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# Masked P(III)/P(V) frustrated Lewis pairs for C–H and X–H bond cleavage and catalytic hydroarylation of alkenes

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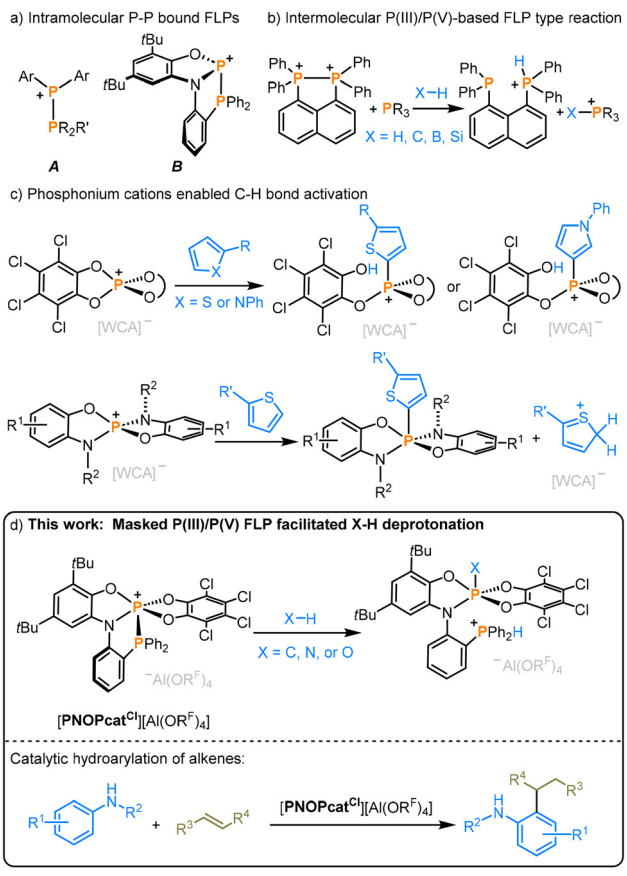
Frustrated Lewis pairs (FLPs) have been realized for a wide range of element combinations, yet systems constructed from two phosphorus centers in distinct oxidation states remain unexplored. Here, we report an intramolecular dative $R_3P \rightarrow PR_4^+$ bond that functions as a masked FLP. The architecture enables the heterolytic activation of C–H and X–H bonds (X = O, N), affording phosphonium/phosphorane products. The cooperative reactivity is further exploited in the hydroarylation of alkenes, demonstrating how P–P frameworks featuring mixed phosphorus oxidation states can be harnessed for main-group catalysis.



The chemistry of phosphorus-based Lewis pairs has driven sustained research interest in recent years.[1] Heteropolar phosphorus–phosphorus bonded systems—exhibiting Lewis acidic and basic character at distinct P centres—have emerged as a promising subclass. With sufficient lability, such systems can be regarded as "masked" or "hidden" frustrated Lewis pairs (FLPs).[2] Indeed, phosphine stabilized phosphenium ions ($R_3P \rightarrow PR_2^+$) undergo ligand exchange,[3] silane activation[4] and addition across C≡C and N=N bonds (Scheme 1a, **A**).[5] Constraining such P–P bonds within a rigid ligand framework allowed extending this chemistry to the phosphino-phosphination of a broad range of unsaturated substrates (Scheme 1a, **B**).[6] A ferrocene-bridged $R_3P \rightarrow PR_2^+$ was found to be air-stable and to react selectively with water.[7] Notably, diphosphorus dications combined with external phosphines form intermolecular FLPs capable of activating H–H, C–H, B–H, and Si–H bonds (Scheme 1b).[8] In contrast to this relatively explored field of $R_3P \rightarrow PR_2^+$ pairs, mixed-valence $R_3P \rightarrow PR_4^+$ adducts (phosphine stabilized phosphonium ions) have rarely been investigated.[9]

We recently reported the reactivity of catechol or aminophenol substituted P(v) cations in the site-selective C–H activation of thiophene and pyrrole substrates (Scheme 1c).[10] Subsequently, we introduced a phosphine-tethered derivative, [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$], which was used as a Z-type ligand for coordination to palladium(0) (Scheme 1d).[11] Building on this platform, we now demonstrate its ability to mediate FLP-type activation of C–H and X–H bonds and showcase its utility in catalytic hydroarylation reactions.




**Scheme 1** (a) Intramolecular P(III)/P(III) bound FLPs. (b) P-based FLP type activation of X–H bonds. (c) C–H activation using P(v) phosphonium ions. (d) This work: X–H bond activation *via* a masked P(III)/P(v) frustrated Lewis pair and catalytic hydroarylation of alkenes.

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Initial efforts were directed toward the reaction of [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] with C–H bonds. While exhibiting inertness with non-activated arenes like benzene, the salt showed selective reactivity with nitrogen-containing heterocyclic compounds (Fig. 1). Exposure of *N*-methylpyrrole to a dichloromethane solution of [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] triggers the formation of phosphonium-phosphorane **1** ($^1J_{P-H}$ = 511 Hz), as confirmed by single crystal X-ray diffraction (Fig. 1b). In contrast to the catechol-substituted P(v) cations reported previously,[10a] the tethered phosphine donor in [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] partially attenuates the Lewis acidity of the phosphorus center. While this is expressed in slower reaction times, the hemilabile interaction provides a mechanism to moderate reactivity while preserving access to Lewis-acid-driven transformations. The observed distorted trigonal-bipyramidal geometry in **1**, compared to the square-pyramidal structure of the *N*-phenylpyrrole-activation product observed with the donor-free cations,[10a] can be associated with the different electronic structure of the substituents. Likewise, [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] reacted with *N*-methylindole, affording product **2** in good isolated yield (see Fig. 1c for the crystal structure). The reactions were found to yield a single rotamer, wherein the PH$^+$ unit is oriented in the same direction as the phosphorane carbon substituent (*cis*-rotamer around the C–N bond). The reaction of [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] with electron-rich arene $Ph_3N$ at 100 °C in toluene for 4 days occurred selectively at the *para*-position of one phenyl ring, yielding the C–H deprotonation product **3**, as displayed in Fig. 1d. In this case, two diastereomers, now also including the C–N bond *trans*-rotamer, were observed by NMR spectroscopy after the reaction. The occurrence of this second diastereomer was attributed to the higher reaction temperature, resulting in the formation of the *trans*-rotamer, which appears entropically favoured (see SI 2.1). Thiophene and furan exhibited no reactivity toward [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$], even upon heating at 100 °C overnight, contrasting with the behaviour of the earlier systems.[10] We explain this observation by the lowered Lewis acidity of [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] due to intramolecular P-coordination.

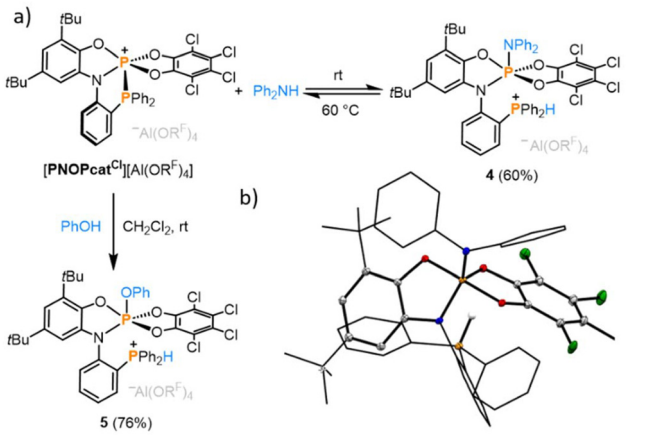



**Fig. 2** (a) Reaction of [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] with $Ph_2NH$ and PhOH. (b) Thermal ellipsoid plots of the solid-state structures of **4** displayed at 50% probability. All carbon-based hydrogen atoms and the counterion [Al(OR$^F$)$_4$]$^-$ have been omitted for clarity.

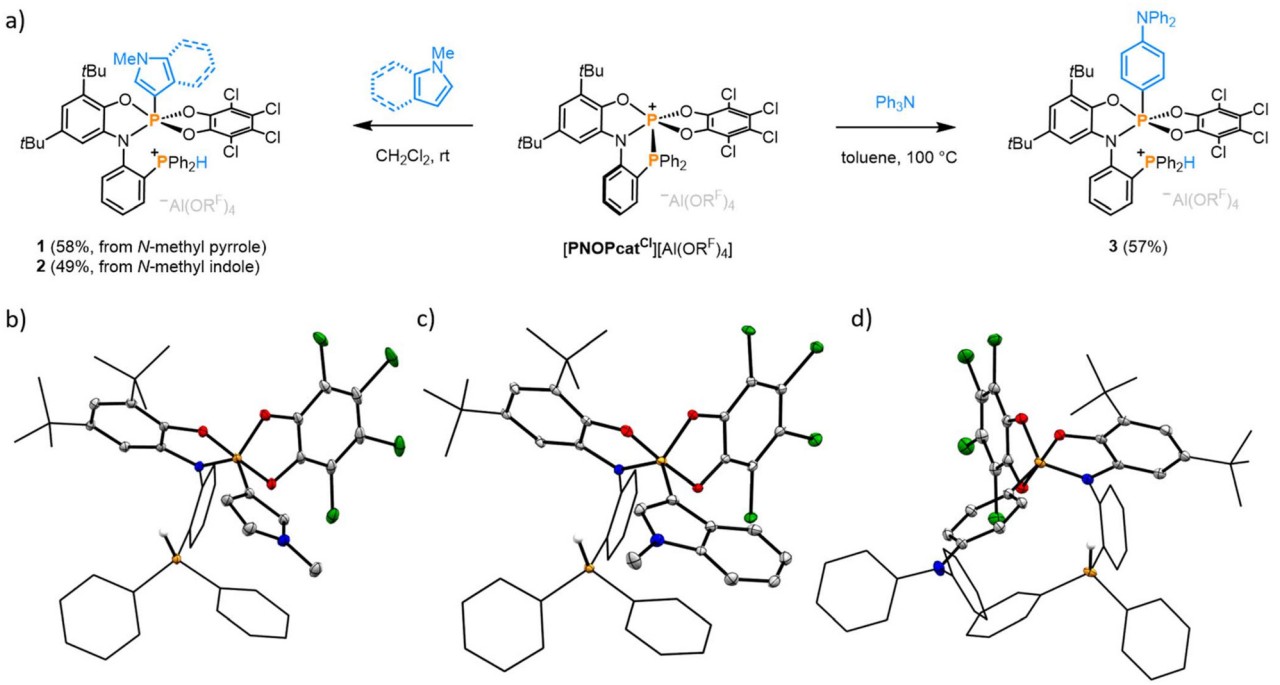



**Fig. 1** (a) Deprotonation of *N*-methyl pyrrole, *N*-methyl indole, and $PPh_3N$. Thermal ellipsoid plots of the solid-state structures of (b) **1**, (c) **2**, and (d) **3** displayed at 50% probability. All carbon-based hydrogen atoms and the counterion [Al(OR$^F$)$_4$]$^-$ have been omitted for clarity.

Next, X–H compounds were investigated. [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] reacted smoothly with $Ph_2NH$ to form the N–H deprotonated product **4** (Fig. 2a). Single crystals suitable for X-ray diffraction were grown by gas phase diffusion of *n*-pentane into $CH_2Cl_2$ solvent (Fig. 2b). Interestingly, a reversible behaviour was observed in the reaction with $Ph_2NH$: product **4** formed at room temperature, reverted to the starting materials upon heating to 60 °C, and regenerated **4** at room temperature (see SI S3.3.1 for more details). The reaction with phenol afforded product **5** as a white solid, for which multinuclear NMR spectroscopy indicated the presence of two isomeric products in a 2.2 : 1 ratio, again attributed to rotamerism around the C–N bond (see SI 2.2). An unselective reaction was observed with an aliphatic alcohol (EtOH).

Finally, we examined the reactivity of this phosphonium salt towards unsaturated functional groups (Fig. 3). On addition of phenylacetylene to a $CH_2Cl_2$ solution of [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$], the yellow solution was discharged and the $^{31}P\{^1H\}$ NMR spectrum showed a complex pattern consistent with the formation of multiple phosphorus-containing species. By gas phase diffusion of *n*-pentane into the $CH_2Cl_2$ solution, white crystals suitable for X-ray diffraction formed, providing structural confirmation of a P-functionalized heteroarene **6** in 30% yield (Fig. 3b). In the $^1H$ NMR spectrum of **6**, signal broadening for the olefin-bound phenyl group and the adjacent *tert*-butyl group suggested restricted rotational motion in the highly rigid product. It represents a unique C–O bond cleavage and oxygen atom migration, likely initiated by a phosphorus–ligand cooperative addition–elimination pathway, reminiscent of earlier findings.[10b] Carbonyl compounds were also examined, with benzaldehyde serving as the representative substrate. While NMR spectroscopic data indicated multiple products, a colourless species **7** crystallized from the $CH_2Cl_2$ solution at −40 °C. Single crystals of **7** analysed by X-ray diffraction revealed complete cleavage of the C=O bond, with the oxygen migrating to P(v), and the PhCH-part inserted within N and $PPh_2$ (Fig. 3c). Interestingly, while the unquenched P(v)-catechol and amidophenolate systems were found to be highly reactive towards olefins,[10] [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] did not show any reactivity with styrene at rt, but only spurious signs of styrene-polymerization upon heating to 60 °C. This compatibility represents a distinct advantage compared to our previous systems,[10] which can be attributed to the tempered Lewis acidity due to intramolecular P → P coordination. Combined with the selective cleavage of X–H bonds, our next attempts focused on catalytic transfer reactions. Building on the role of Brønsted and Lewis acids as catalysts in the hydroarylation of alkenes,[12] we explored the capacity of [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] in this process.

At the outset of our studies, we chose di-*p*-tolylamine and styrene as substrates, with 10 mol% [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] as the catalyst. After heating the reaction mixture in toluene at 80 °C overnight, the hydroarylation product **10a** was isolated in 49% yield (Scheme 2). Of note, any signals related to styrene polymerization were fully suppressed. Optimization of the reaction conditions afforded the target product with an improved isolated yield of 90% (see SI S3.1). Using 4 equiv. of the diarylamines was found to be critical for reducing the formation of bis-alkylated products. When diphenylamine was employed as the substrate, *ortho-C*-alkylation took place and **10b** was obtained as the major product with a yield of 67%. The *para-C*-alkylation product **10b′** was detected with a yield of approximately 26%, as determined by $^1H$ NMR spectroscopy. The observed preference for *ortho*-alkylation is notable, as it contrasts with *para*-alkylation with simple phosphonium cata-

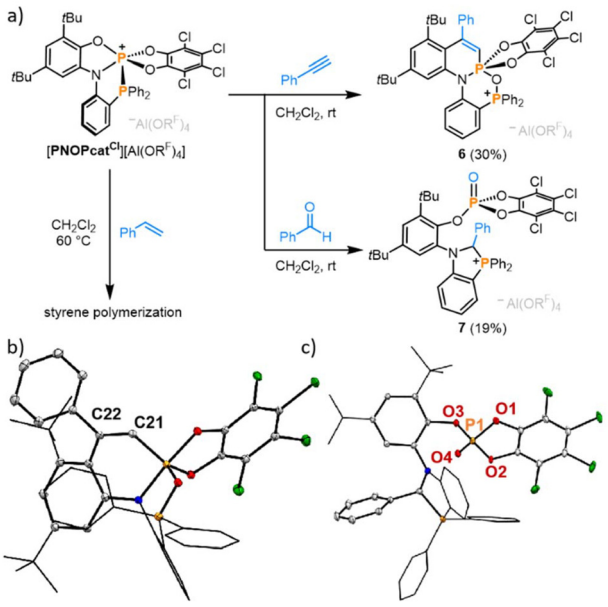
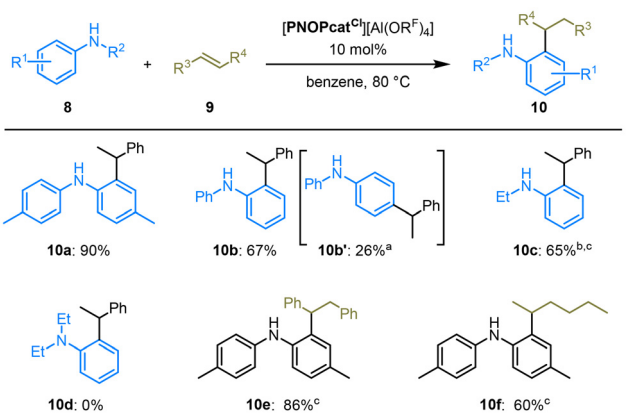



**Fig. 3** (a) Reactions of [**PNOPcat$^{Cl}$**][Al(OR$^F$)$_4$] with styrene, phenylacetylene, and benzaldehyde. Thermal ellipsoid plots of the solid-state structures of (b) **6** and (c) **7** displayed at 50% probability. All hydrogen atoms and the counterion [Al(OR$^F$)$_4$]$^-$ have been omitted for clarity. Selected bond lengths [Å] of **6**: *d*(C21–C22) = 1.357(2) and **7**: *d*(P1–O4) = 1.4495(17), *d*(P1–O1) = 1.6161(17), *d*(P1–O2) = 1.6136(17), and *d*(P1–O3) = 1.5562(17).




**Scheme 2** Scope and limitations of the hydroarylation of alkenes. Isolated yields are given. [a] Yield based on $^1H$ NMR spectroscopy. [b] Yield for *para-C*-alkylation product **10c′** is less than 5%. [c] 120 °C.

lysts *via* electrophilic alkene activation.[12g] Further substrate scope investigations revealed that the alkylarylamine *N*-ethylaniline participated efficiently in the reaction to deliver product **10c** in good yield. By stark contrast, tertiary amines (**10d**) gave no product under the catalytic conditions, implying that the presence of the N–H proton is critical for turnover. Moreover, *cis*-stilbene and the non-activated 1-hexene were found to be competent alkene reagents, giving the desired products **10e** and **10f** in 60–86% yields. Interestingly, the more nucleophilic 1,1-disubstituted α-methylstyrene afforded only trace amounts of the product, even after several days of heating at 120 °C, indicating pronounced steric influences for successful transformation. This observation suggests that the transformation does not proceed *via* a freely equilibrating carbocation intermediate but rather involves a concerted or tightly coupled protonation-bond-forming event, for which steric congestion at the tertiary benzylic center disfavors productive nucleophile capture.

Based on the above results, two mechanisms are plausible (see SI S3.4): scenario (1): the [**PNOPcat**$^{\mathbf{Cl}}$][Al(OR$^{\mathrm{F}}$)$_4$] catalyst first undergoes N–H bond activation to a product of type **4**, which subsequently transfers a proton and the P-bound aryl amide *via* Friedel–Crafts chemistry. Scenario (2): upon heating, the activated amine is released from **4**, and [**PNOPcat**$^{\mathbf{Cl}}$][Al(OR$^{\mathrm{F}}$)$_4$] activates the olefin for hydroarylation. While a clear-cut mechanistic conclusion would require further investigations, the lack of reactivity with tertiary amines and 1,1-disubstituted olefins, the absence of hydroamination products, and the preferred *ortho*-selectivity, including for substrates that are not blocked at the *para*-position, support scenario 1. A concerted pathway, as postulated in previous work under Brønsted acidic conditions,[12a,i] is assumed for the latter step, explaining those observations. The hydroarylation of alkynes has not been found to be successful, but irreversibly delivers product **6**, in line with a faster reaction rate compared to a hydroarylation pathway.

## Conclusions

Herein, we report a masked frustrated Lewis pair type X–H (X = C, N, or O) bond cleavage by employing a phosphino-phosphonium cation. Furthermore, [**PNOPcat**$^{\mathbf{Cl}}$][Al(OR$^{\mathrm{F}}$)$_4$] exhibits unique reactivity toward phenylacetylene and benzaldehyde, and enables catalytic hydroarylation of non-activated alkenes with aryl amines. Since the products contain stereogenic centers, the potentially concerted substrate-transfer pathway suggests opportunities for enantioselective transformations, *e.g.*, by replacing the catechol with BINOL derivatives in the ligand framework.

## Author contributions

L. Y. and L. G. devised the project and designed the experiments. L. Y. performed the experimental work and wrote the draft. Both authors contributed to discussions and to finalizing the manuscript, and both authors agreed to the submitted content.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: **https://doi.org/10.1039/d6qi00241b**.

CCDC 2523825–2523830 contain the supplementary crystallographic data for this paper.[13a–f]

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