftb)₄] (1 equiv.) in DCM at 0 °C (Scheme 2), which

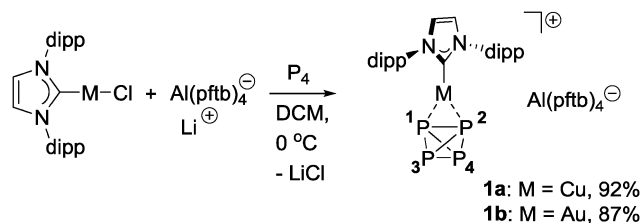
^a Department of Chemistry and Pharmaceutical Sciences Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands. E-mail: K.Lammertsma@vu.nl

^b Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

^c Department of Chemistry, University of Johannesburg, Auckland Park, Johannesburg, 2006 South Africa

† Electronic supplementary information (ESI) available. CCDC 1440355 and 1440356. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc10037b





Scheme 2 Synthesis of cationic η^2 -P₄ complexes of copper and gold (pftb = OC(CF₃)₃; dipp = 2,6-diisopropylphenyl).

resulted in a sharp downfield shifted singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in the case of Cu(I) (−483.1 ppm), and a lower field and broadened singlet for Au(I) (−464.4 ppm), indicating both P₄ tetrahedra to be coordinated dynamically to the cationic metal centers (free P₄ in CD₂Cl₂: −522.0 ppm). The dynamics were confirmed by VT NMR spectroscopy at −90 °C,¹³ revealing broadening of the ^{31}P signal for Cu-P₄ complex **1a**, and two broad triplets for Au-P₄ analogue **1b** (δ ^{31}P : −453.3 and −462.1 ppm, 2:2 ratio; $^1J_{\text{P,P}}$ = −209.8 Hz). Both novel complexes were isolated as white powders in 92% (**1a**) and 87% (**1b**) yield, respectively, and are unique examples of heteroleptic cationic P₄ coinage metal complexes, complementing the homoleptic series $[\text{M}(\eta^2\text{-P}_4)_2]^+$ reported by Krossing^{14a-d} (M = Ag, Cu) and Slattery *et al.*^{14e} (M = Au), and the neutral copper complex $[\text{NacnacCu}(\eta^2\text{-P}_4)]$ isolated by Scheer and coworkers.^{14f}

The A₂B₂ spin-system of gold(I) complex **1b** observed at low temperature by ^{31}P NMR spectroscopy is indicative of η^2 -P₄ coordination, which was confirmed by a single-crystal X-ray analysis (Fig. 1)¹⁵ that showed nearly equal Au1–P1 (2.4043(17) Å) and Au1–P2 (2.4286(19) Å), a distorted trigonal planar Au center with a short Au1–C1 bond (2.037(5) Å), and an acute P1–Au1–P2 angle (57.79(7)°). A comparison of the P–P bonds in “free” P₄ (2.1994(3) Å, determined by gas-phase electron diffraction¹⁶) with those in **1b**⁺ shows a contraction of the P3–P4 bond (2.148(3) Å), as well as shortened P1/P2–P3/P4 bonds (2.155(3)–2.167(4) Å), but an elongated P1–P2 bond (2.335(3) Å) due to coordination to gold, albeit less pronounced than the one found in $[\text{Au}(\eta^2\text{-P}_4)_2][\text{GaCl}_4]$ (*i.e.* 2.410(1) Å^{14e}).

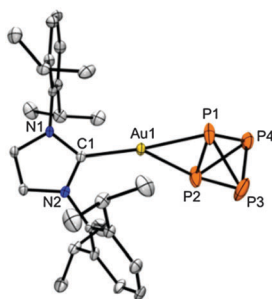


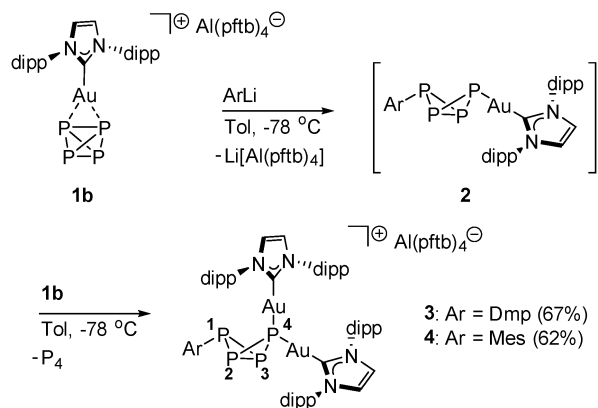
Fig. 1 Molecular structure of **1b**⁺ in the crystal¹⁵ (ellipsoids are set at 50% probability; $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ counter-ion and CH₂Cl₂ solvent molecule omitted). Selected bond lengths [Å] and angles [°]: P1–P2 (2.335(3)), P3–P4 (2.148(3)), P1–P3/P4 (2.167(4)/2.164(3)), P2–P3/P4 (2.156(4)/2.155(3)), Au1–P1/P2 (2.4043(17)/2.4286(19)), C1–Au1 (2.037(5)), C1–Au1–P1 (156.75(14)), C1–Au1–P2 (141.92(14)), P1–Au1–P2 (57.79(7)).

To analyze the bonding situation of **1** in more detail, we resorted to AIM analyses^{17,18} on the gas-phase optimized structures of **1a**⁺ and **1b**⁺,¹⁹ which revealed bond critical points (BCP) between P1 and P2 (ρ = 0.079 a.u. (ϵ = 1.10) in **1a**⁺ and 0.074 a.u. (ϵ = 0.93) in **1b**⁺) with only a slightly lower electron density compared to that computed for the naked P₄ (ρ = 0.105 a.u.; ϵ = 0.10),¹³ confirming the coordinating P₄ fragments to remain intact, disfavoring oxidative addition by P–P bond cleavage. Interestingly, examination of the Laplacian of the electron densities ($\nabla^2\rho$) in the P1–P2 BCPs indicated a stronger P₄–M⁺ interaction in gold complex **1b**⁺ (0.056 a.u.) than in Cu derivative **1a**⁺ (0.033 a.u.), which is in agreement with the observed $^{31}\text{P}\{^1\text{H}\}$ NMR shifts (−483.1 vs. −464.4 ppm for **1a** and **1b**, respectively). ETS-NOCV²⁰ analyses of the M⁺–P₄ bonds concur with these observations,¹⁸ revealing indeed a higher bonding energy for the Au complex ($\Delta\Delta E$ = 1.2 kcal mol^{−1}), with the most prominent difference found for the orbital interactions, showing larger contributions for σ donation (**1b**⁺ −36.7; **1a**⁺ −25.9 kcal mol^{−1}) and concurrent π back-donation (**1b**⁺ −21.4; **1a**⁺ −20.7 kcal mol^{−1}), attributable to the influence of relativistic effects on the valence shell of Au(I).^{21,22}

This difference in bonding energy is also reflected in the stability of **1a** vs. **1b**. Namely, dissolving **1a** in toluene directly led to complete displacement of P₄ at room temperature, whereas **1b** is indefinitely stable under those conditions,²³ rendering Au complex **1b** a suitable building block for the functionalization of P₄. As proof of concept, we first selected the bulky DmpLi to react with **1b**, which proved successful in the synthesis of the LA-stabilized Li⁺ $[\text{DmpP}_4\cdot\text{B}(\text{C}_6\text{F}_5)_3]^-$.^{10a} Hence, a solution of DmpLi (1 equiv.) in toluene was slowly added to a solution of **1b** (1 equiv.) in toluene at −78 °C, revealing an AMX₂ spin system in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (−105.5 (P1), −118.7 (P4) and −327.9 (P2, P3) ppm in a 1:1:2 ratio, respectively), indicative for a non-symmetrically substituted P₄ butterfly.^{10,25} Interestingly, ^1H NMR analysis revealed the presence of two NHC moieties instead of only one needed for the anticipated neutral DmpP₄AuIPr **2** (Scheme 3), which suggests the formation of a doubly coordinated RP₄ complex.

Indeed, X-ray crystal structure determination of colorless crystals obtained by layering a DCM solution with *n*-pentane, displayed the non-symmetrical $[\text{DmpP}_4\cdot(\text{AuIPr})_2][\text{Al}(\text{pftb})_4]$ **3** (Fig. 2) featuring a unique bimetallic gold fragment, with similar P₄–Au1/Au2 distances (2.2924(7)/2.2860(7) Å) and a Au1–P4–Au2 angle of 128.02(3)°, which is larger than found in the triaurated cation $[\text{RP}(\text{AuPPh}_3)_3]^+$ (av. 106°),²⁴ likely due to the steric repulsion between the large NHC ligands. The P₄–P2/P3 bonds (2.1919(10)/2.2077(10) Å) are slightly contracted compared to the P1–P2/P3 bonds (2.2140(10)/2.2240(11) Å), and are similar in length to the bridgehead P2–P3 bond (2.1992(11) Å). These structural parameters are akin to those reported for the cationic $[\text{Mes}_2\text{P}_4\text{Cl}]^+$ of Schulz *et al.*^{25a} as well as to those of the bis-LA complexed anions $[\text{Mes}_2\text{P}_4\cdot(\text{LA})_2]^-$ (LA = BH₃, W(CO)₅) reported by us.^{10b} Intriguingly, the bicyclic P₄ entity in **3**⁺ is sterically highly shielded, as illustrated by a space-filling model (Fig. 2, right), reminiscent of the incorporation of white phosphorus in the self-assembled $[\text{Fe}_4\text{L}_6]^{8+}$ container reported by Nitschke and co-workers.²⁶





Scheme 3 Functionalization of P_4 by reaction of $ArLi$ with **1b**, with the proposed intermediate **2** in brackets (pftb = $OC(CF_3)_3$; dipp = 2,6-diisopropyl(phenyl)).

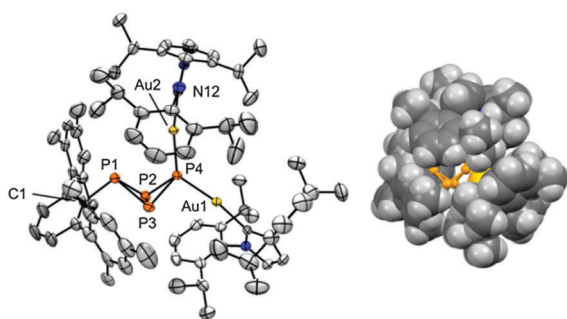


Fig. 2 Left: Molecular structure of **3⁺** in the crystal¹⁵ (ellipsoids are set at 50% probability; $[Al(OC(CF_3)_3)_4]^-$ counter-ion and disordered solvent molecules omitted). Selected bond lengths [Å], angles and torsion angle [°]: P1–P2/P3 (2.2140(10)/2.2240(11)), P4–P2/P3 (2.1919(10)/2.2077(10)), P2–P3 (2.1992(11)), Au1–P4 (2.2924(7)), Au2–P4 (2.2860(7)), C13–P1 (1.865(3)), Au1–P4–Au2 (128.02(3)), P1–P2–P3–P4 (100.98(4)). Right: Space-filling model of **3⁺**.

The formation of **3** could be optimized by using two equivalents of **1b**, which allowed its isolation in 67% yield. Bis-gold complex **3** is likely formed *via* neutral *exo,exo*- ArP_4AuIPr **2** (Scheme 3) that displaces a P_4 molecule from a second equivalent of gold complex **1b**, which was computed to be energetically favorable by $-43.1 \text{ kcal mol}^{-1}$,²⁷ and acts as a monodentate ligand (*via* P4) for $[IPrAu]^+$, displaying reactivity analogous to the recent coordination of bicyclic Mes_2P_4 to $GaCl_3$ ^{25b} shown by Schulz *et al.*, and of $[Cp''Fe(CO)_2]_2(\mu, \eta^{1:1}-P_4)$ toward $[Cu(MeCN)]^+$ presented by the group of Scheer.²⁸

Next, we assessed the reactivity of **1b** toward the less encumbered nucleophile $MesLi$,²⁹ which was not feasible in our original approach (**E**, Scheme 1)¹⁰ as combining $MesLi$ with P_4 in the presence of BPh_3 exclusively produces $Li^+[MesBPh_3]^-$.¹³ Gratifyingly, formation of the bicyclic tetraphosphane $[MesP_4(AuIPr)_2][Al(pftb)_4]$ (**4**) proceeded readily upon mixing $MesLi$ and **1b** (2 equiv.) in toluene at -78°C , showing a distinct set of three $^{31}P\{^1H\}$ resonances at -110.6 (P1), -119.9 (P4) and -314.5 (P2, P3) ppm (1 : 1 : 2 ratio), and an additional signal for free P_4 . The product could be isolated in 62% yield, and was confirmed to contain only one

mesityl unit by mass spectrometry (ESI) and 1H NMR spectroscopy, and two flanking $IPrAu$ moieties.¹³ In contrast to related $Aryl_2P_4$ species, which feature either bulky 2,4,6-*t*Bu₃C₆H₃ (*Mes*)^{7c,10,25a,b} or terphenyl^{4,9,10a} groups, **4** is the first example of a mesityl-substituted P_4 butterfly, which illustrates the merit of this novel P_4 -functionalization strategy in controlling direct P–C bond formation using organolithium reagents.

In summary, addition of *Dmp* or mesityl lithium to the coinage metal based P_4 –LA adduct **1b** gives the unique bimetallic ArP_4 –butterfly cations **3** and **4**. This novel approach allows for varied bulk on the organosubstituents in a single controlled step, showing facile functionalization of P_4 . Currently, we are defining the scope of this new methodology and are exploring the application of **1** in new P_4 transformations.

Notes and references

- For reviews, see: (a) N. A. Giffin and J. D. Masuda, *Coord. Chem. Rev.*, 2011, **255**, 1342; (b) B. M. Cossairt, N. A. Piro and C. C. Cummins, *Chem. Rev.*, 2010, **110**, 4164; (c) M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. Rev.*, 2010, **110**, 4178; (d) M. Scheer, G. Balázs and A. Seitz, *Chem. Rev.*, 2010, **110**, 4236; (e) M. Peruzzini, L. Gonsalvi and A. Romerosa, *Chem. Soc. Rev.*, 2005, **34**, 1038.
- (a) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 7052; (b) O. Back, G. Kuchenbeiser, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2009, **48**, 5530; (c) C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold and G. Bertrand, *Chem. Commun.*, 2013, **49**, 4486; (d) C. L. Dorsey, B. M. Squires and T. W. Hudnall, *Angew. Chem., Int. Ed.*, 2013, **52**, 4462.
- S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner and M. Scheer, *Angew. Chem., Int. Ed.*, 2014, **53**, 7639.
- B. M. Cossairt and C. C. Cummins, *New J. Chem.*, 2010, **34**, 1533.
- D. Tofan and C. C. Cummins, *Angew. Chem., Int. Ed.*, 2010, **49**, 7516.
- D. E. C. Corbridge, *Phosphorus*, Elsevier, Amsterdam, 2000.
- (a) M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, 1963, **28**, 471; (b) M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, 1963, **28**, 473; (c) R. Riedel, H.-D. Hausen and E. Fluck, *Angew. Chem., Int. Ed.*, 1985, **24**, 1056.
- M. Arrowsmith, M. S. Hill, A. L. Johnson, G. Kociok-Köhn and M. F. Mahon, *Angew. Chem., Int. Ed.*, 2015, **54**, 7882.
- A. R. Fox, R. J. Wright, E. Rivard and P. P. Power, *Angew. Chem., Int. Ed.*, 2005, **117**, 7907.
- (a) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg and K. Lammertsma, *Angew. Chem., Int. Ed.*, 2014, **53**, 12836; (b) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg and K. Lammertsma, *Angew. Chem., Int. Ed.*, 2016, **55**, 613.
- I. Krossing, *Chem. – Eur. J.*, 2001, **7**, 490.
- I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066.
- See the ESI[†] for further details.
- (a) I. Krossing, *J. Am. Chem. Soc.*, 2001, **123**, 4603; (b) I. Krossing and L. van Wüllen, *Chem. – Eur. J.*, 2002, **8**, 700; (c) A. Bihlmeier, M. Gonsior, I. Raabe, N. Trapp and I. Krossing, *Chem. – Eur. J.*, 2004, **10**, 5041; (d) G. Santiso-Quinones, A. Reisinger, J. Slattery and I. Krossing, *Chem. Commun.*, 2007, 5046; (e) L. C. Forfar, T. J. Clark, M. Green, S. M. Mansell, C. A. Russell, R. A. Sanguramath and J. M. Slattery, *Chem. Commun.*, 2012, **48**, 1970; (f) F. Spitzer, M. Sierka, M. Latronico, P. Mastroianni, A. V. Virovets and M. Scheer, *Angew. Chem., Int. Ed.*, 2015, **54**, 4392.
- CCDC 1440355 (compound **1b**) and 1440356 (compound **3**) contain the supplementary crystallographic data for this paper.
- B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. M. Mitzel and G. Wu, *J. Am. Chem. Soc.*, 2010, **132**, 8459.
- R. F. W. Bader, *Atoms in Molecules*, Clarendon Press, Oxford, 1994.
- The AIM and ETS-NOCV analysis was performed at ωB97X-D/6-31+G(2d,p) TZ2P using ADF2013.01; see the ESI[†] for details.
- Geometry optimizations were performed at ωB97X-D/6-31+G(2d,p) (LanL2DZ for Cu and Au); J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615; see the ESI[†] for details.



- 20 M. P. Mitoraj, A. Michalak and T. Ziegler, *J. Chem. Theory Comput.*, 2009, **5**, 962.
- 21 This trend was also found in a computational study on homoleptic P_4 complexes of group 11 cations: H.-C. Tai, I. Krossing, M. Seth and D. V. Deubel, *Organometallics*, 2004, **23**, 2343.
- 22 (a) P. Pyykkö, *Chem. Rev.*, 1988, **88**, 563; (b) P. Pyykkö, *Angew. Chem., Int. Ed.*, 2004, **43**, 4412.
- 23 Direct dissociation was observed for both complexes in Et_2O , THF and MTBE.
- 24 H. Schmidbaur, G. Weidenhiller and O. Steigelmann, *Angew. Chem., Int. Ed.*, 1991, **30**, 433.
- 25 Selected examples: (a) J. Bresien, K. Faust, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2015, **54**, 6926; (b) J. Bresien, K. Faust, C. Hering-Junghans, J. Rothe, A. Schulz and A. Villinger, *Dalton Trans.*, 2016, DOI: 10.1039/C5DT02757H; (c) D. Holschumacher, T. Bannenberg, K. Ibrom, C. G. Daniliuc, P. G. Jones and M. Tamm, *Dalton Trans.*, 2010, **39**, 10590; (d) M. B. Power and A. R. Barron, *Angew. Chem., Int. Ed.*, 1991, **30**, 1353.
- 26 P. Mal, B. Breiner, K. Rissanen and J. R. Nitschke, *Science*, 2009, **324**, 1697.
- 27 To reduce the computation time, all aryl substituents were replaced by phenyl groups. DFT calculations were performed at $\omega B97X-D/6-311+G(2d,p)//6-31G(d)$ (LanL2DZ for Au) using Gaussian09 (Revision D.01); see the ESI,[†] for details.
- 28 C. Schwarzmaier, S. Heinl, G. Balázs and M. Scheer, *Angew. Chem., Int. Ed.*, 2015, **54**, 13116.
- 29 Lerner *et al.* isolated $[Li_3][Mes_3P_4]$ by reaction of P_4 with 3 equiv. of MesLi: A. Hübner, T. Bernert, I. Sängner, E. Alig, M. Bolte, L. Fink, M. Wagner and H.-W. Lerner, *Dalton Trans.*, 2010, **39**, 7528.

