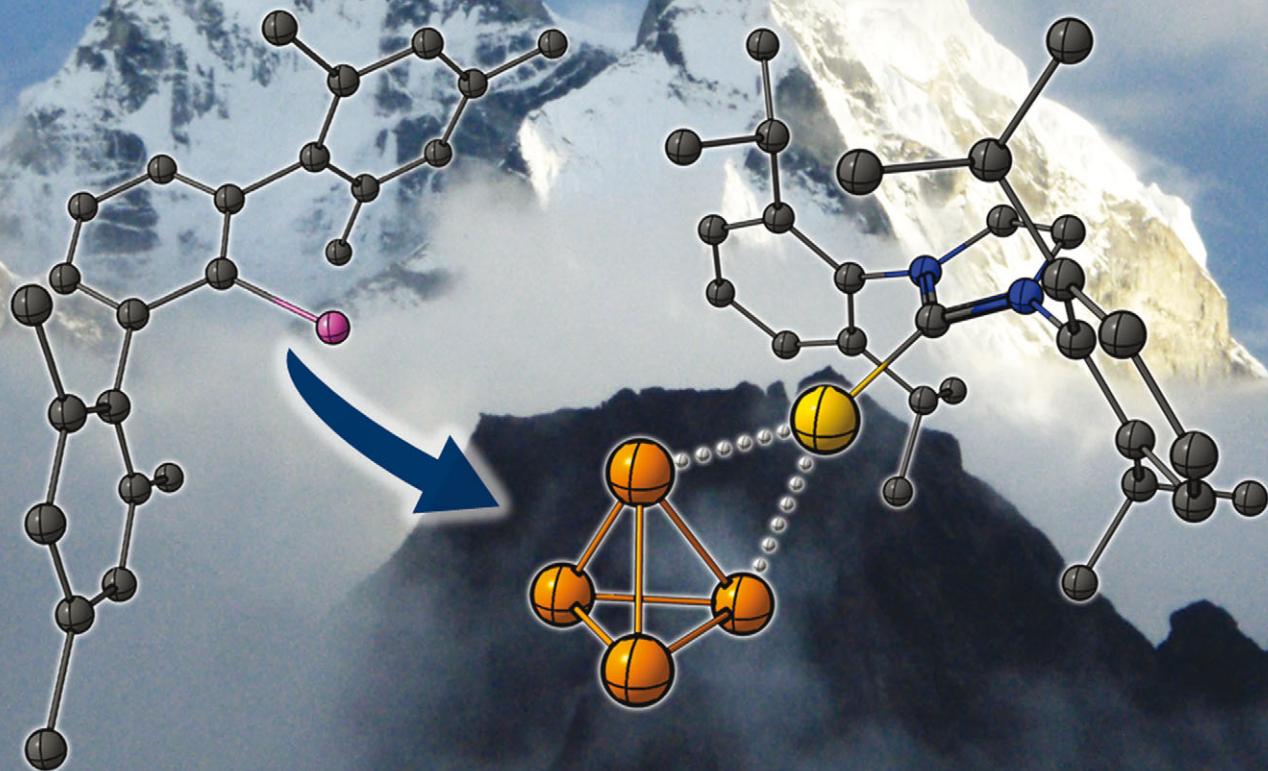


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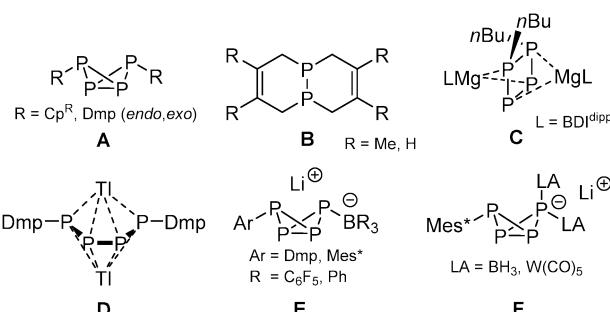
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Selective functionalization of white phosphorus is achieved by addition of ArLi to unique cationic coinage metal $\eta^2\text{-P}_4$ complexes. This novel approach allows controlled P-C bond formation using the bulky DmpLi ($\text{Dmp} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$) and the unencumbered MesLi, giving sterically diverse doubly complexed RP_4 butterfly derivatives in a single step.

Controlling direct P-C bond formation using P_4 as starting material is of interest in avoiding chlorinated intermediates, such as PCl_3 , for the production of organophosphorus compounds. Yet this task is extremely challenging due to the highly reactive nature of the P_4 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 P_4 reported by Scheer *et al.* (**A**; $\text{R} = \text{Cp}^{\text{R}}$, Scheme 1)³ as well as by Cummins and co-workers ($\text{R} = \text{Dmp}$),⁴ who also demonstrated facile P-functionalization chemistry by embedding photochemically generated P_2 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 P_4 .⁷ An intriguing exception was recently described by Hill, who achieved selective activation of P_4 using a β -diketiminato organomagnesium compound, producing the $[\text{nBu}_2\text{P}_4]^{2-}$ dianion **C**,⁸ which is related to the thallium tetraphosphabutadienediide $[\text{Ar}_2\text{P}_4]^{2-}$ salt **D** reported by Power *et al.*⁹ We showed that the reactivity of bulky ArLi reagents

Functionalization of P_4 in the coordination sphere of coinage metal cations[†]

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Scheme 1 Methods allowing selective direct P-C bond formation using P_4 . $\text{Dmp} = 2,6\text{-dimesitylphenyl}$; $\text{BDI}^{\text{dipp}} = \text{HC}(\text{C}(\text{Me})\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3))_2$; $\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$; $\text{Cp}^{\text{R}} = \text{Cp}^{\text{BIG}}$, Cp'' , Cp^* , $\text{Cp}^{4\text{IPr}}$.

toward P_4 can be controlled in the presence of Lewis acids ($\text{B}(\text{C}_6\text{F}_5)_3$ and BPh_3), giving the LA-stabilized bicyclo[1.1.0]tetraphosphabutanides $[\text{ArP}_4\text{LA}]^-$ **E** that can subsequently be functionalized selectively generating the neutral disubstituted bicyclic phosphanes ArP_4R (type **A**) and the doubly coordinated tetraphosphides $[\text{ArP}_4\text{LA}]_2^-$ **F**.¹⁰ Key in this approach is the irreversible formation of the transient phosphide $[\text{RP}_4]^-$ that is directly trapped by the Lewis acid. Note that P_4 does not form an adduct with BPh_3 or even $\text{B}(\text{C}_6\text{F}_5)_3$,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 P_4 as synthon that now tolerate varied bulk on the ArLi reagents, as demonstrated by the selective addition of Dmp ($\text{Dmp} = 2,6\text{-dimesitylphenyl}$) and mesityl lithium, resulting in the formation of unique doubly complexed RP_4 butterfly cations.

Commercially available IPrMCl ($\text{M} = \text{Cu, Au}$; $\text{IPr} = 1,3\text{-bis}(\text{diisopropylphenyl})\text{imidazol-2-ylidene}$) in combination with $\text{Li}^+ [\text{Al}(\text{pftb})_4]^-$ ($\text{pftb} = \text{perfluoro-}tert\text{-butoxy}$)^{11,12} as chloride scavenger were found to be suitable starting materials allowing the isolation of readily available LA- P_4 adducts. The complexation of P_4 was achieved by dropwise addition of a solution of IPrMCl (1 equiv.; $\text{M} = \text{Cu, Au}$) in DCM to a suspension of white phosphorus (1.1 equiv.) and $\text{Li}[\text{Al}(\text{pftb})_4]$ (1 equiv.) in DCM at 0 °C (Scheme 2), which

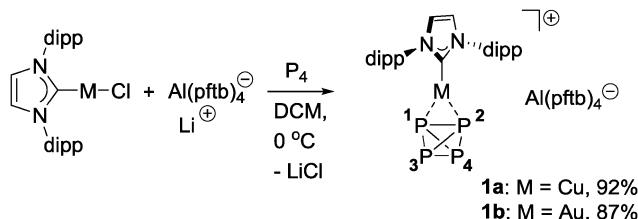
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† Electronic supplementary information (ESI) available. CCDC 1440355 and 1440356. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc10037b





Scheme 2 Synthesis of cationic 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 ³¹P{¹H} 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 ³¹P signal for Cu–P₄ complex **1a**, and two broad triplets for Au–P₄ analogue **1b** (δ ³¹P: −453.3 and −462.1 ppm, 2:2 ratio; $^1J_{P,P}$ = −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 [M(η^2 -P₄)₂]⁺ reported by Krossing^{14a–d} (M = Ag, Cu) and Slattery *et al.*^{14e} (M = Au), and the neutral copper complex [NacnacCu(η^2 -P₄)] isolated by Scheer and coworkers.^{14f}

The A₂B₂ spin-system of gold(i) complex **1b** observed at low temperature by ³¹P 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 distances (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 [Au(η^2 -P₄)₂][GaCl₄] (*i.e.* 2.410(1) Å^{14e}).

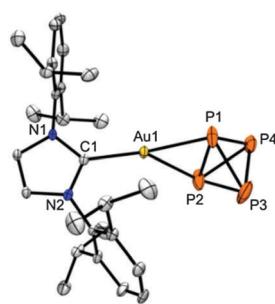


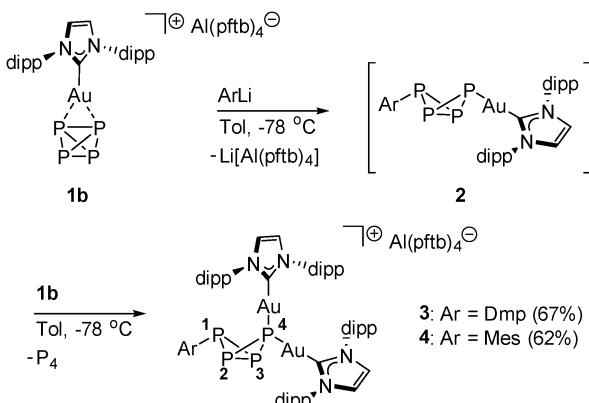
Fig. 1 Molecular structure of **1b**⁺ in the crystal¹⁵ (ellipsoids are set at 50% probability; [Al(OC(CF₃)₃)₄][−] counter-ion and CH₂Cl₂ solvent molecule omitted). Selected bond lengths [Å] and angles [°]: P1–P2 (2.335(3)), P3–P4 (2.148(3)), P1–P3/P4 (2.167(4)/2.164(3)), P2–P3/P4 (2.156(4)/2.155(3)), 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 ³¹P{¹H} 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⁺ [DmpP₄·B(C₆F₅)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 ³¹P{¹H} 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 [DmpP₄·(AuIPr)₂][Al(pftb)] **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 [RP(AuPPh₃)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 [Mes*₂P₄Cl]⁺ of Schulz *et al.*^{25a} as well as to those of the bis-LA complexed anions [Mes*P₄·(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 [Fe₄L₆]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 = $\text{OC}(\text{CF}_3)_3$; dipp = 2,6-diisopropylphenyl).

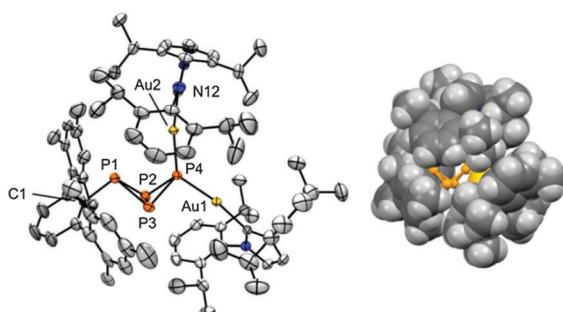


Fig. 2 Left: Molecular structure of 3^+ in the crystal¹⁵ (ellipsoids are set at 50% probability; $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ counter-ion and disordered solvent molecules omitted). Selected bond lengths [\AA], angles and torsion angle [$^\circ$]: P1–P2/P3 (2.2140(10)/2.2240(11)), P4–P2/P3 (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* P_4) for $[\text{IPrAu}]^+$, displaying reactivity analogous to the recent coordination of bicyclic Mes^*P_4 to GaCl_3 ^{25b} 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.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 $\text{Li}^+[\text{MesBPh}_3]^-$.¹³ Gratifyingly, formation of the bicyclic tetraphosphane $[\text{MesP}_4^-(\text{AuIPr})_2]\text{Al}(\text{pftb})_4$ (**4**) proceeded readily upon mixing MesLi and **1b** (2 equiv.) in toluene at -78°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 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 Arly_2P_4 species, which feature either bulky $2,4,6-t\text{Bu}_3\text{C}_6\text{H}_3$ (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 $\text{P}-\text{C}$ 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.

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