

The Hexaphenyl-1,2-Diphosponium Dication $[\text{Ph}_3\text{P}-\text{PPh}_3]^{2+}$

Fabian Dankert,^a Simon P. Muhm,^a Chandan Nandi,^a Sergi Danés,^b Sneha Mullassery,^a Petra Herbeck-Engel,^c Bernd Morgenstern,^d Robert Weiss,^{*e} Pedro Salvador,^{*b} Dominik Munz^{*a}

^a Saarland University, Coordination Chemistry, Campus C4.1, D-66123 Saarbrücken, Germany;

^b Institut de Química Computacional i Catàlisi, Departament de Química, Universitat de Girona, C/M. Aurelia Capmany 69, 17003, Girona, Spain;

^c INM Leibniz Institute for New Materials, Campus D2.2, 66123 Saarbrücken, Germany;

^d Saarland University, Inorganic Solid-State Chemistry, Campus C4.1, D-66123 Saarbrücken, Germany;

^e Friedrich-Alexander-Universität (FAU) Erlangen-Nürnberg, Nikolaus-Fiebiger-Str. 10, 91058 Erlangen, Germany.

Radicals, Lewis-Acids, Elementorganic Chemistry, Main Group Chemistry, Bond Activation

ABSTRACT: The oxidation of triphenylphosphine by perfluorinated phenazinium^F aluminate in difluorobenzene affords the hexaaryl-1,2-diphosponium dialuminate **1**. Dication **1**²⁺ is isoelectronic with elusive hexaphenylethane, where instead the formation of a mixture of the trityl radical and Gomberg's dimer is favored. Quantum-chemical calculations in combination with Raman/IR spectroscopies rationalize the stability of the P–P bonded dimer in **1**²⁺ and suggest, akin to the halogens, facile homolytic as well as heterolytic scission. Thus, **1**²⁺ serves as a surrogate of both the triphenylphosphorandilylium dication (Ph_3P^{2+}) and the triphenylphosphine radical monocation ($\text{Ph}_3\text{P}^{\bullet+}$). Treating **1** with dimethylaminopyridine (DMAP) replaces triphenylphosphine under heterolytic P–P bond scission. Qualifying as a superoxidant (E vs. $\text{Fc}/\text{Fc}^+ = +1.44$ V), **1** oxidizes trimethylphosphine. Based on halide abstraction experiments ($-\text{BF}_4$, $-\text{PF}_6$, $-\text{SbCl}_6$, $-\text{SbF}_6$) as well as the deoxygenation of triethylphosphine oxide, triflate anions as well as toluic acid, **1** also features Lewis superacidity. The controlled hydrolysis affords Hendrickson's reagent, which itself finds broad use as dehydration agent. Formally homolytic P–P bond scission is induced by diphenyldisulfide (PhSSPh), dihydrogen, and the triple bond in acetonitrile. The irradiation by light cleaves the P–P bond homolytically and generates transient triphenylphosphine radical cations, which engage in H-atom abstraction as well as CH phosphoranylation.

Introduction

In quest for hexaphenylethane (Figure 1, I), Moses Gomberg reported the triphenylmethyl (trityl) radical **II** in 1900.¹ The discovery of "trivalent carbon" is considered nowadays the beginning of organic radical chemistry. Later scrutiny revealed that the trityl radical had been obtained only in marginal yield, as it dimerizes instead through addition to the *para*-position of one phenyl substituent (Gomberg's dimer **III**).² Whereas heavier hexaphenylsilaethane is isolable,³ corresponding addition reactions to the *para*-position occur also for the isoelectronic triphenylboryl radical anion⁴ and the triphenylamine radical cation.⁵ Later in the 1970s, it was found that the decoration of the phenyl substituents allows to shift the equilibrium to respective hexaarylethane dimers.⁶ Phenyl group decoration similarly allows to shift the equilibrium toward monocationic triarylamine radical monomers⁷ and dianionic diboron(6) dimers.⁸

In stark contrast, both the hexaphenyl-1,2-diphosponium dication as well as the triphenylphosphine radical cation remain elusive.⁹ Triphenylphosphine radical cations are believed though to serve as transient key intermediates in (photo)redox and electro-catalysis,¹⁰ as well as even arene hydrogenation by water.¹¹ It is known furthermore that the sterically encumbered trimesitylphosphine radical cation

does not dimerize.¹² This radical may be obtained in crystalline form upon treating $(\text{Mes})_3\text{P}$ with $\text{Al}(\text{C}_6\text{F}_5)_3$,^{12b} thus bridging the fields of Frustrated Lewis Pair (FLP)¹³ and radical chemistry.¹⁴

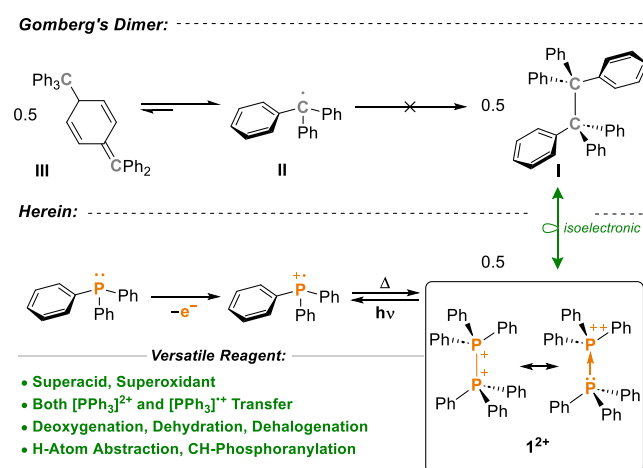


Figure 1. Opposed to the triphenylmethyl radical, which associates to Gomberg's dimer (top), the isoelectronic triphenylphosphine radical cation affords the hexaphenyl-1,2-diphosponium dimer (bottom).

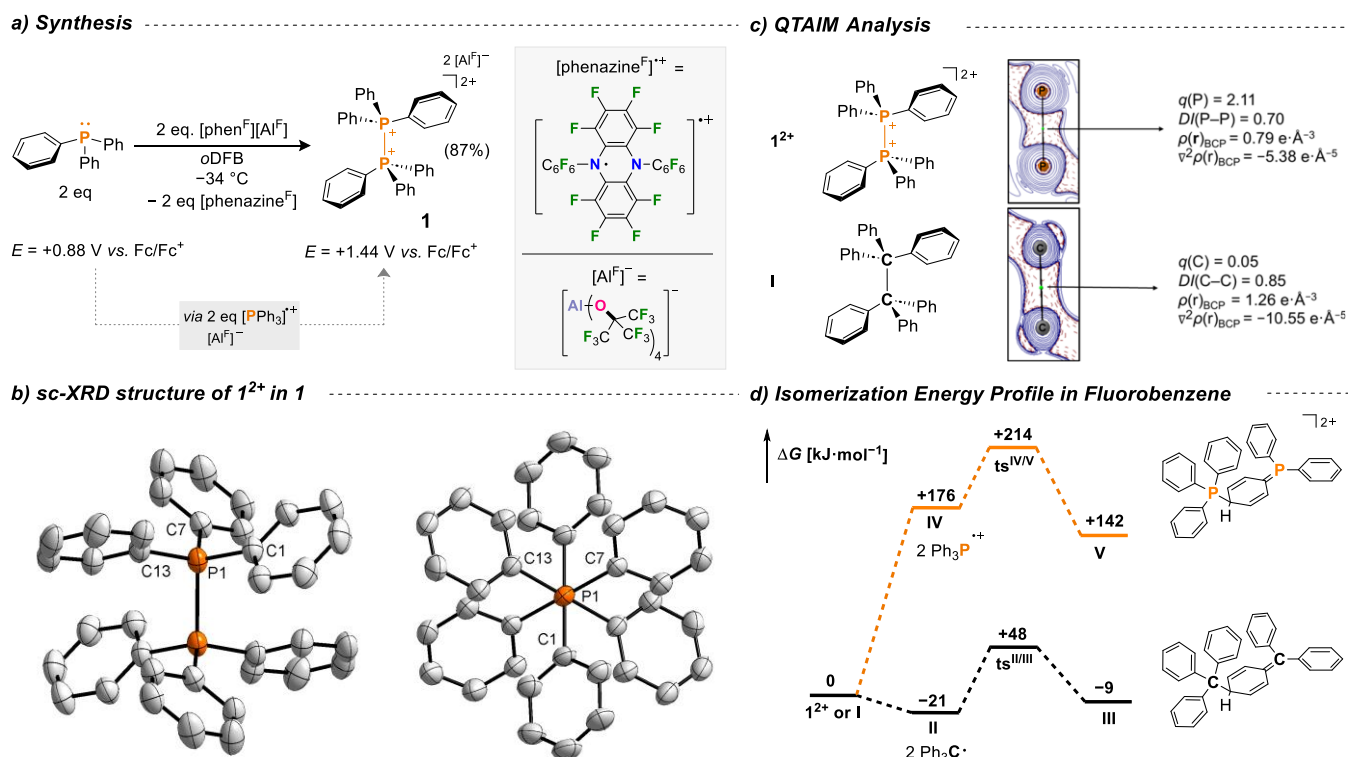
Further, a phosphine radical cation with three bulky halogenated naphthyl substituents, where the halogen-substituents interact with the radical site, was reported.¹⁵ The permethylation of diphosphines R_2P-PR_2 by an excess of methyl triflate ($R = Me$) affords peraliphatic $+P-P+$ vicinal diphosphonium dications.¹⁶ Whereas the reactivity of these compounds remains essentially unexplored beyond treating them with nucleophiles,^{10b,17} the electronic nature of the unusual vicinal dicationic¹⁸ $+P-P+$ bond has been investigated computationally and spectroscopically.¹⁹ It has been argued that (i) the $+P-P+$ bond is more susceptible for homolytic than heterolytic cleavage, and (ii) that the vicinal cationic charges infer covalency. Enforcing two phosphorus centers into proximity by a rigid bridge represents an alternative approach to 1,2-diphosphonium dications.²⁰ Treating the naphthalene-linked P^V/P^{III} precursor $(Ph_2F_2P)(C_{10}H_6)(PPh_2)$ with the triethylsilylium cation afforded the respective $+P-P+$ dication, which was described as a purely phosphorus-based and Lewis-acidic²¹ as well as hydridophilic FLP. Encouraged by the rich bond-activation chemistry by formal phosphorus dications²² and typically constrained phosphonium monocations and related compounds,²³ the emergence of organonpictogen redox catalysis,²⁴ as well as reports on formal carbon dications,²⁵ we turned our attention toward oxidizing triphenylphosphine by an innocent oxidant. The fluorinated phenazinium radi-

cal cations reported by the Crossing group appeared a promising choice,²⁶ as they are prepared with stable aluminate anions.²⁷ Here, we report that triphenylphosphine is swiftly oxidized by such "deelectronators", thereby affording the hexaaryl-1,2-diphosphonium dication 1^{2+} . Spectroscopic as well as computational investigations rationalize the stability of 1^{2+} in respect to Gomberg's dimer. Reactivity studies demonstrate (i) both homo- as well as heterolytic cleavage of the P-P bond, (ii) Lewis (super-)acidity, (iii) H-atom abstraction capabilities, and (iv) that dication 1^{2+} serves as powerful deoxygenation and phosphoranylation agent.

Results and Discussion

Treating triphenylphosphine in cold *ortho*-difluorobenzene (*o*DFOB) or 1,2,3,4-tetrafluorobenzene (TFB) with two equivalents of $[phen^F][Al^F]$ ($[phen^F] = [perfluoro-5,10-bis(perfluorophenyl)-5,10-dihydrophenazinium]^+$; $[Al^F] = [Al\{OC(CF_3)_3\}_4]^-$) (Scheme 1, a) afforded a faint yellow solution. A crystalline colorless precipitate formed upon slowly warming the solution to room temperature. The precipitate was identified as **1** according to the ³¹P NMR spectroscopic analysis with a signal at 17.6 ppm (*c.f.* $[Me_3P-PMe_3][OTf]_2$ 28.4 ppm),^{16a} and was isolated in 87% crystalline yield after workup. Single-crystal X-Ray diffraction (sc-XRD) confirmed the formation of the hexaphenyl-1,2-diphosphonium dialuminate $[Ph_3P-PPh_3][Al^F]_2$ (**1**, Scheme 1, b).

Scheme 1. a) Synthesis of 1, b) sc-XRD structure of 1^{2+} in single-crystals of $1 \cdot C_6H_2F_4$ illustrated with a Side (left) and Top View (right), c) QTAIM analysis of 1^{2+} in comparison to Ph_3C-CPh_3 , and d) Energy Profile for the formation of Gomberg's dimer at the CPCM(Fluorobenzene)-PBE0-D3(BJ)/def2-TZVP//PBE0/def2-SVP Level of Theory. Anions and Cocrystallized $C_6H_2F_4$ are Omitted for Clarity, Thermal Ellipsoids are Given at 50% Probability. Selected Bond Lengths [Å] and Angles [°] in **1: P1-P1, 2.262(3); P1-C1, 1.794(4); P1-C7, 1.786(4); P1-C13, 1.794(4); C1-P1-C7, 111.5(2); C7-P1-C13, 113.2(2); C1-P1-C13, 112.2(2); C13-P1-P1, 105.8(2); C7-P1-P1, 106.6(2); C13-P1-P1, 105.8(2); C13-P1-P1-C13, 180°.**



In the solid-state structure, an inversion center is found between the two phosphorus atoms, which infers a staggered conformation of the phenyl groups. The P–P bond of 2.262(3) Å is elongated in comparison to the PMe₃-congener (2.198(2) Å).^{16a} The comparison with triphenylphosphine reveals that the P–C bonds in **1** are shorter (**1**, 1.794(4); 1.786(4); 1.794(4) Å; PPh₃, ~1.823 Å) and that the C–P–C angles (**1**, 111.5(2), 113.2(2), 112.2(2)°; PPh₃, ~102°) are larger, thus indicating significant planarization and charge-delocalization.

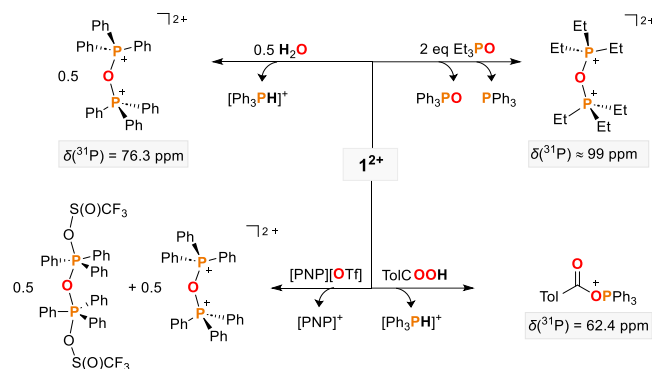
The Raman (IR, respectively; Figs. S15 S16, S17) vibrational spectroscopy revealed bands at $\tilde{\nu} = 191$ and 611 cm⁻¹, and a weak feature at 450 cm⁻¹. Based on computations (*vide infra*), we assign these signals to the P–P stretch, which couples with phenyl-based modes ($\tilde{\nu}_{\text{calc}} = 202, 581$ and 449 cm⁻¹; Fig. S111). Whereas it has been argued^{3b, 19b} that neither the P–P bond length nor corresponding stretching frequency (Badger’s and Gordy’s rules) are an accurate measure for the P–P bond’s strength, we note that these values are similar to the ones reported for the diphosphonium dication in [Me₃P–PMe₃][OTf]₂ ($\tilde{\nu} = 207, 456, 692$ cm⁻¹; $\tilde{\nu}_{\text{calc}} = 212, 444, 670$ cm⁻¹; Fig. S112). The cyclovoltammetric analysis in PFB (Fig. S97) revealed that dimeric **1** is a potent oxidant with a redox potential of $E = +1.44$ V vs. Fc/Fc⁺, which exceeds the one of monomeric PPh₃ ($E = \sim 0.88$ V vs. Fc/Fc⁺) by almost 0.6 V.

Quantum chemical calculations at the density functional level of theory (DFT) were performed to understand the stability of **1**²⁺. The topological analysis of the electron density (QTAIM; Scheme 1, c) affords a bond critical point (bcp) connecting the two phosphorus atoms. The negative sign of the Laplacian at the bcp ($\nabla^2\rho(r_{\text{bcp}}) = -5.38$ e Å⁻⁵) and the bond order ($DI = 0.70$) are consistent with a covalent interaction and local charge accumulation, coupled to charge depletion in the area opposed to the P–P bond. The QTAIM descriptors are similar to those reported for [Me₃P–PMe₃]²⁺ ($\rho(r_{\text{bcp}}) = 0.82$ e Å⁻³; $\nabla^2\rho(r_{\text{bcp}}) = -4.45$ e Å⁻⁵), yet enhanced covalency is found for carbon-congener **1** ($\rho(r_{\text{bcp}}) = 1.26$ e Å⁻³; $\nabla^2\rho(r_{\text{bcp}}) = -10.55$ e Å⁻⁵; $DI = 0.85$). According to Energy Decomposition Analysis coupled with Natural Orbitals for Chemical Valence (EDA-NOCV;²⁸ Tables S4–S9) in the gas-phase, the P–P interaction ($\Delta E_{\text{int}} = -122$ kJ mol⁻¹) is largely governed by dispersion ($\Delta E_{\text{disp}} = -80$ kJ mol⁻¹), and stronger than in [Me₃P–PMe₃]²⁺ ($\Delta E_{\text{int}} = -42$ kJ mol⁻¹, $\Delta E_{\text{disp}} = -27$ kJ mol⁻¹). Further, the electrostatic contribution is more favorable ($\Delta E_{\text{elstat}} = -206$ kJ mol⁻¹ vs. +7 kJ mol⁻¹) due to charge delocalization within the phenyl rings in **1**²⁺. In the case of hexaphenylethane **I**, the dispersion contribution ($\Delta E_{\text{disp}} = -81$ kJ mol⁻¹) is essentially the same as in **1**²⁺. Yet, and although the C–C interaction is strong ($\Delta E_{\text{int}} = -378$ kJ mol⁻¹), the monomers’ preparation energies compromise the stability of the dimer **I** ($-E_{\text{prep}} = +329$ kJ mol⁻¹).

Scheme 1d shows the free-energy profile for the formation of Gomberg’s dimer **III** and the corresponding P-congener **V** in fluorobenzene solution. Solvation renders the homolytic P–P bond cleavage in **1**²⁺ strongly endergonic (**IV**, $\Delta G = +176$ kJ mol⁻¹), which stands in stark contrast to the gas phase, where this reaction is facile (Fig. S104; $\Delta G_{\text{gas}} = +33$ kJ mol⁻¹). As dearomatization is not coupled to efficient charge-delocalization, also the addition product **V** is very high in energy ($\Delta G = +142$ kJ mol⁻¹). Opposed to **1**²⁺, solvation does not play a crucial role for the dissociation of neutral **I** into trityl

radicals **II** ($\Delta G = -21$ kJ mol⁻¹ Fig. S105; $\Delta G_{\text{gas}} = -14$ kJ mol⁻¹; Fig. S106) and neither for the further transformation to Gomberg’s dimer **III** ($\Delta G = -9$ kJ mol⁻¹, Fig. S105; $\Delta G_{\text{gas}} = -5$ kJ mol⁻¹, Fig. S106), which profits from the generation of a strong C=C double bond.

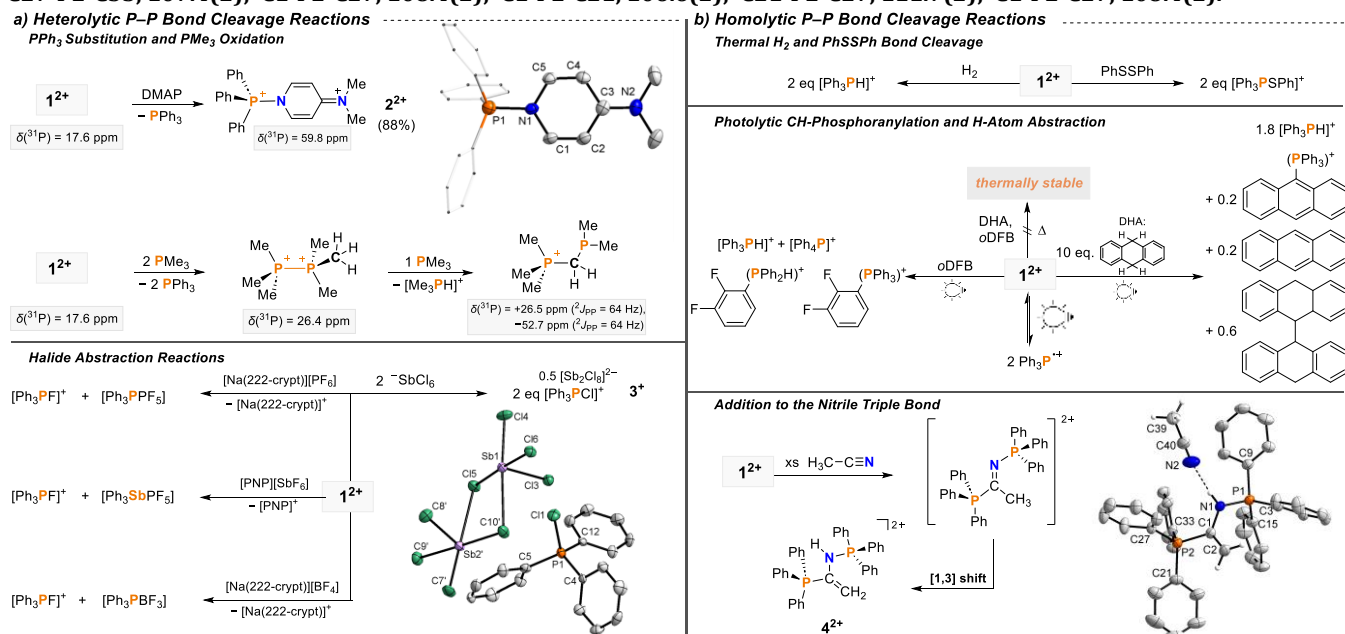
Efforts were conducted to gauge the Lewis-acidity²⁹ as well as oxophilicity of **1** (Ph₃P²⁺, respectively)³⁰ through either the addition of *para*-fluorobenzonitrile³¹ or triethylphosphine oxide (Gutmann–Beckett method).³² However, no reaction was observed with fluorobenzonitrile, whereas triethylphosphine oxide leads to oxygen transfer, thereby generating a stoichiometric mixture of triphenylphosphine oxide, triphenylphosphine and [Et₃P–O–PEt₃]²⁺ (Scheme 2). **Scheme 2. Deoxygenation of Et₃PO, Water, *p*-Toluic Acid and [PNP][OTf] by **1**²⁺; [Al^F] Anions are Omitted for Clarity, all Reactions were Conducted in *o*DFB at Ambient Temperature and Occur Instantaneously and Quantitatively.**



We consequently explored also the reaction with other oxygen-containing molecules such as water,¹¹ a triflate salt, and *p*-toluic acid. The controlled partial hydrolysis cleanly generated the aluminate analogue of Hendrickson’s reagent [(Ph₃P)₂O][OTf]₂ (“POP”)³³ and a stoichiometric amount of triphenylphosphonium salt [Ph₃PH]⁺. This reaction is remarkable, as Hendrickson’s reagent itself finds use for challenging dehydration reactions.³⁴ In fact, and highlighting exceeding oxophilicity, we observed the instantaneous abstraction of oxygen atoms upon adding the triflate salt [PNP][OTf] (PNP = [Ph₃PNPPh₃]⁺) to **1**.³⁵ The reaction with *p*-toluic acid generated the respective acyloxyphosphonium salt, which serves as the activated mixed-anhydride intermediate in the Appel³⁶ and Mitsunobu³⁷ reactions.

Further detailed reactivity studies were conducted to gauge the interplay of heterolytic *versus* homolytic P–P bond cleavage. Dimethylaminopyridine (DMAP) readily replaces triphenylphosphine under heterolytic P–P bond cleavage to afford the DMAP adduct **2** in *o*DFB solution at room temperature (Scheme 3, a). In the solid-state structure of **2**, both the P–N (1.719(2) Å) as well as C=NMe₂ (1.320(4) Å) bonds are consistent with the values found for [Me₃P(DMAP)][OTf]₂ (P–N, 1.720(3); C=NMe₂ 1.319(4) Å),^{17a} thus indicating pronounced delocalization of cationic charge onto the DMAP substituent. Note however that the equilibrium lies in case of [Me₃P(DMAP)][OTf]₂ at the side of [Me₃P–PMe₃][OTf]₂. The substitution of PPh₃ proceeds according to quantum-chemical calculations barrierless through an S_N2-type mechanism (Fig. S114), thereby highlighting the Lewis-acidity of **1**.

Scheme 3. Heterolytic (a) and Homolytic (b) Bond Cleavage Reactions of 1; [Al^F] Anions are omitted for clarity. All Reactions were Performed in *o*DFB and Proceed Quantitatively. Most Hydrogen Atoms within Crystal Structure Representations are Omitted for Clarity, Thermal Ellipsoids are Given at 50% Probability. Only one of Four Independent [PPh₃Cl]⁺ Moieties and a Symmetry Generated Part of the Anion are Shown for Clarity (see ESI for Details). Selected Bond Lengths [Å] and Angles [°]: 2²⁺; P1–N1, 1.719(2); P1–C8, 1.772(3); P1–C14, 1.780(3); P1–C20, 1.779(3); N1–C1, 1.384(4); N1–C5, 1.387(4); C1–C2, 1.339(4); C2–C3, 1.423(4); C4–C5, 1.329(4); C3–C4, 1.433(4); C3–N2, 1.320(4); C14–P1–C20, 113.6(1); C20–P1–C8, 113.9(1); C8–P1–C14, 109.9(1); C8–P1–N1, 108.1(1); C20–P1–N1, 104.0(1); C14–P1–N1, 106.8(1). 3⁺; P1–Cl1, 1.995(2); P1–C4, 1.780(5); P1–C5, 1.757(7); P1–C12, 1.776(7); Sb1–Cl3, 2.369(2); Sb1–Cl4, 2.420(2); Sb1–Cl5, 2.775(2); Sb1–Cl6, 2.492(2); Sb2'–C7', 2.394(2); Sb2'–C8', 2.381(2); Sb2'–C9', 2.488(2); Sb2'–C5, 2.986(2); Sb2'–C10', 2.776(2); Cl1–P1–C4, 107.64(2); Cl1–P1–C5, 107.2(2); Cl1–P1–C12, 107.1(2). 4²⁺; P1–N1, 1.650(4); P1–C3, 1.783(4); P1–C9, 1.787(5); P1–C15, 1.788(5); N1–C1, 1.424(6); C1–C2, 1.324(7); P2–C1, 1.817(4); P2–C21, 1.790(5); P2–C27, 1.793(5); P2–C33, 1.794(5); C39–C40, 1.457(9); C40–N2, 1.119(9); N1…N2, 2.844(6); P1–N1–C1, 123.6(3); N1–C1–P2, 116.3(3); N1–C1–C2, 123.9(4); C39–C40–N2, 179.4(7); C3–P1–C9, 108.8(2); C3–P1–C15, 108.8(2); C9–P1–C15, 114.8(2); C3–P1–N1, 112.4(2); C9–P1–N1, 103.5(2); C15–P1–N1, 108.3(2); P2–C1–N1, 116.3(3); P2–C1–C2, 119.7(3); C21–P2–C27, 111.7(2); C21–P2–C33, 111.7(2); C27–P2–C33, 107.4(2); C1–P2–C27, 108.4(2); C1–P2–C21, 106.6(2); C21–P2–C27, 111.7(2); C1–P2–C27, 108.4(2).



We analyzed the P–P bond polarization along the reaction coordinate by the occupations of σ -type effective-fragment orbitals (EFOs)³⁸ of the triphenylphosphine fragments (Fig. S115).³⁹ DMAP polarizes the P–P bond already at long distance ($d_{P-N} = 2.931$ Å), rendering former **12⁺** effectively a triphenylphosphine-stabilized triphenylphosphorandiylum dication. Upon treating **1** with two equivalents of trimethylphosphine, the stoichiometric formation of $[\text{Me}_3\text{P}-\text{PMe}_3]^{2+}$ and PPh_3 was observed, which reveals that **12⁺** is a stronger oxidant (less stable, respectively) than $[\text{Me}_3\text{P}-\text{PMe}_3]^{2+}$. Treatment with overall three equivalents of PMe_3 generated $[\text{Me}_3\text{PH}]^+$ and $[\text{Me}_3\text{PCH}_2\text{PMe}_2]^+$.^{16c,d} Eventually, salt **1** was found to cleanly and instantaneously generate corresponding halotriphenylphosphonium salts in the halide abstraction reactions with the $-\text{BF}_4$, $-\text{PF}_6$, $-\text{SbCl}_6$ and even $-\text{SbF}_6$ anions, which commonly serves as benchmark for Lewis-supercidity.⁴⁰ Compound **1** also engages in formally homolytic P–P bond cleavage reactions (Scheme 3, b). Both the S–S bond in diphenyldisulfide as well as the H–H bond in dihydrogen are readily cleaved (oxidized, respectively),⁴¹ thereby affording the $[\text{Ph}_3\text{PSPH}]^+$ and $[\text{Ph}_3\text{PH}]^+$ phosphonium cations, respectively. Exploring the reactivity with C–H bonds, salt **1** was heated to reflux in *o*DFB in the presence of 9,10-dihydroanthracene (DHA; $BDFE = 305$ kJ mol⁻¹; $E = 0.88$ V vs. H₂)⁴². However, the NMR spectroscopic analysis revealed that **1** is stable under these conditions. In stark con-

trast, irradiating **1** by a Xenon-lamp in the presence of 50 equivalents of DHA afforded $[\text{Ph}_3\text{PH}]^+$ and anthracene within less than 30 min at room temperature. The NMR-spectroscopic analysis revealed thereby the major formation of the homo-coupled anthracenyl dimer, thus confirming a radical H-atom abstraction pathway (Fig. S82–87). The formation of $[\text{Ph}_3\text{PH}]^+$ was observed also in the control experiment, that is in the absence of DHA. In this case however, the reaction required 3 h to achieve quantitative conversion and is due to phosphoranylation of *o*DFB solvent molecules, followed by partial metathetical aryl group exchange. The formally electrophilic aromatic substitution is unusual, as it proceeds with an electron-deficient arene. It thus prospects synthetically useful substitution reactions with electron-rich arenes. Homolytic P–P bond cleavage under the transfer of two Ph_3P^{2+} substituents also was observed in the reaction with an unsaturated π -system. Keeping **1** at room temperature over two days in acetonitrile led to quantitative conversion to the nitrile-addition product **4**. Following the reaction by ¹H NMR spectroscopy substantiated thereby the presence of an intermediate, which is assigned to the initial addition product, which then tautomerizes (Fig. S72). Paralleling the CH phosphoranylation of *o*DFB, this reaction again highlights the group-transfer capabilities of **12⁺**, as electron-deficient acetonitrile usually is considered exceedingly difficult to activate under oxidative conditions.

Conclusion

We report that the oxidation of triphenylphosphine furnishes the hexaphenyl-1,2-diphosphonium dication in the form of its perfluorinated alkoxy aluminate salt **1**. This reaction involves the dimerization of the transient triphenylphosphine radical cation. Highlighting cooperativity, this dimerization boosts the redox-potential by +0.6 V and hence generates a potent oxidant with $E = +1.44$ V vs. Fc/Fc⁺, which oxidizes trimethylphosphine and activates dihydrogen. Quantum chemical calculations rationalize that **1**²⁺, isoelectronic with hexaphenylethane, does not form the equivalent of Gomberg's dimer, as the phosphorus addition product is thermodynamically disfavored. Mimicking halogens, salt **1** may react by both heterolytic and homolytic pathways. Heterolytic P–P bond cleavage dominates thermally, that is the compound is to be understood here a phosphorus-only Frustrated Lewis Pair (FLP) and a surrogate of the triphenylphosphorandiylium dication Ph₃P²⁺. It hence serves as a (super-)acidic halide- and powerful oxygen abstraction and/or dehydration reagent. Diphosphoranylation of the electron-deficient C≡N multiple bond occurs in the reaction with acetonitrile. The irradiation with UV-light induces homolytic P–P bond cleavage to triphenylphosphine radical cations Ph₃P^{•+}, which engage in H-atom abstraction and arene CH phosphoranylation. In short, compound **1** complements our knowledge on the trityl radical, improves our understanding of oxidation catalysis with ubiquitous triphenylphosphine and corresponding transient triphenylphosphine radical cations. It thereby presents itself as a powerful Lewis-acid, oxidant, as well as deoxygenation- and phosphoranylation agent.

ASSOCIATED CONTENT

Supporting Information. Synthetic procedures, spectroscopic data, computational and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* dominik.munz@uni-saarland.de

* pedro.salvador@udg.edu

* weiss@chemie.uni-erlangen.de

Funding Sources

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Program (grant no. 948185). B.M. and F.D. thank for the instrumentation and technical assistance for this work, provided by the Service Center X-ray Diffraction, with financial support from Saarland University and the German Science Foundation DFG (project number INST 256/506-1 and INST 256/582-1). We gratefully acknowledge scientific support and HPC resources provided by the Erlangen National High Performance Computing Center (NHR@FAU) of the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU). We thank the NHR funding provided by federal and Bavarian state authorities. The NHR@FAU hardware is partially funded by the German Research Foundation (DFG) – 440719683.

ACKNOWLEDGMENT

We thank C. W. M. Kay and K. Hollemeyer (Servicestelle Massenspektrometrie) for support with EPR and HRMS-measurements, and I. Crossing and M. Sellin for helpful discussions.

ABBREVIATIONS

[AlF]⁻, [Al{OC(CF₃)₃}₄]⁻; bcp, bond critical point; BDFE, bond dissociation free energy; DHA, 9,10-dihydroanthracene; DMAP, dimethylaminopyridine; DFT, density functional theory; DHA, dihydroanthracene; EDA-NOCV, energy decomposition analysis with natural orbitals for chemical valence; Fc, ferrocene; FLP, frustrated Lewis pair; IR, infrared; *o*DFB, 1,2-difluorobenzene; [phen^F]⁺, [perfluoro-5,10-bis(perfluorophenyl)-5,10-dihydrophenazinium]⁺; PFB, pentafluorobenzene; NMR, nuclear magnetic resonance; QTAIM, quantum theory of atoms in molecules; sc-XRD, single-crystal X-ray diffractometry; TFB, 1,2,3,4-tetrafluorobenzene.

REFERENCES

- (a) Gomberg, M. An instance of trivalent carbon: triphenylmethyl *J. Am. Chem. Soc.* **1900**, *22*, 757-771. (b) Gomberg, M. Triphenylmethyl, ein Fall von dreiwertigem Kohlenstoff. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3150-3163.
- Lankamp, H.; Nauta, W. T.; MacLean, C. A new interpretation of the monomer-dimer equilibrium of triphenylmethyl- and alkylsubstituted-diphenyl methyl-radicals in solution. *Tetrahedron Lett.* **1968**, *9*, 249-254.
- (a) Schlenk, W.; Renning, J.; Racky, G. Über das Hexaphenyl-silicoäthan und einige Biphenyl-Substitutionsprodukte des gewöhnlichen Äthans und Äthylens. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1178-1182. (b) Rummel, L.; Schumann, J. M.; Schreiner, P. R. Hexaphenylditetrels – When Longer Bonds Provide Higher Stability. *Chem. Eur. J.* **2021**, *27*, 13699-13702.
- Eisch, J. J.; Dluzniewski, T.; Behrooz, M. The nature of Krause's adducts: The structure of the 1:1 adduct of triphenylborane with sodium metal. *Heteroat. Chem.* **1993**, *4*, 235-241.
- (a) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. Anodic Oxidation Pathways of Aromatic Amines. Electrochemical and Electron Paramagnetic Resonance Studies. *J. Am. Chem. Soc.* **1966**, *88*, 3498-3503. (b) Marcoux, L. S.; Adams, R. N.; Feldberg, S. W. Dimerization of Triphenylamine Cation Radicals. Evaluation of Kinetics Using the Rotating Disk Electrode. *J. Phys. Chem.* **1969**, *73*, 2611-2614.
- (a) Stein, M.; Winter, W.; Rieker, A. Hexakis(2,6-di-tert-butyl-4-biphenyl)ethane—The First Unbridged Hexaarylethane. *Angew. Chem. Int. Ed.* **1978**, *17*, 692-694. (b) Grimme, S.; Schreiner, P. R. Steric Crowding Can Stabilize a Labile Molecule: Solving the Hexaphenylethane Riddle. *Angew. Chem. Int. Ed.* **2011**, *50*, 12639-12642. (c) Uchimura, Y.; Takeda, T.; Katoono, R.; Fujiwara, K.; Suzuki, T. New Insights into the Hexaphenylethane Riddle: Formation of an α,o -Dimer. *Angew. Chem. Int. Ed.* **2015**, *54*, 4010-4013. (d) Rösel, S.; Balestrieri, C.; Schreiner, P. R. Sizing the role of London dispersion in the dissociation of all-meta tert-butyl hexaphenylethane. *Chem. Sci.* **2017**, *8*, 405-410. (e) Rösel, S.; Becker, J.; Allen, W. D.; Schreiner, P. R. Probing the Delicate Balance between Pauli Repulsion and London Dispersion with Triphenylmethyl Derivatives. *J. Am. Chem. Soc.* **2018**, *140*, 14421-14432.
- (a) Vasiļevska, A.; Slanina, T. Structure–property–function relationships of stabilized and persistent C- and N-based triaryl radicals. *Chem. Commun.* **2024**, *60*, 252-264. (b) Heuer, A. M.; Coste, S. C.; Singh, G.; Mercado, B. Q.; Mayer, J. M. A Guide to Tris(4-Substituted)-triphenylmethyl Radicals. *J. Org. Chem.* **2023**, *88*, 9893-9901.

8. Li, S.; Shiri, F.; Xu, G.; Yiu, S.-M.; Lee, H. K.; Ng, T. H.; Lin, Z.; Lu, Z. Reactivity of a Hexaaryldiboron(6) Dianion as Boryl Radical Anions. *J. Am. Chem. Soc.* **2024**, *146*, 17348-17354.
9. (a) Powell, R. L.; Hall, C. D. Phosphonium radical cation. *J. Am. Chem. Soc.* **1969**, *91*, 5403-5404. (b) Reichl, K. D.; Ess, D. H.; Radosevich, A. T. Catalyzing Pyramidal Inversion: Configurational Lability of P-Stereogenic Phosphines via Single Electron Oxidation. *J. Am. Chem. Soc.* **2013**, *135*, 9354-9357. (c) Yasui, S.; Tojo, S.; Majima, T. Reaction of Triarylphosphine Radical Cations Generated from Photoinduced Electron Transfer in the Presence of Oxygen. *J. Org. Chem.* **2005**, *70*, 1276-1280.
10. (a) Schiavon, G.; Zecchin, S.; Cogoni, G.; Bontempelli, G. Anodic oxidation of triphenylphosphine at a platinum electrode in acetonitrile medium. *J. Electroanal. Chem. Interf. Electrochem.* **1973**, *48*, 425-431. (b) Nikitin, E. V.; Romakhin, A. S.; Zagumenov, V. A.; Babkin, Y. A. Electrochemical synthesis of diphosphonium salts, their reactivity and role in organic electrosynthesis. *Electrochim. Acta* **1997**, *42*, 2217-2224. (c) Leca, D.; Fensterbank, L.; Lacôte, E.; Malacria, M. Recent advances in the use of phosphorus-centered radicals in organic chemistry. *Chem. Soc. Rev.* **2005**, *34*, 858-865. (d) Luo, K.; Yang, W.-C.; Wu, L. Photoredox Catalysis in Organophosphorus Chemistry. *Asian J. Org. Chem.* **2017**, *6*, 350-367. (e) Rossi-Ashton, J. A.; Clarke, A. K.; Unsworth, W. P.; Taylor, R. J. K. Phosphoranyl Radical Fragmentation Reactions Driven by Photoredox Catalysis. *ACS Catal.* **2020**, *10*, 7250-7261. (f) Hu, X.-Q.; Hou, Y.-X.; Liu, Z.-K.; Gao, Y. Recent advances in phosphoranyl radical-mediated deoxygenative functionalisation. *Org. Chem. Front.* **2020**, *7*, 2319-2324. (g) Pan, D.; Nie, G.; Jiang, S.; Li, T.; Jin, Z. Radical reactions promoted by trivalent tertiary phosphines. *Org. Chem. Front.* **2020**, *7*, 2349-2371. (h) Roediger, S.; Le Saux, E.; Boehm, P.; Morandi, B. Coupling of unactivated alkyl electrophiles using frustrated ion pairs. *Nature* **2024**, *636*, 108-114.
11. Zhang, J.; Mück-Lichtenfeld, C.; Studer, A. Photocatalytic phosphine-mediated water activation for radical hydrogenation. *Nature* **2023**, *619*, 506-513.
12. (a) Pan, X.; Chen, X.; Li, T.; Li, Y.; Wang, X. Isolation and X-ray Crystal Structures of Triarylphosphine Radical Cations. *J. Am. Chem. Soc.* **2013**, *135*, 3414-3417. (b) Ménard, G.; Hatnean, J. A.; Cowley, H. J.; Lough, A. J.; Rawson, J. M.; Stephan, D. W. C-H bond activation by radical ion pairs derived from $R_3P/Al(C_6F_5)_3$ frustrated Lewis pairs and N_2O . *J. Am. Chem. Soc.* **2013**, *135*, 6446-6449. (c) Liu, L.; Cao, L. L.; Shao, Y.; Ménard, G.; Stephan, D. W. A Radical Mechanism for Frustrated Lewis Pair Reactivity. *Chem* **2017**, *3*, 259-267. (d) Holtrop, F.; Jupp, A. R.; Kooij, B. J.; van Leest, N. P.; de Bruin, B.; Slootweg, J. C. Single-Electron Transfer in Frustrated Lewis Pair Chemistry. *Angew. Chem. Int. Ed.* **2020**, *59*, 22210-22216. (e) Das, B.; Makol, A.; Kundu, S. Phosphorus radicals and radical ions. *Dalton Trans.* **2022**, *51*, 12404-12426.
13. (a) Stephan, D. W.; Erker, G. Frustrated Lewis Pair Chemistry: Development and Perspectives. *Angew. Chem. Int. Ed.* **2015**, *54*, 6400-6441. (b) Stephan, D. W. The broadening reach of frustrated Lewis pair chemistry. *Science* **2016**, *354*, aaf7229.
14. (a) Jupp, A. R.; Stephan, D. W. New Directions for Frustrated Lewis Pair Chemistry. *Trends Chem.* **2019**, *1*, 35-48. (b) Ju, M.; Lu, Z.; Novaes, L. F. T.; Martinez Alvarado, J. I.; Lin, S. Frustrated Radical Pairs in Organic Synthesis. *J. Am. Chem. Soc.* **2023**, *145*, 19478-19489. (c) van der Zee, L. J. C.; Pahar, S.; Richards, E.; Melen, R. L.; Slootweg, J. C. Insights into Single-Electron-Transfer Processes in Frustrated Lewis Pair Chemistry and Related Donor-Acceptor Systems in Main Group Chemistry. *Chem. Rev.* **2023**, *123*, 9653-9675.
15. Ham, G.; Kim, Y.; Jang, W.-D.; Kim, S. An Isolable Triarylphosphine Radical Cation Electronically Stabilized by Through-Space Radical Delocalization. *J. Am. Chem. Soc.* **2024**, *146*, 31405-31411.
16. (a) Weigand, J. J.; Riegel, S. D.; Burford, N.; Decken, A. Prototypical Phosphorus Analogues of Ethane: General and Versatile Synthetic Approaches to Hexaalkylated P-P Diphosphonium Cations. *J. Am. Chem. Soc.* **2007**, *129*, 7969-7976. (b) Dyker, C. A.; Burford, N. catena-Phosphorus Cations. *Chem. Asian J.* **2008**, *3*, 28-36. (c) Robertson, A. P. M.; Chitnis, S. S.; Jenkins, H. A.; McDonald, R.; Ferguson, M. J.; Burford, N. Establishing the Coordination Chemistry of Antimony(V) Cations: Systematic Assessment of $Ph_4Sb(OTf)$ and $Ph_3Sb(OTf)_2$ as Lewis Acceptors. *Chem. Eur. J.* **2015**, *21*, 7902-7913. (d) Chitnis, S. S.; Robertson, A. P. M.; Burford, N.; Weigand, J. J.; Fischer, R. Synthesis and reactivity of cyclo-tetra(stibinophosphonium) tetracations: redox and coordination chemistry of phosphine-antimony complexes. *Chem. Sci.* **2015**, *6*, 2559-2574.
17. (a) Weigand, J. J.; Burford, N.; Decken, A.; Schulz, A. Preparation and Characterization of a Ligand-Stabilized Trimethylphosphane Dication. *Eur. J. Inorg. Chem.* **2007**, *2007*, 4868-4872. (b) Weigand, J. J.; Burford, N.; Mahnke, D.; Decken, A. Coordination Complexes of the Dimethylthiophosphonium Cation and Ligand Exchange. *Inorg. Chem.* **2007**, *46*, 7689-7691.
18. Munz, D.; Meyer, K. Charge frustration as a concept for ligand design and functional group transfer. *Nat. Rev. Chem.* **2021**, *5*, 422-439.
19. (a) Wolstenholme, D. J.; Weigand, J. J.; Davidson, R. J.; Pearson, J. K.; Cameron, T. S. Understanding the Electronic Structure, Reactivity, and Hydrogen Bonding for a 1,2-Diphosphonium Dication. *J. Phys. Chem. A* **2008**, *112*, 3424-3431. (b) Chitnis, S. S.; Whalen, J. M.; Burford, N. Influence of charge and coordination number on bond dissociation energies, distances, and vibrational frequencies for the phosphorus-phosphorus bond. *J. Am. Chem. Soc.* **2014**, *136*, 12498-12506.
20. Holthausen, M. H.; Bayne, J. M.; Mallov, I.; Dobrovetsky, R.; Stephan, D. W. 1,2-Diphosphonium Dication: A Strong P-Based Lewis Acid in Frustrated Lewis Pair (FLP)-Activations of B-H, Si-H, C-H, and H-H Bonds. *J. Am. Chem. Soc.* **2015**, *137*, 7298-7301.
21. (a) Caputo, C. B.; Hounjet, L. J.; Dobrovetsky, R.; Stephan, D. W. Lewis Acidity of Organofluorophosphonium Salts: Hydrodefluorination by a Saturated Acceptor. *Science* **2013**, *341*, 1374-1377. (b) Bayne, J. M.; Stephan, D. W. Phosphorus Lewis acids: emerging reactivity and applications in catalysis. *Chem. Soc. Rev.* **2016**, *45*, 765-774. (c) Burford, N.; Ragogna, P. J. New synthetic opportunities using Lewis acidic phosphines. *J. Chem. Soc., Dalton Trans.* **2002**, 4307-4315.
22. (a) Zhou, J.; Liu, L. L.; Cao, L. L.; Stephan, D. W. A Phosphorus Lewis Super Acid: η^5 -Pentamethylcyclopentadienyl Phosphorus Dication. *Chem* **2018**, *4*, 2699-2708. (b) Mehlmann, P.; Witteler, T.; Wilm, L. F. B.; Dielmann, F. Isolation, characterization and reactivity of three-coordinate phosphorus dications isoelectronic to alanes and silylium cations. *Nat. Chem.* **2019**, *11*, 1139-1143. (c) Đorđević, N.; Ganguly, R.; Petković, M.; Vidović, D. E-H (E = B, Si, C) Bond Activation by Tuning Structural and Electronic Properties of Phosphenium Cations. *Inorg. Chem.* **2017**, *56*, 14671-14681. (d) Chitnis, S. S.; Krischer, F.; Stephan, D. W. Catalytic Hydrodefluorination of C-F Bonds by an Air-Stable P^{III} Lewis Acid. *Chem. Eur. J.* **2018**, *24*, 6543-6546. (e) Waked, A. E.; Chitnis, S. S.; Stephan, D. W. P(V) dications: carbon-based Lewis acid initiators for hydrodefluorination. *Chem. Commun.* **2019**, *55*, 8971-8974. (f) Chitnis, S. S.; LaFortune, J. H. W.; Cummings, H.; Liu, L. L.; Andrews, R.; Stephan, D. W. Phosphorus Coordination Chemistry in Catalysis: Air Stable P(III)-Dications as Lewis Acid Catalysts for the Allylation of C-F Bonds. *Organometallics* **2018**, *37*, 4540-4544. (g) Humphries, A. L.; Tellier, G. A.; Smith, M. D.; Chianese, A. R.; Peryshkov, D. V. N-H Bond Activation of Ammonia by a Redox-Active Carboranyl Diphosphine. *J. Am. Chem. Soc.* **2024**, *146*, 33159-33162.
23. (a) Arduengo, A. J., III; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Culley, S. A.; Mizzen, M. B. The synthesis, structure, and chemistry of 10-Pn-3 systems: tricoordinate hypervalent pnictogen compounds. *J. Am. Chem. Soc.* **1987**, *109*, 627-647. (b) Dunn, N. L.; Ha, M.; Radosevich, A. T. Main Group Redox Catalysis: Reversible P^{III}/P^V Redox Cycling at a Phosphorus Platform. *J. Am. Chem. Soc.* **2012**, *134*, 11330-11333. (c) Zhao, W.; McCarthy, S. M.;

- Lai, T. Y.; Yennawar, H. P.; Radosevich, A. T. Reversible Intermolecular E-H Oxidative Addition to a Geometrically Deformed and Structurally Dynamic Phosphorous Triamide. *J. Am. Chem. Soc.* **2014**, *136*, 17634-17644. (d) Volodarsky, S.; Dobrovetsky, R. Amphiphilic geometrically constrained phosphonium cation. *Chem. Commun.* **2018**, *54*, 6931-6934. (e) Roth, D.; Stirn, J.; Stephan, D. W.; Greb, L. Lewis Superacidic Catecholato Phosphonium Ions: Phosphorus-Ligand Cooperative C-H Bond Activation. *J. Am. Chem. Soc.* **2021**, *143*, 15845-15851. (f) Abbenseth, J.; Townrow, O. P. E.; Goicoechea, J. M. Thermoneutral N-H Bond Activation of Ammonia by a Geometrically Constrained Phosphine. *Angew. Chem. Int. Ed.* **2021**, *60*, 23625-23629. (g) McCarthy, S. M.; Lin, Y.-C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. Intermolecular N-H Oxidative Addition of Ammonia, Alkylamines, and Arylamines to a Planar σ^3 -Phosphorus Compound via an Entropy-Controlled Electrophilic Mechanism. *J. Am. Chem. Soc.* **2014**, *136*, 4640-4650. (h) Volodarsky, S.; Bawari, D.; Dobrovetsky, R. Dual Reactivity of a Geometrically Constrained Phosphonium Cation. *Angew. Chem. Int. Ed.* **2022**, *61*, e202208401. (i) Chulsky, K.; Malahov, I.; Bawari, D.; Dobrovetsky, R. Metallomimetic Chemistry of a Cationic, Geometrically Constrained Phosphine in the Catalytic Hydrodefluorination and Amination of Ar-F Bonds. *J. Am. Chem. Soc.* **2023**, *145*, 3786-3794. (j) Bawari, D.; Toami, D.; Jaiswal, K.; Dobrovetsky, R. Hydrogen splitting at a single phosphorus centre and its use for hydrogenation. *Nat. Chem.* **2024**, *16*, 1261-1266. (k) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. Phosphine Coordination Complexes of the Diphenylphosphonium Cation: A Versatile Synthetic Methodology for P-P Bond Formation. *J. Am. Chem. Soc.* **2003**, *125*, 14404-14410. (l) Pearce, K. G.; Borys, A. M.; Clark, E. R.; Shepherd, H. J. Exploring the Reactivity of Donor-Stabilized Phosphonium Cations: Lewis Acid-Catalyzed Reduction of Chlorophosphanes by Silanes. *Inorg. Chem.* **2018**, *57*, 11530-11536. (m) Lee, V. Y.; Sugawara, H.; Gapurenko, O. A.; Minyaev, R. M.; Minkin, V. I.; Gornitzka, H.; Sekiguchi, A. A Cationic Phosphapyramidane. *Chem. Eur. J.* **2016**, *22*, 17585-17589. (n) Olaru, M.; Mebs, S.; Beckmann, J. Cationic Carbene Analogues: Donor-Free Phosphonium and Arsenium Ions. *Angew. Chem. Int. Ed.* **2021**, *60*, 19133-19138. (o) Clark, E. R.; Borys, A. M.; Pearce, K. Donor-substituted phosphanes – surprisingly weak Lewis donors for phosphonium cation stabilisation. *Dalton Trans.* **2016**, *45*, 16125-16129. (p) Wünsche, M. A.; Witteler, T.; Dielmann, F. Lewis Base Free Oxophosphonium Ions: Tunable, Trigonal-Planar Lewis Acids. *Angew. Chem. Int. Ed.* **2018**, *57*, 7234-7239.
24. (a) Abbenseth, J.; Goicoechea, J. M. Recent developments in the chemistry of non-trigonal pnictogen pincer compounds: from bonding to catalysis. *Chem. Sci.* **2020**, *11*, 9728-9740. (b) Lipshultz, J. M.; Li, G.; Radosevich, A. T. Main Group Redox Catalysis of Organopnictogens: Vertical Periodic Trends and Emerging Opportunities in Group 15. *J. Am. Chem. Soc.* **2021**, *143*, 1699-1721.
25. (a) Loh, Y. K.; Melaimi, M.; Gembicky, M.; Munz, D.; Bertrand, G. A crystalline doubly oxidized carbene. *Nature* **2023**, *623*, 66-70. (b) Gong, Y.; Langwald, J.; Mulks, F. F. On the road to isolable geminal carbodocations. *Chem* **2024**, *10*, 3294-3308.
26. (a) Schorpp, M.; Heizmann, T.; Schmucker, M.; Rein, S.; Weber, S.; Krossing, I. Synthesis and Application of a Perfluorinated Ammoniumyl Radical Cation as a Very Strong Deelectronator. *Angew. Chem. Int. Ed.* **2020**, *59*, 9453-9459. (b) Sellin, M.; Friedmann, C.; Mayländer, M.; Richert, S.; Krossing, I. Towards clustered carbonyl cations $[M_3(CO)_{14}]^{2+}$ (M = Ru, Os): the need for innocent deelectronation. *Chem. Sci.* **2022**, *13*, 9147-9158. (c) Rall, J. M.; Schorpp, M.; Keilwerth, M.; Mayländer, M.; Friedmann, C.; Daub, M.; Richert, S.; Meyer, K.; Krossing, I. Synthesis and Characterization of Stable Iron Pentacarbonyl Radical Cation Salts. *Angew. Chem. Int. Ed.* **2022**, *61*, e202204080. (d) Armbruster, C.; Sellin, M.; Seiler, M.; Würz, T.; Oesten, F.; Schmucker, M.; Sterbak, T.; Fischer, J.; Radtke, V.; Hunger, J.; Krossing, I. Pushing redox potentials to highly positive values using inert fluorobenzenes and weakly coordinating anions. *Nat. Commun.* **2024**, *15*, 6721. (e) Sellin, M.; Willrett, J.; Röhner, D.; Heizmann, T.; Fischer, J.; Seiler, M.; Holzmann, C.; Engesser, T. A.; Radtke, V.; Krossing, I. Utilizing the Perfluoronaphthalene Radical Cation as a Selective Deelectronator to Access a Variety of Strongly Oxidizing Reactive Cations. *Angew. Chem. Int. Ed.* **2024**, *63*, e202406742.
27. Engesser, T. A.; Lichtenthaler, M. R.; Schleep, M.; Krossing, I. Reactive p-block cations stabilized by weakly coordinating anions. *Chem. Soc. Rev.* **2016**, *45*, 789-899.
28. Mitoraj, M. P.; Michalak, A.; Ziegler, T. A Combined Charge and Energy Decomposition Scheme for Bond Analysis. *J. Chem. Theory Comput.* **2009**, *5*, 962-975.
29. Greb, L. Lewis Superacids: Classifications, Candidates, and Applications. *Chem. Eur. J.* **2018**, *24*, 17881-17896.
30. Erdmann, P.; Schmitt, M.; Sigmund, L. M.; Krämer, F.; Breher, F.; Greb, L. How to Deal with Charge in the Ranking of Lewis Acidity: Critical Evaluation of an Extensive Set of Cationic Lewis Acids. *Angew. Chem. Int. Ed.* **2024**, *63*, e202403356.
31. Künzler, S.; Rathjen, S.; Merk, A.; Schmidtman, M.; Müller, T. An Experimental Acidity Scale for Intramolecularly Stabilized Silyl Lewis Acids. *Chem. Eur. J.* **2019**, *25*, 15123-15130.
32. (a) Mayer, U.; Gutmann, V.; Gerger, W. The acceptor number – A quantitative empirical parameter for the electrophilic properties of solvents. *Monatsh. Chem.* **1975**, *106*, 1235-1257. (b) Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Sukumar Varma, K. A convenient n.m.r. method for the measurement of Lewis acidity at boron centres: correlation of reaction rates of Lewis acid initiated epoxide polymerizations with Lewis acidity. *Polymer* **1996**, *37*, 4629-4631. (c) Erdmann, P.; Greb, L. What Distinguishes the Strength and the Effect of a Lewis Acid: Analysis of the Gutmann-Beckett Method. *Angew. Chem. Int. Ed.* **2022**, *61*, e202114550.
33. Hendrickson, J. B.; Schwartzman, S. M. Triphenyl phosphine ditriflate: A general oxygen activator. *Tetrahedron Lett.* **1975**, *16*, 277-280.
34. Hendrickson, J. B.; Mistry, S. N.; Moussa, Z.; Al-Masri, H. T. Triphenylphosphonium Anhydride Trifluoromethanesulfonate. In *Encyclopedia of Reagents for Organic Synthesis*, 2014.
35. Moussa, Z.; Ahmed, S. A.; ElDouhaibi, A. S.; Al-Raqa, S. Y. NMR Studies and electrophilic properties of triphenylphosphine-trifluoromethanesulfonic anhydride; a remarkable dehydrating reagent system for the conversion of aldoximes into nitriles. *Tetrahedron Lett.* **2010**, *51*, 1826-1831.
36. Appel, R. Tertiary Phosphane/Tetrachloromethane, a Versatile Reagent for Chlorination, Dehydration, and P-N Linkage. *Angew. Chem. Int. Ed.* **1975**, *14*, 801-811.
37. Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; Kumar, K. V. P. Mitsunobu and Related Reactions: Advances and Applications. *Chem. Rev.* **2009**, *109*, 2551-2651.
38. Mayer, I. Atomic Orbitals from Molecular Wave Functions: The Effective Minimal Basis. *J. Phys. Chem.* **1996**, *100*, 6249-6257.
39. Gimferrer, M.; Danés, S.; Andrada, D. M.; Salvador, P. Unveiling the Electronic Structure of the Bi(+1)/Bi(+3) Redox Couple on NCN and NNN Pincer Complexes. *Inorg. Chem.* **2021**, *60*, 17657-17668.
40. (a) Erdmann, P.; Greb, L. Multidimensional Lewis Acidity: A Consistent Data Set of Chloride, Hydride, Methide, Water and Ammonia Affinities for 183 p-Block Element Lewis Acids. *ChemPhysChem* **2021**, *22*, 935-943. (b) Erdmann, P.; Leitner, J.; Schwarz, J.; Greb, L. An Extensive Set of Accurate Fluoride Ion Affinities for p-Block Element Lewis Acids and Basic Design Principles for Strong Fluoride Ion Acceptors. *ChemPhysChem* **2020**, *21*, 987-994.
41. (a) Zander, E.; Bresien, J.; Zhivonitko, V. V.; Fessler, J.; Villinger, A.; Michalik, D.; Schulz, A. Rational Design of Persistent Phosphorus-Centered Singlet Tetradicals and Their Use in Small-Molecule Activation. *J. Am. Chem. Soc.* **2023**, *145*, 14484-14497. (b) Zhivonitko, V. V.; Beer, H.; Zakharov, D. O.; Bresien, J.; Schulz, A. Hyperpolarization Effects in Parahydrogen Activation with Pnictogen Biradicaloids: Metal-free PHIP and SABRE.

ChemPhysChem **2021**, *22*, 813-817. (c) Li, Z.; Chen, X.; Andrada, D. M.; Frenking, G.; Benkő, Z.; Li, Y.; Harmer, J. R.; Su, C.-Y.; Grützmacher, H. (L)₂C₂P₂: Dicarbondiphosphide Stabilized by N-Heterocyclic Carbenes or Cyclic Diamido Carbenes. *Angew. Chem. Int. Ed.* **2017**, *56*, 5744-5749. (d) Hinz, A.; Schulz, A.; Villinger, A. Metal-Free Activation of Hydrogen, Carbon Dioxide, and Ammonia by the Open-Shell Singlet Biradicaloid [P(μ-NTer)]₂. *Angew. Chem. Int. Ed.* **2016**, *55*, 12214-12218. (e) Rey Planells, A.; Espinosa

Ferao, A.; Streubel, R.; Frontera, A. Internal Coulombic assistance in intermolecular frustrated Lewis pair activation of dihydrogen. *New J. Chem.* **2024**, *48*, 4675-4679.

42. Agarwal, R. G.; Coste, S. C.; Groff, B. D.; Heuer, A. M.; Noh, H.; Parada, G. A.; Wise, C. F.; Nichols, E. M.; Warren, J. J.; Mayer, J. M. Free Energies of Proton-Coupled Electron Transfer Reagents and Their Applications. *Chem. Rev.* **2022**, *122*, 1-49.

$[\text{Ph}_3\text{P}-\text{PPh}_3]^{2+}$

- ✓ Superacid, Superoxidant
- ✓ O-Atom Abstraction
- ✓ Ph_3P^{2+} Transfer Reagent
- ✓ $\text{Ph}_3\text{P}^{\bullet+}$ Transfer Reagent
- ✓ sc-XRD, Raman, DFT

