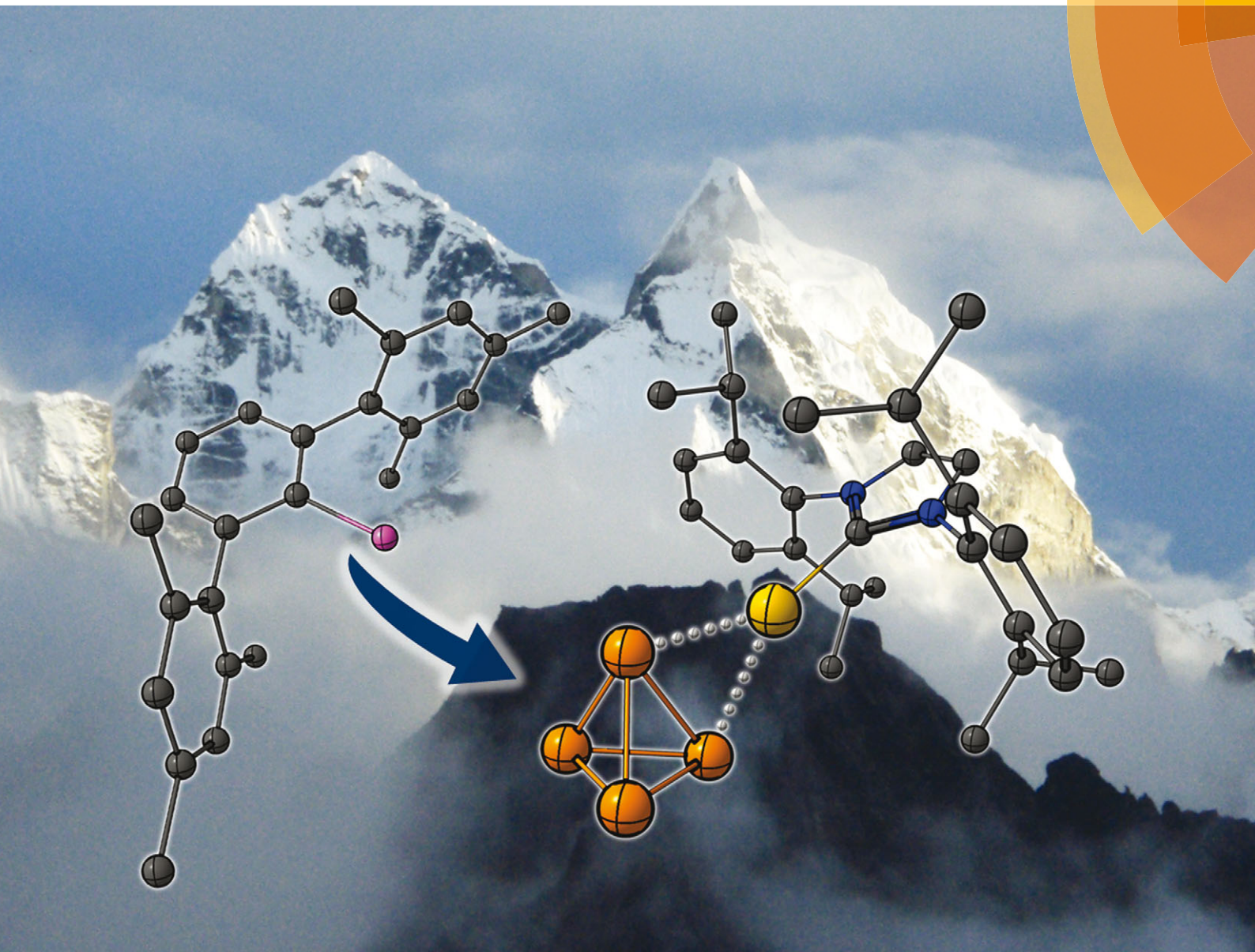


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Functionalization of  $P_4$  in the coordination sphere of coinage metal cations

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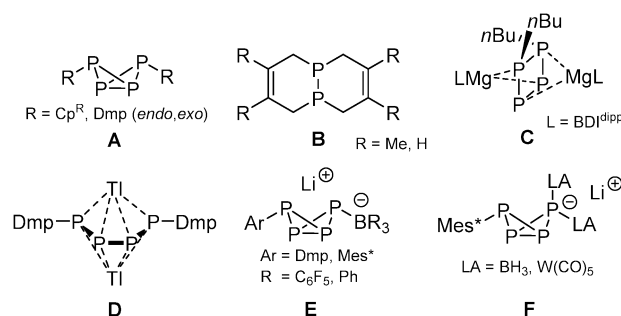
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**Selective functionalization of white phosphorus is achieved by addition of ArLi to unique cationic coinage metal  $\eta^2$ -P<sub>4</sub> complexes. This novel approach allows controlled P–C bond formation using the bulky DmpLi (Dmp = 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and the unencumbered MesLi, giving sterically diverse doubly complexed RP<sub>4</sub> butterfly derivatives in a single step.**

Controlling direct P–C bond formation using P<sub>4</sub> as starting material is of interest in avoiding chlorinated intermediates, such as PCl<sub>3</sub>, for the production of organophosphorus compounds. Yet this task is extremely challenging due to the highly reactive nature of the P<sub>4</sub> tetrahedron.<sup>1</sup> Currently, several selective methods have been developed, like the use of ambiphilic carbenes pioneered by the group of Bertrand,<sup>2</sup> and the metal-mediated radical functionalization of P<sub>4</sub> reported by Scheer *et al.* (A; R = Cp<sup>R</sup>, Scheme 1)<sup>3</sup> as well as by Cummins and co-workers (R = Dmp),<sup>4</sup> who also demonstrated facile P-functionalization chemistry by embedding photochemically generated P<sub>2</sub> fragments into organic frameworks (B).<sup>5</sup> In contrast, conventional methods for the formation of P–C bonds,<sup>6</sup> 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 P<sub>4</sub>.<sup>7</sup> An intriguing exception was recently described by Hill, who achieved selective activation of P<sub>4</sub> using a  $\beta$ -diketiminato organomagnesium compound, producing the [nBu<sub>2</sub>P<sub>4</sub>]<sup>2-</sup> dianion C,<sup>8</sup> which is related to the thallium tetraphosphabutadienediide [Ar<sub>2</sub>P<sub>4</sub>]<sup>2-</sup> salt D reported by Power *et al.*<sup>9</sup> We showed that the reactivity of bulky ArLi reagents



Scheme 1 Methods allowing selective direct P–C bond formation using P<sub>4</sub>. Dmp = 2,6-dimesitylphenyl; BDI<sup>dipp</sup> = HC(CMe)N(2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>; Mes\* = 2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; Cp<sup>R</sup> = Cp<sup>BIG</sup>, Cp<sup>'''</sup>, Cp\*, Cp<sup>4iPr</sup>.

toward P<sub>4</sub> can be controlled in the presence of Lewis acids (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and BPh<sub>3</sub>), giving the LA-stabilized bicyclo[1.1.0]tetraphosphabutanes [ArP<sub>4</sub>(LA)]<sup>-</sup> E that can subsequently be functionalized selectively generating the neutral disubstituted bicyclic phosphanes ArP<sub>4</sub>R (type A) and the doubly coordinated tetraphosphides [ArP<sub>4</sub>(LA)<sub>2</sub>]<sup>2-</sup> F.<sup>10</sup> Key in this approach is the irreversible formation of the transient phosphide [RP<sub>4</sub>]<sup>-</sup> that is directly trapped by the Lewis acid. Note that P<sub>4</sub> does not form an adduct with BPh<sub>3</sub> or even B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>10</sup> 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 P<sub>4</sub> 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 RP<sub>4</sub> butterfly cations.

Commercially available IPrMCl (M = Cu, Au; IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) in combination with Li<sup>+</sup> [Al(pftb)<sub>4</sub>]<sup>-</sup> (pftb = perfluoro-*tert*-butoxy)<sup>11,12</sup> as chloride scavenger were found to be suitable starting materials allowing the isolation of readily available LA–P<sub>4</sub> adducts. The complexation of P<sub>4</sub> 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)<sub>4</sub>] (1 equiv.) in DCM at 0 °C (Scheme 2), which

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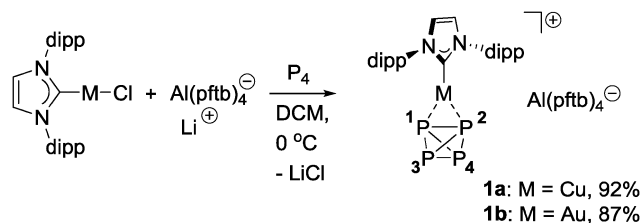
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† Electronic supplementary information (ESI) available. CCDC 1440355 and 1440356. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc10037b



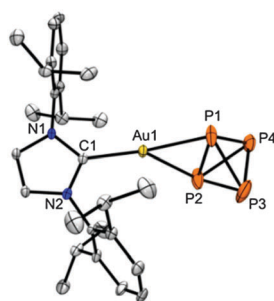




**Scheme 2** Synthesis of cationic  $\eta^2$ - $P_4$  complexes of copper and gold (pftb = OC(CF<sub>3</sub>)<sub>3</sub>; dipp = 2,6-diisopropylphenyl).

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  $P_4$  tetrahedra to be coordinated dynamically to the cationic metal centers (free  $P_4$  in  $\text{CD}_2\text{Cl}_2$ :  $-522.0$  ppm). The dynamics were confirmed by VT NMR spectroscopy at  $-90$  °C,<sup>13</sup> revealing broadening of the  $^{31}\text{P}$  signal for Cu- $P_4$  complex **1a**, and two broad triplets for Au- $P_4$  analogue **1b** ( $\delta$   $^{31}\text{P}$ :  $-453.3$  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  $P_4$  coinage metal complexes, complementing the homoleptic series  $[\text{M}(\eta^2\text{-}P_4)_2]^+$  reported by Krossing<sup>14a-d</sup> (M = Ag, Cu) and Slattery *et al.*<sup>14e</sup> (M = Au), and the neutral copper complex  $[\text{NacnacCu}(\eta^2\text{-}P_4)]$  isolated by Scheer and coworkers.<sup>14f</sup>

The  $A_2B_2$  spin-system of gold(I) complex **1b** observed at low temperature by  $^{31}\text{P}$  NMR spectroscopy is indicative of  $\eta^2$ - $P_4$  coordination, which was confirmed by a single-crystal X-ray analysis (Fig. 1)<sup>15</sup> 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”  $P_4$  (2.1994(3) Å, determined by gas-phase electron diffraction<sup>16</sup>) with those in **1b**<sup>+</sup> 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<sup>14e</sup>).



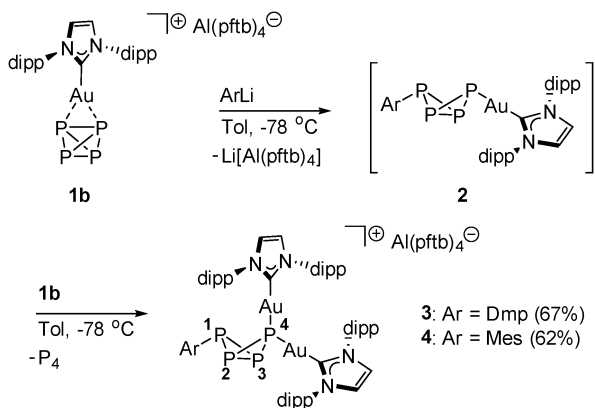
**Fig. 1** Molecular structure of **1b**<sup>+</sup> in the crystal<sup>15</sup> (ellipsoids are set at 50% probability;  $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$  counter-ion and  $\text{CH}_2\text{Cl}_2$  solvent molecule omitted). Selected bond lengths [Å] and angles [°]: P1-P2 (2.335(3)), P3-P4 (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<sup>17,18</sup> on the gas-phase optimized structures of **1a**<sup>+</sup> and **1b**<sup>+</sup>,<sup>19</sup> which revealed bond critical points (BCP) between P1 and P2 ( $\rho = 0.079$  a.u. ( $\epsilon = 1.10$ ) in **1a**<sup>+</sup> and 0.074 a.u. ( $\epsilon = 0.93$ ) in **1b**<sup>+</sup>) with only a slightly lower electron density compared to that computed for the naked  $P_4$  ( $\rho = 0.105$  a.u.;  $\epsilon = 0.10$ ),<sup>13</sup> confirming the coordinating  $P_4$  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  $P_4$ -M<sup>+</sup> interaction in gold complex **1b**<sup>+</sup> (0.056 a.u.) than in Cu derivative **1a**<sup>+</sup> (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-NOCV<sup>20</sup> analyses of the M<sup>+</sup>- $P_4$  bonds concur with these observations,<sup>18</sup> revealing indeed a higher bonding energy for the Au complex ( $\Delta\Delta E = 1.2$  kcal mol<sup>-1</sup>), with the most prominent difference found for the orbital interactions, showing larger contributions for  $\sigma$  donation (**1b**<sup>+</sup>  $-36.7$ ; **1a**<sup>+</sup>  $-25.9$  kcal mol<sup>-1</sup>) and concurrent  $\pi$  back-donation (**1b**<sup>+</sup>  $-21.4$ ; **1a**<sup>+</sup>  $-20.7$  kcal mol<sup>-1</sup>), attributable to the influence of relativistic effects on the valence shell of Au(I).<sup>21,22</sup>

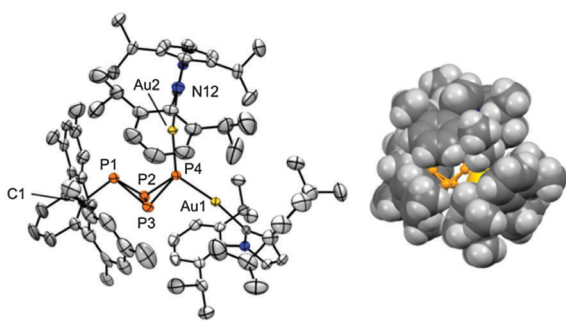
This difference in bonding energy is also reflected in the stability of **1a** vs. **1b**. Namely, dissolving **1a** in toluene directly led to complete displacement of  $P_4$  at room temperature, whereas **1b** is indefinitely stable under those conditions,<sup>23</sup> rendering Au complex **1b** a suitable building block for the functionalization of  $P_4$ . 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<sup>+</sup>  $[\text{DmpP}_4\text{B}(\text{C}_6\text{F}_5)_3]^-$ .<sup>10a</sup> 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 AMX<sub>2</sub> 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  $P_4$  butterfly.<sup>10,25</sup> Interestingly,  $^1\text{H}$  NMR analysis revealed the presence of two NHC moieties instead of only one needed for the anticipated neutral DmpP<sub>4</sub>AuIPr **2** (Scheme 3), which suggests the formation of a doubly coordinated RP<sub>4</sub> complex.

Indeed, X-ray crystal structure determination of colorless crystals obtained by layering a DCM solution with *n*-pentane, displayed the non-symmetrical  $[\text{DmpP}_4(\text{AuIPr})_2][\text{Al}(\text{pftb})_4]$  **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°),<sup>24</sup> 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.*<sup>25a</sup> as well as to those of the bis-LA complexed anions  $[\text{Mes}^*\text{P}_4(\text{LA})_2]^-$  (LA = BH<sub>3</sub>, W(CO)<sub>5</sub>) reported by us.<sup>10b</sup> Intriguingly, the bicyclic  $P_4$  entity in **3**<sup>+</sup> 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.<sup>26</sup>





**Scheme 3** Functionalization of  $\text{P}_4$  by reaction of  $\text{ArLi}$  with **1b**, with the proposed intermediate **2** in brackets (pftb =  $\text{OC}(\text{CF}_3)_3$ ; diippr = 2,6-diisopropylphenyl).



**Fig. 2** Left: Molecular structure of  $\mathbf{3}^+$  in the crystal<sup>15</sup> (ellipsoids are set at 50% probability;  $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$  counter-ion and disordered solvent molecules omitted). Selected bond lengths [ $\text{\AA}$ ], angles and torsion angle [ $^\circ$ ]:  $\text{P1-P2/P3}$  (2.2140(10)/2.2240(11)),  $\text{P4-P2/P3}$  (2.1919(10)/2.2077(10)),  $\text{P2-P3}$  (2.1992(11)),  $\text{Au1-P4}$  (2.2924(7)),  $\text{Au2-P4}$  (2.2860(7)),  $\text{C13-P1}$  (1.865(3));  $\text{Au1-P4-Au2}$  (128.02(3));  $\text{P1-P2-P3-P4}$  (100.98(4)). Right: Space-filling model of  $\mathbf{3}^+$ .

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*- $\text{ArP}_4\text{AuIPr}$  **2** (Scheme 3) that displaces a  $\text{P}_4$  molecule from a second equivalent of gold complex **1b**, which was computed to be energetically favorable by  $-43.1 \text{ kcal mol}^{-1}$ ,<sup>27</sup> and acts as a monodentate ligand (*via*  $\text{P4}$ ) for  $[\text{IPrAu}]^+$ , displaying reactivity analogous to the recent coordination of bicyclic  $\text{Mes}_2\text{P}_4$  to  $\text{GaCl}_3$ ,<sup>25b</sup> shown by Schulz *et al.*, and of  $[\{\text{Cp}''\text{Fe}(\text{CO})_2\}_2(\mu, \eta^{1:1}\text{-P}_4)]$  toward  $[\text{Cu}(\text{MeCN})]^+$  presented by the group of Scheer.<sup>28</sup>

Next, we assessed the reactivity of **1b** toward the less encumbered nucleophile  $\text{MesLi}$ ,<sup>29</sup> which was not feasible in our original approach (**E**, Scheme 1)<sup>10</sup> as combining  $\text{MesLi}$  with  $\text{P}_4$  in the presence of  $\text{BPh}_3$  exclusively produces  $\text{Li}^+[\text{MesBPh}_3]^-$ .<sup>13</sup> Gratifyingly, formation of the bicyclic tetraphosphane  $[\text{MesP}_4(\text{AuIPr})_2][\text{Al}(\text{pftb})_4]$  (**4**) proceeded readily upon mixing  $\text{MesLi}$  and **1b** (2 equiv.) in toluene at  $-78^\circ\text{C}$ , showing a distinct set of three  $^{31}\text{P}\{^1\text{H}\}$  resonances at  $-110.6$  (P1),  $-119.9$  (P4) and  $-314.5$  (P2, P3) ppm (1 : 1 : 2 ratio), and an additional signal for free  $\text{P}_4$ . The product could be isolated in 62% yield, and was confirmed to contain only one

mesityl unit by mass spectrometry (ESI) and  $^1\text{H}$  NMR spectroscopy, and two flanking  $\text{IPrAu}$  moieties.<sup>13</sup> In contrast to related  $\text{Aryl}_2\text{P}_4$  species, which feature either bulky 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>3</sub> ( $\text{Mes}^*$ )<sup>7c,10,25a,b</sup> or terphenyl<sup>4,9,10a</sup> groups, **4** is the first example of a mesityl-substituted  $\text{P}_4$  butterfly, which illustrates the merit of this novel  $\text{P}_4$ -functionalization strategy in controlling direct P-C bond formation using organolithium reagents.

In summary, addition of  $\text{Dmp}$  or mesityl lithium to the coinage metal based  $\text{P}_4$ -LA adduct **1b** gives the unique bimetallic  $\text{ArP}_4$ -butterfly cations **3** and **4**. This novel approach allows for varied bulk on the organosubstituents in a single controlled step, showing facile functionalization of  $\text{P}_4$ . Currently, we are defining the scope of this new methodology and are exploring the application of **1** in new  $\text{P}_4$  transformations.

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- 29 Lerner *et al.* isolated [Li<sub>3</sub>][Mes<sub>3</sub>P<sub>4</sub>] by reaction of P<sub>4</sub> with 3 equiv. of MesLi: A. Hübner, T. Bernert, I. Sängler, E. Alig, M. Bolte, L. Fink, M. Wagner and H.-W. Lerner, *Dalton Trans.*, 2010, **39**, 7528.

