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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-Mes), 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 PCl₅, for the production of organophosphorus compounds. Yet, this task is extremely challenging due to the highly reactive nature of the P₄ tetrahedron. Currently, several selective methods have been developed, like the use of amphoteric carbenes pioneered by the group of Bertrand, and the metal-mediated radical functionalization of P₄ reported by Scheer et al. [A; R = Cp⁺, Scheme 1] as well as by Cummins and co-workers (R = Dmp), who also demonstrated facile P-functionalization chemistry by embedding photochemically generated P₂ fragments into organic frameworks [B]. In contrast, conventional methods for the formation of P–C bonds, 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. An intriguing exception was recently described by Hill, who achieved selective activation of P₄ using a β-diketiminato organonitrogen compound, producing the [nBu₂P₂]₂-di cation C, which is related to the thallium tetraphosphabutadienediide [Ar₂P₄]²⁻ salt D reported by Power et al. We showed that the reactivity of bulky ArLi reagents toward P₄ can be controlled in the presence of Lewis acids (B(C₆F₅)₃) and BPh₄⁻, giving the LA-stabilized bicyclo[1.1.0]tetraphosphabutadiene [Ar₃P₄-LA]⁻ that can subsequently be functionalized selectively generating the neutral disubstituted bicyclic phosphines Ar₃P₂R (type A) and the doubly coordinated tetraphosphides [Ar₃P₂-LA]⁻ F. Key in this approach is the irreversible formation of the transient phosphide [RP₃]⁻ that is directly trapped by the Lewis acid. Note that P₄ does not form an adduct with BPh₃ or even B(C₆F₅)₃, 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 synthons 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.

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

Jaap E. Borger,† Martijn S. Bakker, Andreas W. Ehlers, Martin Lutz, J. Chris Slootweg* and Koop Lammertse²,a

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-Mes) and the unencumbered MesLi, giving sterically diverse doubly complexed RP₄ butterfly derivatives in a single step.

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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 P₄ coinage metal complexes, complementing the homoleptic series [M(η²-P₄)]⁺ reported by Krossing et al. (M = Ag, Cu) and Slattery et al. (M = Au), and the neutral copper complex [NacnacCu(η²-P₄)] isolated by Scheer and coworkers.¹⁴

\[
\text{Scheme 2} \quad \text{Synthesis of cationic } \eta^2\text{-P₄ complexes of copper and gold } (\text{ptfb} = 0\text{C(CF}_3)_2\text{)} \text{, dipp = 2,6-diisopropylphenyl)}.
\]

The AₓB₂ spin-system of gold(I) complex 1b observed at low temperature by ³¹P NMR spectroscopy is indicative of η²-P₄ coordination, which was confirmed by a single-crystal X-ray analysis (Figure 1) 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 C1–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 diffraction¹⁰ 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) Å), an elongated P1–P2 bond (2.335(3) Å) due to coordination to gold, albeit less pronounced than the one found in [Au(η²-P₄)][GaCl₃] (i.e. 2.410(1) Å).¹⁴

\[
\text{Scheme 3} \quad \text{Functionalization of P₄ by reaction of ArLi with 1b, with the proposed intermediate 2 in brackets } (\text{ptfb} = 0\text{C(CF}_3)_2\text{, dipp = 2,6-diisopropylphenyl)}.
\]

Indeed, X-ray crystal structure determination of colorless crystals obtained by layering a DCM solution with n-pentane, displayed the non-symmetrical [DmpP₄(AuIPr)][Al(ptfb)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 [RfPpH₃]⁺ (av. 106.5°) likely due to the steric repulsion between the large NHC ligands. The P₄–P₃ bond (2.1919(10)/2.2077(10) Å) are slightly contracted compared to the P1–P2/P3–P4 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 [Mes₄⁺P₄Cl]⁺ of Schulz et al.25b as well as to those of the bis-LA complexed anions [Mes₄⁺P₄(LA)₂−] (LA = BH₃, W(CO)₃) reported by us.¹⁰ Intriguingly, the bicyclic P₄ 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,La]8+ container reported by Nitschke and co-workers.26

Fig 2: Left: Molecular structure of 3 in the crystal (ellipsoids are set at 50% probability; [Al(OC(CF3))4] counter-ion and disordered solvent molecules omitted). Selected bond lengths [Å], angles and torsion angle [(µ,η ω)]: P1–P2/P3 (2.1404(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)), Cl3–P1 (1.8653(3)), Au1–P1–Au2 (1.2860(23)), P1–P2–P3–P4 (1.0098(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. Biggold complex 3 is likely formed via neutral exoexo-ArP4AuPr2 (Scheme 1) 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), displaying reactivity analogous to the novel coordination of bicycl[4]cate
catalysed by GaCl3,28 shown by Schulz et al., and of [(C≡P=P(CO)]2(µ111–P4)] toward [Cu(MeCN)]+ presented by the Schaefer.28

Next, we assessed the reactivity of 1b toward the less encumbered nucleophile MesLi,29 which was not feasible in our original approach (Scheme 1)30 as combining MesLi with P4 in the presence of BPh3 exclusively produces Li[MesBPh3].31 Gratifyingly, formation of the bicyclic tetraphosphane [MesP2(AlPr)2][Al(Ph)][4] proceeded readily upon mixing MesLi and 1b (2 equiv.) in toluene at −78 °C, showing a distinct set of three 31P{[1]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 P4. The product could be isolated in 62% yield, and was confirmed to contain only one mesityl unit by mass spectroscopy (ESI) and 31P NMR spectroscopy, and two flanking [P3Au] moieties.32 In contrast to related Ar3P7 species, which feature either bulky 2.4,6-Bu3C4H4 (Mes3)55,60a-b or terphenyl8,10b,9a groups, 4 is the first example of a mesityl-substituted P4 butterfly, which illustrates the merit of this novel P4-functionlization strategy in controlling direct P–C bond formation using organonitrogen reagents.

In summary, addition of Dmp or mesityl lithium to the coinage metal based P=LA adduct 1b gives the unique bimetallic Ar3P–Ar=P=LA cationcs 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.

Notes and references


9 The AIM and ETS-NOVC analysis was performed at ZORA-BP66-D3/TZ2P using ADF2013.01; see the SI for details.

10 Geometry optimizations were performed at o99T(X)/6-31+G(dp) (LanL2DZ for Au) using Gaussian09 (Revision D.01); see the SI for details.

11 The trend was also found in a computational study on homoleptic P4 complexes of group 11 cations: H+ –C. T. I. Krossing, M. Scheer and D. V. Deubel, Organometallics, 2004, 23, 2343.


13 Direct dissociation was observed for both complexes in Et2O/THF and MTBE.


17 To reduce the computation time, all aryl substituents were replaced by phenyl groups. DFT calculations were performed at o99T(X)/6-311+G(d,p)//6-31G(d) (LanL2DZ for Au) using Gaussian09 (Revision D.01); see the SI for details.
