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Catalyzing Pyramidal Inversion: Configurational Lability of P-Stereogenic Phosphines via Single Electron Oxidation

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S *Supporting Information*

ABSTRACT: We report that pyramidal inversion of trivalent phosphines may be catalyzed by single electron oxidation. Specifically, a series of *P*-stereogenic (aryl)-methylphenyl phosphines are shown to undergo rapid racemization at ambient temperature when exposed to catalytic quantities of a single electron oxidant in solution. Under these conditions, transient phosphoniumyl radical cations ($R_3P^{\bullet+}$) are formed, and computational models indicate that the pyramidal inversion barriers for these open-shell intermediates are on the order of ~5 kcal/mol. The observed 10^{20}-fold rate enhancement over uncatalyzed pyramidal inversion opens new opportunities for the dynamic stereochemistry of phosphines and may hold additional implications for the configurational stability of *P*-stereogenic phosphine ligands on high-valent oxidizing transition metals.

The stereodynamic behavior of chiral compounds underpins numerous techniques in stereoselective synthesis,[1] chiral sensing,[2] and chiroptical switching.[3] Pyramidal inversion of trivalent group 15 compounds, in which C_{3v}-symmetric ground states interconvert via a planar D_{3h}-symmetric transition state (Figure 1), is an archetypal example of dynamic stereoisomerism.[4−8] Whereas pyramidal trivalent nitrogen compounds commonly undergo inversion with low barriers, heavier group 15 analogues experience signficant energetic penalties for inversion.[9] Indeed, Mislow demonstrated in a series of landmark papers that the barrier to pyramidal inversion for trivalent aryl and alkyl phosphorus compounds is on the order of 30−40 kcal/mol.[10] These high barriers impart differentially substituted trivalent phosphines with persistent chirality, a feature that makes them valuable chiral ligands in enantioselective synthesis and coordination polymers[11,12] but otherwise limits their use in stereodynamic processes to specialized *P*-substituted derivatives with atypically low inversion barriers.[13−15] The ability to trigger facile dynamic stereoisomerism of underivatized *P*-stereogenic aryl and alkyl phosphines at ambient temperature would open the door to utilization of this important class of compounds in diverse dynamic stereochemical applications.[16]

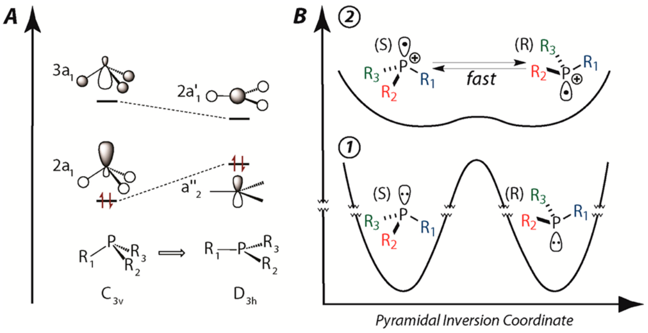

Figure 1. (A) Frontier orbital correlation diagram for trisubstituted phosphine. (B) Energy coordinate diagram for pyramidal inversion of neutral phosphine (1) and phosphoniumyl radical cation (2).

The inversion barrier of trivalent group 15 compounds is often described within the context of a second-order Jahn−Teller effect (Figure 1a).[7,8] Deformation of the pyramidal C_{3v}-symmetric ground state to the planar D_{3h}-symmetric transition state involves an energetic penalty associated with raising of the HOMO energy due to loss of HOMO−LUMO orbital mixing. This energy penalty is significant for phosphorus compared with nitrogen due to the large ground-state HOMO−LUMO mixing.[5] Congruent with this electronic understanding, theoretical and experimental results have indicated that open-shell phosphoniumyl radical cations ($R_3P^{\bullet+}$),[17] which may be accessed by removal of one electron[18] from the closed-shell neutral phosphine, may exhibit a decreased electronic penalty for planarization (Figure 1b).[19−21] Indeed, the racemization of a *P*-stereogenic phosphine by TCNQ/HCl has previously been suggested to involve phosphoniumyl radical cations,[22] although the analysis in this circumstance is made ambiguous by the possible intervention of closed-shell phosphonium or phosphorane intermediates.[23,24] We show that under diverse conditions of outer-sphere single electron transfer, the pyramidal inversion of *P*-stereogenic phosphines may be efficiently catalyzed with barriers of only ~5 kcal/mol.[25] This demonstration opens new opportunities for the use of dynamic stereochemistry of underivatized phosphines and may have further implications for the suitability of *P*-stereogenic phosphines as chiral ligands for redox-active transition metals.

As an exemplar of the catalyzed pyramidal inversion of phosphines, we focused initially on the stereodynamic behavior of (ferrocenyl)methylphenylphosphine (**1**). The solution potential and reversibility of the redox couple $\mathbf{1} \rightleftharpoons \mathbf{1}^{\bullet+}$ was electrochemically interrogated. A cyclic voltammogram (CV) of **1** (1 mM **1** in MeCN, 0.1 M [nBu$_4$N][PF$_6$], T = 293 K, scan

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rate = 100 mV/s, stationary glassy carbon working electrode) is dominated by an irreversible anodic feature at +0.09 V vs $Cp_2Fe^{0/+}$ (Figure 2A). In accord with previous reports on the reactivity of electrogenerated phosphoniumyl radical cations,[26] we supposed that the observed electrochemical irreversibility for **1** was due to a rapid chemical reaction with adventitious water[27] following initial one-electron oxidation. Consistent with this notion, the anodic current at +0.09 V vs $Cp_2Fe^{0/+}$ is diminished upon successive scans of **1** (taken without pause in a quiescent solution) as a new reversible wave grows in at +0.21 V vs $Cp_2Fe^{0/+}$. A voltammogram recorded on independently synthesized (ferrocenyl)methylphenylphosphine oxide (FcMePhP=O) supports the assignment of the wave at +0.21 V vs $Cp_2Fe^{0/+}$ as this species. Despite the sensitivity of the electrogenerated phosphoniumyl radical cation $\mathbf{1}^{\bullet+}$ to oxide formation, increasing reversibility for the couple $\mathbf{1} \rightleftharpoons \mathbf{1}^{\bullet+}$ may be demonstrated at faster scan rates (Figure 2B). A return cathodic wave becomes apparent upon increasing scan rate from 100 to 1000 mV/s, indicating that the phosphoniumyl radical cation is persistent at least on the millisecond time-scale.[28]

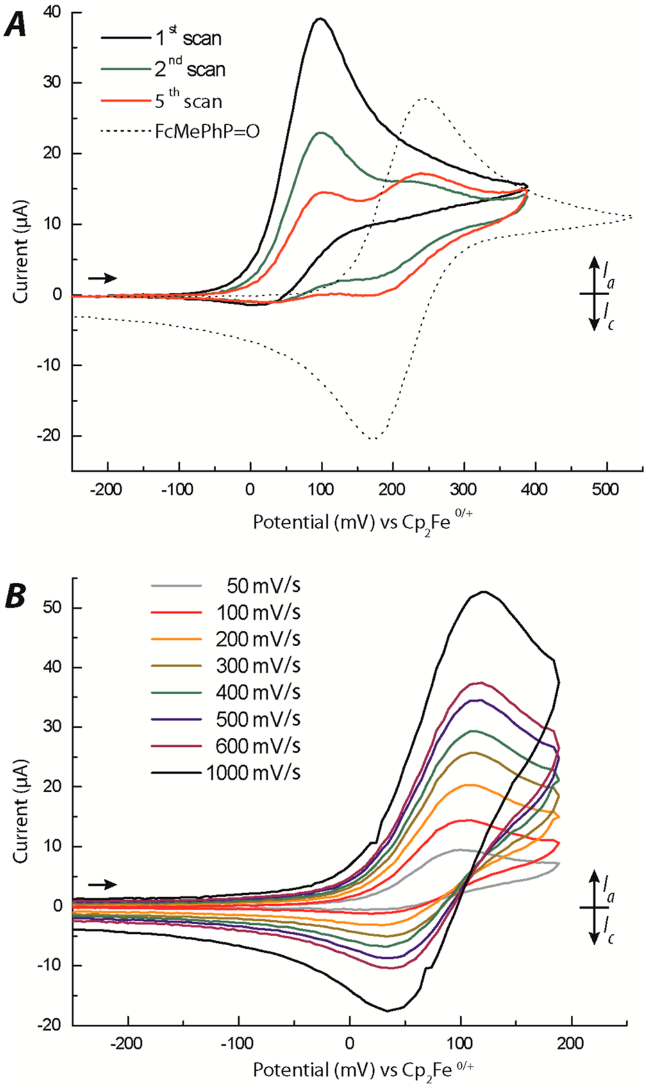
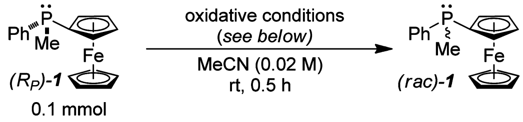


Figure 2. (A) CV of **1**. (B) Scan rate dependence on observed electrochemical reversibility for the couple $\mathbf{1} \rightleftharpoons \mathbf{1}^{\bullet+}$.

In order to probe the stereochemical lability of **1** under catalytic single electron oxidation, a sample of enantioenriched (R_P)-**1** was prepared in 96% *ee*.[29] This compound is configurationally stable in solution at ambient temperature, with an experimentally determined barrier to thermal inversion of 31.4 kcal/mol.[30] However, exposure of **1** to 25 mol % of $[Cp_2Fe][PF_6]$ in acetonitrile solution at ambient temperature results in rapid and significant erosion of optical activity (Table 1, entry 1). Under these conditions, we suggest that thermal electron transfer (ET) from **1** to $[Cp_2Fe]^+$ generates transient $\mathbf{1}^{\bullet+}$, for which racemization via a low-energy pyramidal inversion pathway (vide infra) precedes return ET. Consistent with this proposed outer-sphere ET mechanism, the racemization of **1** may also by catalyzed by oxidation with organic aminium oxidant $[(p\text{-}MeOC_6H_4)_3N][PF_6]$ (entry 2). Additionally, copper(II) triflate was found to catalyze racemization of **1** (entry 3). Since oxidizing metal salts including Cu(II) are frequently employed in conjunction with *P*-stereogenic ligands for the preparation of chiral catalysts,[31] this latter result suggests that stereochemical fidelity may not necessarily be assumed across all classes of *P*-stereogenic phosphine/metal complexes.[32,33]

Table 1. ET-Catalyzed Pyramidal Inversion[a]

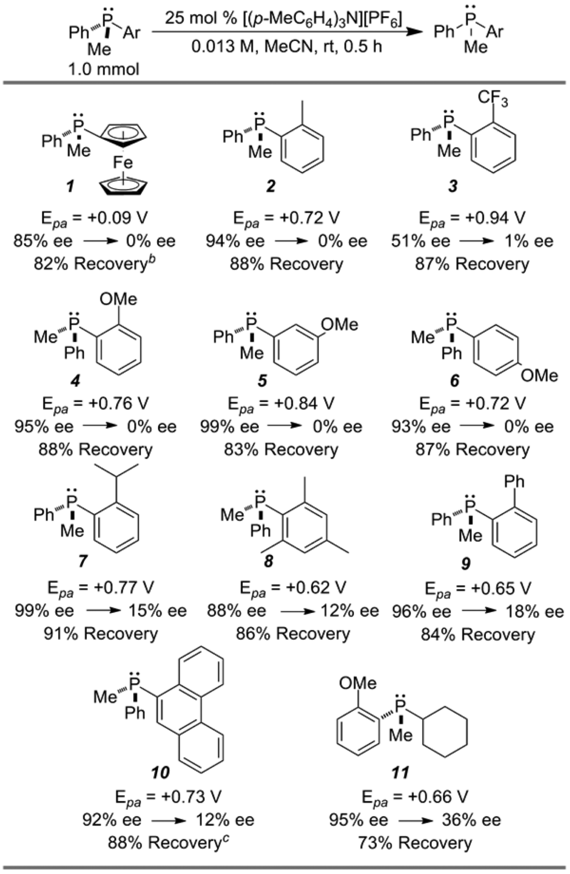


entry	catalytic oxidant	Δ*ee*[b]
1	25 mol % $[Cp_2Fe][PF_6]$	96% → 12%
2	25 mol % $[(p\text{-}MeOC_6H_4)_3N][PF_6]$	96% → 8%
3	25 mol % $Cu(OTf)_2$	96% → 2%

[a]See Supporting Information for full experimental details. [b]Determined by HPLC of isolated **1** following protection as the BH_3-adduct.

A survey of the racemization of *P*-stereogenic (aryl)-methylphenylphosphines (**2**−**10**) with diverse steric and electronic properties further indicates the generality of the catalyzed pyramidal inversion (Table 2). The anodic peak potentials for phosphines **2**−**10** range from 620 to 940 mV vs $Cp_2Fe^{0/+}$ as determined by CV. At these potentials, ferrocenium ion is ineffective at promoting electron transfer; prolonged exposure to acetonitrile solutions of $[Cp_2Fe][PF_6]$ did not result in any observable erosion of stereochemistry for any of the phosphines **2**−**10**. By contrast, the use of 25 mol % of tri(*p*-tolyl)aminium hexafluorophosphate ($[p\text{-}MeC_6H_4)_3N][PF_6]$, $E_{1/2}$ = +0.37 V vs $Cp_2Fe^{0/+}$), proved effective at catalyzing the pyramidal inversion in acetonitrile solution on a 1 mmol scale within 30 min. In all cases, good mass recovery of the racemized phosphines is observed with the only minor byproduct being ∼10−12% of the corresponding phosphine oxide. Phosphines substituted with both electron-donating (**4**−**6**) and electron-withdrawing substituents (**3**) are rendered configurationally labile under these conditions. In addition, the dialkylarylphosphine **11** (CAMP) experiences significant erosion of stereochemistry, indicating that the catalyzed pyramidal inversion is not limited to diarylalkylphosphines. We note that highly sterically encumbered phosphines (**7**−**10**) undergo incomplete racemization under these conditions, an outcome that we attribute primarily to retarded rates of intermolecular ET for these bulky species.[34]

Table 2. Examples of ET-Catalyzed Pyramidal Inversion[a]



compound	E_{pa}	ee	recovery
1	+0.09 V	85% ee → 0% ee	82% Recovery[b]
2	+0.72 V	94% ee → 0% ee	88% Recovery
3	+0.94 V	51% ee → 1% ee	87% Recovery
4	+0.76 V	95% ee → 0% ee	88% Recovery
5	+0.84 V	99% ee → 0% ee	83% Recovery
6	+0.72 V	93% ee → 0% ee	87% Recovery
7	+0.77 V	99% ee → 15% ee	91% Recovery
8	+0.62 V	88% ee → 12% ee	86% Recovery
9	+0.65 V	96% ee → 18% ee	84% Recovery
10	+0.73 V	92% ee → 12% ee	88% Recovery[c]
11	+0.66 V	95% ee → 36% ee	73% Recovery

[a] See Supporting Information for full experimental details. Enantiomeric excess of isolated phosphines was determined by HPLC following protection as BH_3-adduct. [b] Ferrocenium hexafluorophosphate ($[Cp_2Fe][PF_6]$, 25 mol %) was used as oxidant. [c] CH_2Cl_2 was used as solvent.

A preliminary attempt to experimentally determine the rate of ET-catalyzed phosphine inversion evidences a low barrier. When monitored *in situ* by circular dichroism spectroscopy, ET-catalyzed racemization of **1** with $[Cp_2Fe][PF_6]$ is complete within the lag time of mixing and acquisition (~20 s).[35] (U)M06-2X/6-31G(d,p) density functional theory (DFT) calculations[36] in SMD[37] acetonitrile solvent provide a more quantitative estimate of the ET-catalyzed pyramidal inversion barrier.[32,38] Optimized ground states and transition structures for phosphine inversion of **2** and **2**$^{\bullet+}$ are depicted in Figure 3.[39] In accord with previous studies,[19] the removal of one electron from **2** leads to a flattening of the ground-state structure for open-shell **2**$^{\bullet+}$, which adopts a relaxed pyramidal geometry with a ~17° reduction in the PR_3 internal dihedral angle that decreases intramolecular R group repulsion. The relaxation energy associated with this change in structure upon oxidation for **2**/**2**$^{\bullet+}$ is estimated to be >15 kcal/mol. With respect to the inversion transition states, both **2-TS** and **2**$^{\bullet+}$**-TS** are found to have nearly identical geometries, with PR_3 dihedral angles <1° and similar P-R group bond lengths. However, while neutral **2** inverts via Y-shaped **2-TS** with a computed barrier of $\Delta H^{\ddagger}$ = 31.9 kcal/mol, the $\Delta H^{\ddagger}$ for **2**$^{\bullet+}$ via **2**$^{\bullet+}$**-TS** is found to be only 4.3 kcal/mol. Since the $\Delta H^{\ddagger}$ for **2**$^{\bullet+}$ inversion is significantly less than the relaxation energy after electron transfer, it is possible that inversion is coupled mechanistically with geometric relaxation from ET.

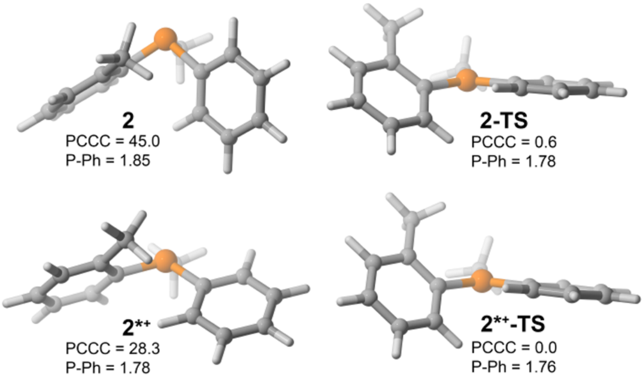


Figure 3. Ground and transition states for inversion of **2** and **2**$^{\bullet+}$.

Examination of the change in M06-2X HOMO energies for **2** to **2-TS** compared with **2**$^{\bullet+}$ to **2**$^{\bullet+}$**-TS** shows qualitative, although not quantitative, agreement with inversion barriers correlated to second-order Jahn−Teller effects. For example, the HOMO energy of **2** is destabilized by 1.8 eV (41.2 kcal/mol) in **2-TS**, while the HOMO of **2**$^{\bullet+}$ is destabilized by 0.7 eV (16.9 kcal/mol) in **2**$^{\bullet+}$**-TS**. In addition to frontier orbital effects, the low barrier for **2**$^{\bullet+}$**-TS** is likely due to less electron repulsion between the phosphine substituents and the singly occupied orbital in the planar transition-state geometry. This electron repulsion effect is in line with the observations of the relaxed ground-state structures.

Related decreases in computed inversion barriers were found for the other phosphines surveyed (e.g., $\Delta H^{\ddagger}$ = 31.3 and 4.9 kcal/mol for inversion of **3** and **3**$^{\bullet+}$, respectively). The calculations also support the speculation that slow intermolecular ET rather than large inversion barriers are the origin of incomplete racemization for phosphines **7**−**10**. For example, **9**$^{\bullet+}$ has an inversion $\Delta H^{\ddagger}$ of 4.0 kcal/mol, which is similar to the inversion barriers computed for **2**$^{\bullet+}$ and **3**$^{\bullet+}$.

In summary, we have shown that the pyramidal inversion of trisubstituted (aryl)alkyl phosphines may be catalyzed by single electron transfer, permitting dynamic stereochemical behavior of *P*-stereogenic phosphines at ambient temperatures. We anticipate that the ability to deliberately control the configurational lability of *P*-stereogenic phosphines will open new opportunities for stereodynamic applications of underivatized phosphines, for instance in stereoselective synthesis and chiroptical switching. Additionally, our results also bear on the suitability of certain *P*-stereogenic phosphines as chiral ligands for certain high-valent transition metals; the stereochemical fidelity of metal-bound *P*-stereogenic phosphines, and by consequence their ability to influence the stereochemical outcome of a metal-catalyzed process, may not necessarily be assumed when ligating oxidizing metal centers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, spectral characterization, HPLC chromatograms, Cartesian coordinates 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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