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Functionalization of P_4 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 η^2 -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

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Scheme 2 Synthesis of cationic $\eta^2\text{-P}_4$ 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 P_4 tetrahedra to be coordinated dynamically to the cationic metal centers (free P_4 in CD_2Cl_2 : −522.0 ppm). The dynamics were confirmed by VT NMR spectroscopy at −90 °C,¹³ revealing broadening of the ^{31}P signal for Cu- P_4 complex **1a**, and two broad triplets for Au- P_4 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 P_4 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 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 (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” P_4 (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 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 $\text{P}_4\text{-M}^+$ 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 $\text{M}^+\text{-P}_4$ 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 $\text{Li}^+ [\text{DmpP}_4\text{-B}(\text{C}_6\text{F}_5)_3]^-$.^{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 AMX_2 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.^{10,25} Interestingly, ^1H NMR analysis revealed the presence of two NHC moieties instead of only one needed for the anticipated neutral $\text{DmpP}_4\text{AuIPr}$ **2** (Scheme 3), which suggests the formation of a doubly coordinated RP_4 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 $\text{P}_4\text{-Au1/Au2}$ 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 $\text{P}_4\text{-P2/P3}$ 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 $[\text{Mes}^*\text{P}_4\text{-(LA)}_2]^-$ (LA = BH_3 , $\text{W}(\text{CO})_5$) reported by us.^{10b} Intriguingly, the bicyclic P_4 entity in **3**⁺ is sterically highly shielded, as illustrated by a space-filling model (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.

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