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Main Group Redox Catalysis: Reversible P^{III}/P^{V} Redox Cycling at a Phosphorus Platform

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Supporting Information

ABSTRACT: A planar, trivalent phosphorus compound is shown to undergo reversible two-electron redox cycling (P^{III}/P^{V}) enabling its use as catalyst for a transfer hydrogenation reaction. The trivalent phosphorus compound activates ammonia-borane to furnish a 10-P-5 dihydridophosphorane, which in turn is shown to transfer hydrogen cleanly to azobenzene, yielding diphenylhydrazine and regenerating the initial trivalent phosphorus species. This result constitutes a rare example of two-electron redox catalysis at a main group compound and suggests broader potential for this nonmetal platform to support bond-modifying redox catalysis of the type dominated by transition metal catalysts.

Homogeneous transition metal catalysis has profoundly impacted chemical synthesis,[1] enabling the construction of covalent bonds with exquisite levels of efficiency and selectivity.[2−5] Methods based on late transition metal catalysts (Rh, Ir, Pd, Pt) are particularly prominent. The facility with which these complexes mediate the making and breaking of covalent bonds stems in part from the ability of d-block metals to readily cycle between *n* and *n* + 2 oxidation states with concomitant expansion and contraction of their primary coordination sphere (Figure 1).[6] This reversible coordinative and oxidative reactivity is intimately linked to the energetic and spatial disposition of the valence d-orbitals about the metal center.[7] Consequently, catalytic two-electron bond modifying redox reactivity has traditionally been considered the exclusive purview of the transition metals.[8]

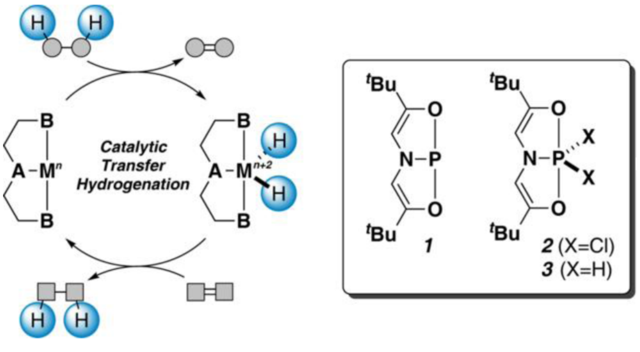

Figure 1. (Left) Schematic representation of redox cycling at a metal complex during transfer hydrogenation. (Right) Phosphorus compounds **1**−**3** employed in this study.

The notion that elements outside the d-block, in particular nonmetal p-block elements, may be able to exhibit the redox reactivity traditionally reserved for the transition metals has recently been articulated by Bertrand,[9] Power,[10] and Stephan and Erker.[11] The elementary steps common to redox catalytic mechanisms (e.g., oxidative addition, reductive elimination) have been demonstrated in stoichiometric fashion for a large number of the p-block elements,[12−14] and recent breakthroughs have further expanded the scope of this reactivity, demonstrating the ability of nonmetals to activate even strong, nonpolar bonds under mild conditions.[15,16] Despite this promising stoichiometric reactivity, catalytic processes employing redox catalysts based on p-block elements remain extremely rare.[17,18] We now report a nonmetal, phosphorus-based platform that participates in reversible, two-electron bond modifying reactivity in analogy to the transition metals. We further show that this ability to cycle freely between P^{III}/P^{V} oxidation states may be harnessed to effect a catalytic transfer hydrogenation reaction where the central redox element is not of the *d*-block.[19] This observation extends the reach of bond activation catalysis beyond the transition metal series, further cementing the role of certain main group compounds as viable metal-catalyst surrogates.[20]

We adopted a structurally unique tricoordinate phosphorus compound **1**, described initially by Arduengo,[21−23] as a point of departure in our study (Figure 1). Whereas three-coordinate phosphorus commonly assumes a pyramidal geometry, compound **1** displays a highly unusual T-shaped geometry. When considered in conjuction with the related 10-P-5 compound **2**, this platform suggested a structural analogy to transition metal pincer complexes,[24] where meridionally ligated metals localize diverse bond activation processes at sites perpendicular to the ligand plane.

Motivated by the perceived analogy to pincer chemistry, we evaluated the capacity of **1** to affect dehydrogenation of small molecule substrates.[25] Three-coordinate **1** is stable in alkane solutions; however, reaction with the alkane isostere ammonia-borane[26] in acetonitrile solution results in conversion to a single new phosphorus-containing compound with a $^{31}P\{^{1}H\}$ NMR resonance at δ −43.7 ppm. This signal evolves in the proton-coupled ^{31}P NMR spectrum to a triplet of triplets with J = 670 and 34 Hz (Figure 2, bottom). In situ monitoring of the reaction progress indicates that no other phosphorus-containing intermediates or products are formed. Spectroscopically pure material may be isolated in 75% yield following

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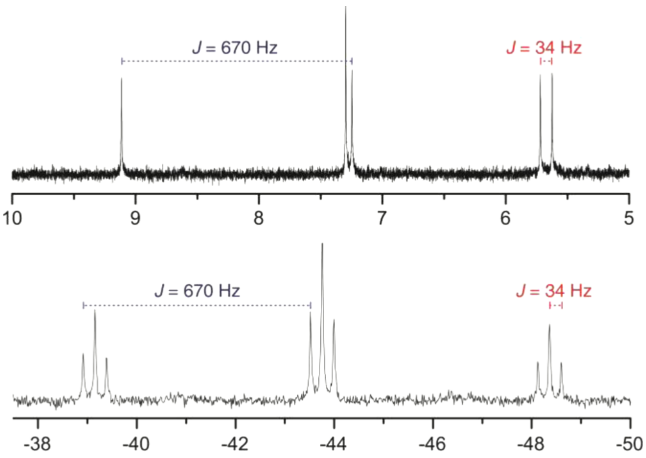
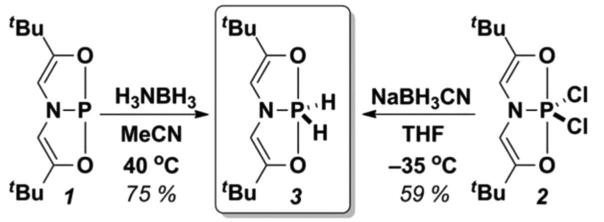


Figure 2. (Top) Abridged ^{1}H NMR spectrum for 3 in $CDCl_3$. An additional ^{1}H signal for $-C(CH_3)_3$ is found at δ 1.06 ppm. (Bottom) Annotated ^{31}P NMR spectrum for 3 in $CDCl_3$. Units are ppm relative to Me_4Si (^{1}H) and H_3PO_4 (^{31}P).

pentane trituration of the crude reaction residue. Alternatively, the action of sodium cyanoborohydride on dichlorophosphorane **2** gives the same species in 59% isolated yield, which we assign as dihydridophosphorane **3** (Scheme 1).[27,28] The magnitude and multiplicity of the ^{31}P NMR resonance are indicative of $^1J_{PH}$ coupling of the phosphorus center with bound hydrogen nuclei of an apparently equivalent pair (i.e., a $-P(H)_2$ unit, vide infra) and longer range $^3J_{PH}$ coupling to the remote vinylic hydrogen nuclei. The complementary coupling securing these assignments is evident in the ^{1}H NMR spectrum (Figure 2, top); phosphorus-coupled doublets are observed at δ 7.95 ppm ($^1J_{PH}$ = 670 Hz) and δ 5.83 ppm ($^3J_{PH}$ = 34 Hz).

Scheme 1. Preparation of Dihydridophosphorane 3



X-ray diffraction of a colorless single crystal obtained by sublimation of **3** in vacuo at 35 °C affords additional structural detail. The structure of **3** is found to deviate, albeit modestly, from an idealized 10-P-5 trigonal bipyramid toward a distorted square pyramid about phosphorus (Figure 3). The phosphorus center resides in a plane defined by the nitrogen atom and the two P−H hydrogen atoms. The positions of the P−H hydrogens, both of which were located on the difference Fourier map, are splayed obliquely with respect to the *O,N,O*-supporting structure and are crystallographically inequivalent ($\angle N{-}P{-}H_1$ = 134.8(1)°; $\angle N{-}P{-}H_2$ = 116.1(1)°).[29] Tridentate binding of the *O,N,O*-motif is evident with oxygen atoms spanning the phosphorus center at an angle of 170.5(1)°. The ring systems experience only a minor puckering with nitrogen displaying slight pyramidalization (φ = 6.7°).[30]

Reaction of dihydridophosphorane **3** with an unsaturated organic substrate results in transfer of hydrogen from phosphorus, regenerating reduced three-coordinate **1**.[31] In a stoichiometric experiment, exposure of **3** to 1 equiv of azobenzene in acetonitrile-d_3 solution at 40 °C for 19 h results in 72 ± 5% conversion of **3** to **1** with concomitant formation of 1,2-diphenylhydrazine in 63 ± 5% yield (eq 1). In the presence of excess azobenzene (which mimics catalytic conditions, vide infra), the conversion of **3** to **1** can be driven cleanly to completion. When monitored by NMR, no other intermediates or products are evident in this hydrogen transfer. The consumption of **3** in acetonitrile-d_3 solution in the presence of excess azobenzene follows pseudo-first order kinetics, and an Eyring analysis over the temperature range 30−60 °C furnishes $\Delta H^\ddagger$ = 12.4 ± 0.7 kcal/mol and $\Delta S^\ddagger$ = −36 ± 7 eu (see Supporting Information (SI)). Although a more detailed mechanistic description awaits further study, the sign and magnitude of the entropy of activation are consistent with a rate-limiting step involving a transition structure from bimolecular reaction.

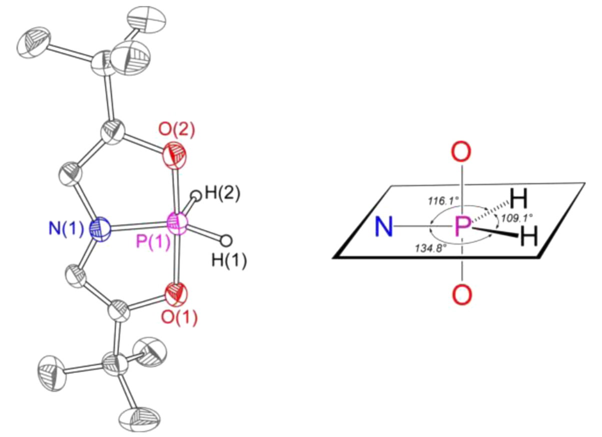
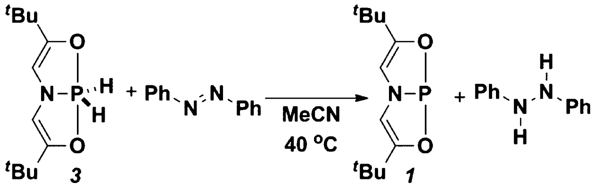


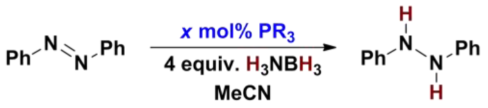
Figure 3. (Left) Thermal ellipsoid plot (50%) of **3**. Hydrogen atoms on carbon omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1) = 1.676(2); P(1)−O(1) = 1.721(1); P(1)−O(2) = 1.699(1); P(1)−H(1) = 1.29(2); P(1)−H(2) = 1.31(2); O(1)−P(1)−O(2) = 170.5(1); N(1)−P(1)−H(1) = 134.8(1); N(1)−P(1)−H(2) = 116.1(1); H(1)−P(1)−H(2) = 109.1(2). (Right) Schematic illustrating bond angles.



(1)

The combined reactivities of **1** as hydrogen acceptor from ammonia-borane and **3** as hydrogen donor to an organic substrate suggested the possibility of employing this phosphorus platform as a redox catalyst for transfer hydrogenation. The direct reaction of azobenzene with a 4-fold excess of ammonia-borane in acetonitrile solution at 80 °C proceeds only to minimal conversion (ca. 5%) after 24 h (Table 1, entry 1). However, the addition of 10 mol % of **1** yields diphenylhydrazine in 80% yield in the same time frame (entry 2), even under less forcing conditions (40 °C). Longer reactions times lead to modestly increased yields (entry 3). Presumably, under these conditions, three-coordinate **1** accepts hydrogen from ammonia-borane forming dihydridophosphorane **3**, then subsequent hydrogen transfer to azobenzene regenerates **1** and closes the catalytic cycle. Consistent with this scheme, the use of a catalytic amount of **3** also promotes

Table 1. Catalytic Transfer Hydrogenation with 1/3



entry	PR$_3$	mol %^{a}	Time (h)	T (°C)	Yield^b
1	none	---	24	80	<5 %
2	***1***	10 mol %	24	40	*80 %*
3	***1***	10 mol %	48	40	*94 %*
4	***3***	10 mol %	24	40	*63 %*
5	***3***	10 mol %	48	40	*81 %*
6	PPh$_3$	100 mol %	24	80	< 5 %
7	P(OMe)$_3$	100 mol %	24	80	< 5 %
8	P(NMe$_2$)$_3$	100 mol %	24	80	24 %

^{a}Loading relative to azobenzene substrate. ^{b}Determined by$_1$H NMR of crude reaction mixtures. Error estimate ±5%.

transfer hydrogenation (entries 4 and 5). Interrogation of the phosphorus speciation by ^{31}P NMR under the catalytic conditions supports this mechanistic outline; the signal corresponding to **1** (δ 186.7 ppm) is replaced by dihydridophosphorane **3** (δ −43.7 ppm) at early time points, after which compound **3** persists in solution as the sole observable phosphorus species in the range +250 to −150 ppm until the catalytic reaction is terminated at 48 h (Figure 4).

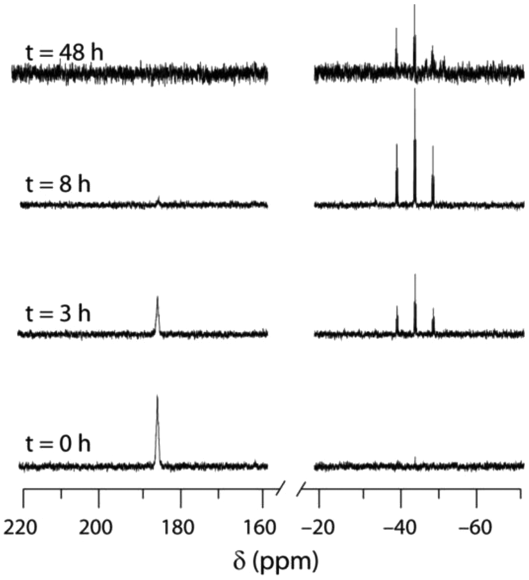


Figure 4. Evolution of phosphorus species during transfer hydrogenation catalysis with **1** (Table 1, entry 3). Time-stacked ^{31}P NMR spectra at t = 0, 3, 8, and 48 h. See SI for full, unabridged spectra.

These results implicate **3** as the resting state of the catalytic cycle. The redox platform **1**/**3** is unique among phosphorus species surveyed in enabling this catalytic transfer hydrogenation reactivity; none of the other trivalent phosphorus compounds examined promote the transfer hydrogenation at a comparable level, even at higher loadings and temperatures (entries 4−6).

These results demonstrate the capacity for a three-coordinate phosphorus compound to support two electron redox chemistry of the type commonly observed in the transition metals. This constitutes a rare example of two-electron bond modifying redox catalysis outside of the d-block. Moreover, whereas phosphines are well-known nucleophilic[32] and frustrated Lewis pair (FLP) catalysts,[33] the behavior of the phosphorus center described above is of a different type. In both nucleophilic and FLP paradigms, the phosphorus behaves exclusively as an electron donor.[34] By contrast, catalysis with **1** results from cycling between discrete tricoordinate P$^{\mathrm{III}}$ and pentacoordinate P$^{\mathrm{V}}$ states, capitalizing on the colocalization of electron-donating and electron-accepting function at a single atomic center. It is precisely this coordinative and oxidative reactivity that enables the valuable two-electron redox transformations observed in transition metal catalysis. The identification of this reactivity in **1** suggests broader potential for this nonmetal platform to support additional bond-modifying redox catalysis of the type currently dominated by transition metal catalysts. Research along these lines is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures and spectra, kinetic data, crystallographic and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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