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Functionalization of P₄ in the Coordination Sphere of Coinage Metal Cations†

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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 = CpR, 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 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.
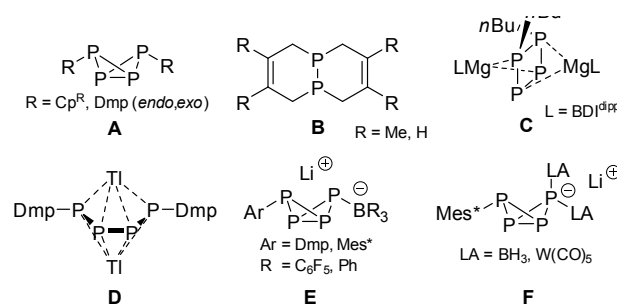
Scheme 1 Methods allowing selective direct P–C bond formation using P₄. Dmp = 2,6-dimesitylphenyl; BDIdipp = HC{C(Me)N(2,6-iPr₂C₆H₃)}₂; Mes* = 2,4,6-tBu₃C₆H₂; CpR = CpBIG, Cp''', Cp*, Cp4iPr.

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 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; ¹JP,P = −209.8 Hz).

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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 $[M(\eta^2\text{-}P_4)_2]^+$ reported by Krossing[14a-d] (M = Ag, Cu) and Slattery et al.[14e] (M = Au), and the neutral copper complex $[NacnacCu(\eta^2\text{-}P_4)]$ isolated by Scheer and coworkers.[14f]
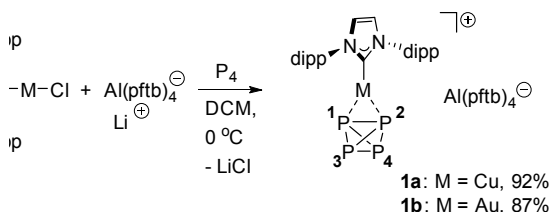
Scheme 2 Synthesis of cationic $\eta^2\text{-}P_4$ complexes of copper and gold (pftb = $OC(CF_3)_3$; dipp = 2,6-diisopropylphenyl).

The A_2B_2 spin-system of gold(I) complex **1b** observed at low temperature by ^{31}P NMR spectroscopy is indicative of $\eta^2\text{-}P_4$ coordination, which was confirmed by a single-crystal X-ray analysis (Figure 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" P_4 (2.1994(3) Å, determined by gas-phase electron diffraction[16]) 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 $[Au(\eta^2\text{-}P_4)_2][GaCl_4]$ (i.e. 2.410(1) Å[14e]).
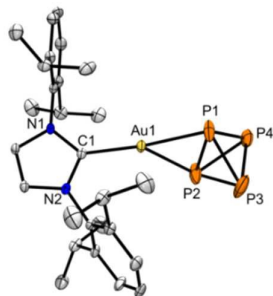

Fig. 1 Molecular structure of **1b+** in the crystal[15] (ellipsoids are set at 50% probability; $[Al(OC(CF_3)_3)_4]^-$ counter-ion and CH_2Cl_2 solvent molecule omitted). Selected bond lengths [Å] and angles [°]: P1–P2 (2.335(3)), P3–P4 (2.148(3)), P1–P3/P4 (2.167(4)/2.164(3)), P2–P3/P4 (2.156(4)/2.155(3)), 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[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 P_4 (ρ = 0.105 a.u.; ε = 0.10),[13] 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^+ 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 $^{31}P\{^1H\}$ NMR shifts (−483.1 vs. −464.4 ppm for **1a** and **1b**, respectively). ETS-NOCV[20] analyses of the M^+–P_4 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 P_4 at room temperature, whereas **1b** is indefinitely stable under those conditions,[23] 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 $Li^+[DmpP_4\cdot B(C_6F_5)_3]^-$.[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 AMX_2 spin system in the $^{31}P\{^1H\}$ 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 P_4 butterfly.[10,25] Interestingly, ^1H NMR analysis revealed the presence of two NHC moieties instead of only one needed for the anticipated neutral $DmpP_4AuIPr$ **2** (Scheme 3), which suggests the formation of a doubly coordinated RP_4 complex.
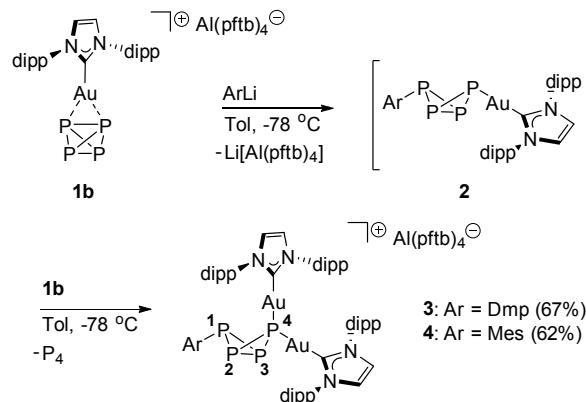
Scheme 3 Functionalization of P_4 by reaction of ArLi with **1b**, with the proposed intermediate **2** in brackets (pftb = $OC(CF_3)_3$; dipp = 2,6-diisopropylphenyl).

Indeed, X-ray crystal structure determination of colorless crystals obtained by layering a DCM solution with n-pentane, displayed the non-symmetrical $[DmpP_4\cdot(AuIPr)_2][Al(pftb)_4]$ **3** (Figure 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 $[RP(AuPPh_3)_3]^+$ (av. 106°),[24] likely due to the steric repulsion between the large NHC ligands. The P4–P2/P3 bonds (2.1919(10)/2.0770(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 $[Mes*_2P_4Cl]^+$ of Schulz et al.[25a] as well as to those of the bis-LA complexed anions $[Mes*P_4\cdot(LA)_2]^-$ (LA = BH_3, $W(CO)_5$) reported by us.[10b] Intriguingly, the bicyclic P_4 entity in **3+** is sterically highly shielded, as illustrated by a space-filling model (Figure 2, right), reminiscent of the incorporation

of white phosphorus in the self-assembled $[Fe_4L_6]^{8+}$ container reported by Nitschke and co-workers.[26]
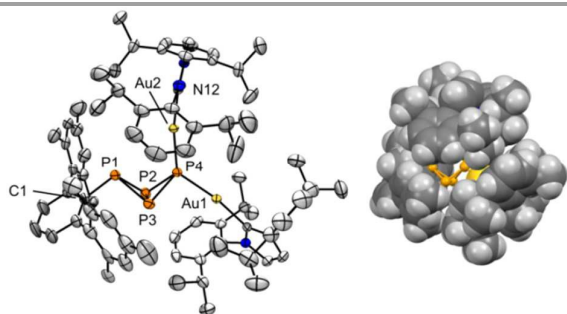
Fig 2. Left: Molecular structure of **3**[+] in the crystal[15] (ellipsoids are set at 50% probability; $[Al(OC(CF_3)_3)_4]^-$ counter-ion and disordered solvent molecules omitted). Selected bond lengths [Å], angles and torsion angle [°]: P1–P2/P3 (2.2140(10)/2.2240(11)), P4–P2/P3 (2.1919(10)/2.2077(10)), 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*-ArP₄AuIPr **2** (Scheme 3) that displaces a P₄ molecule from a second equivalent of gold complex **1b**, which was computed to be energetically favorable by −43.1 kcal·mol⁻¹,[27] and acts as a monodentate ligand (via P4) for [IPrAu]⁺, displaying reactivity analogous to the recent coordination of bicyclic Mes*₂P₄ to GaCl₃[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 P₄ in the presence of BPh₃ exclusively produces Li⁺[MesBPh₃]⁻.[13] Gratifyingly, formation of the bicyclic tetraphosphane [MesP₄·(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 ³¹P{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 P₄. 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 Aryl₂P₄ 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 P₄ butterfly, which illustrates the merit of this novel P₄-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 P₄–LA adduct **1b** gives the unique bimetallic ArP₄-butterfly cations **3** and **4**. This novel approach allows for varied bulk on the organosubstituents in a single controlled step, showing facile functionalization of P₄. Currently, we are defining the scope of this new methodology and are exploring the application of **1** in new P₄ transformations.

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