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Validating the Biphilic Hypothesis of Nontrigonal P(III) Compounds

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Abstract

Constraining σ^3 -P compounds in nontrigonal, entatic geometries has proven to be an effective strategy for promoting biphilic oxidative addition reactions more typical of transition metals. Although qualitative descriptions of the impact of structure and symmetry on σ^3 -P complexes have been proposed, electronic structure variations responsible for biphilic reactivity have yet to be elucidated experimentally. Here we report P K-edge XANES data and complementary TDDFT calculations for a series of structurally-modified P(N)₃ complexes that both validate and quantify electronic structure variations proposed to give rise to biphilic reactions at phosphorus. These data are presented alongside experimentally-referenced electronic structure calculations that reveal nontrigonal structures predicted to further enhance biphilic reactivity in σ^3 -P ligands and catalysts.

Keywords

biphilic; phosphorus; X-ray absorption spectroscopy; main group; TDDFT

Tricordinate phosphorus (σ^3 -P) compounds are indispensable tools in many fields of synthetic chemistry.^{1,2,3,4,5} Despite a diversity of applications, the reactivity of most typical trigonal pyramidal σ^3 -P compounds falls within a narrowly prescribed range, governed overwhelmingly by the nucleophilic reactivity of the stereochemically active lone pair (Figure 1).^{6,7} Complementary electrophilic reactivity of σ^3 -P compounds is comparatively rare;⁸ within trigonal symmetry the phosphorus-based unfilled acceptor orbitals for compounds R₃P are $\sigma^*_{\text{P-R}}$ in character and therefore rather high in energy.^{9–12}

Motivated by the perception that the restriction of phosphorus to local (pseudo)trigonal symmetry places an unnecessary check on the synthetic performance of σ^3 -P compounds,

13,14,15,16,17,18,19,20,21,22,23 we have advanced the hypothesis that descent from trigonal symmetry should colocalize both donor and acceptor reactivity at a single σ^3 -P site (i.e. biphilic²⁴ reactivity). Indeed, we have shown that nontrigonal σ^3 -P compounds (viz. **1** and **2**, Figure 1a) evolve to pentacoordinate phosphorus (σ^5 -P) products through oxidative addition of E–H bonds (E=OR, NHR, Ru),^{25–26,27,28} in some cases reversibly.^{29–35}

Although applications of the biphilic character of nontrigonal σ^3 -P compounds such as **1** and **2** have emerged in reactivity, a direct experimental demonstration of how the $C_{3v} \rightarrow C_s$ structural deformation controls σ^3 -P frontier orbital energies has not been previously presented. With a view toward establishing a rational schema for biphilic σ^3 -P design, we provide here the first explicit spectroscopic evidence validating the descent-in-symmetry hypothesis of biphilicity at σ^3 -P. Through phosphorus K-edge X-ray absorption near-edge structure (XANES) spectroscopy and supporting (TD)DFT demonstrations, we quantify the impact of nontrigonal distortion ($C_{3v} \rightarrow C_s \rightarrow C_{2v}$) on the electronic structure of a series of compositionally related compounds and show that nontrigonal σ^3 -P compounds present inherently contracted frontier orbital energy gaps that colocalize electron–donor and –acceptor behavior at a single σ^3 -P site, engendering biphilic character. Overall, these results codify how structural modifications control σ^3 -P electronic structure and provide a forward-looking blueprint for the development of next generation nontrigonal P(III) catalysts and ligands with exceptional biphilic reactivity.

Phosphorus K-edge XANES³⁶ is an ideal element-specific technique for extracting information concerning electronic structure and chemical bonding in diverse phosphorus compounds.^{37,38,39,40,41–42,43,44} Unoccupied frontier orbital energies are measured by excitation of core P 1s electrons, and transitions are governed by the dipole selection rule so that peak intensity correlates to P 3p character in the associated virtual orbitals.^{45–46} For *tris*-methylanilide P(NMePh)₃⁴⁷, a benchmark crystalline C_3 -symmetric phosphorous triamide, the P K-edge XANES spectrum exhibits an intense pre-edge feature at 2147.0 eV (Figure 2a, blue dashes). TDDFT simulation (B3LYP-D3/6–31G(d,p)) and subsequent natural transition orbital analysis⁴⁸ (NTOs; Figure S12) assigned this transition as an excitation of a core 1s_P electron into excited states with mixing of MOs 94/95 and 100/101, the latter of which correspond to the degenerate *e*-symmetry σ^*_{P-N} orbitals assuming rigorous C_3 point group symmetry. The magnitude of the calculated oscillator strength for each transition stems primarily from the large calculated 3p_P character of MOs 100 and 101 (47.4% and 53.2%, respectively). This is consistent with the analysis of the NTO for the first transition in which the particle state is 53.6% 3p_P. In contrast, MOs 93 (HOMO), 94 (LUMO), and 95 (LUMO +1) have smaller calculated 3p_P character (4.6% - 7.7%) and are best described as aryl π^* (Figure S6). Correspondingly, the P lone pair is better matched to MO 87 (Figure 2d), as reflected by its increased P 3s_P (10.7%) and 3p_P (18.4%) character compared to the HOMO (4.4% and 4.6% for 3s_P and 3p_P, respectively).

Despite the apparent compositional similarity in their local σ^3 -P environments, the P K-edge XANES spectrum of nontrigonal σ^3 -P **1** (Figure 2a, red) revealed a dramatic bathochromic shift of about 1.1 eV for the first pre-edge peak (2145.9 eV) compared to P(NMePh)₃. This difference in XANES pre-edge energies cannot be attributed to variance in P oxidation state; as expected for P compounds with identical valency and local bonding environment, there is

only a small (0.1 eV) difference in the calculated $1s_P$ orbital energies. Rather, the 1.1 eV difference between the first peak energies for **1** and $P(NMePh)_3$ stems primarily from lowering of frontier phosphorus acceptor orbital energy by the nontrigonal distortion of σ^3 -P compound **1**. Upon descent in symmetry, the nearly degenerate P acceptor MOs in $P(NMePh)_3$ splits in **1** to yield a new unoccupied orbital at lower energy (MO 68; Figure 2d); the energy of the remaining P acceptor orbital (MO 73) is relatively unaffected by comparison. TDDFT simulation of the K-edge absorption confirms excitation to MO 68, a transition best described as $1s_P \rightarrow \sigma^*_{P-N}$ (Figure 2b). In effect, the $C_3 \rightarrow C_s$ structure change yields a pronounced decrease in σ^*_{P-N} energy that is consistent with increased biphilicity of **1** relative to $P(NMePh)_3$.

Notably, further deformation of C_s -symmetric **1** to a C_{2v} -symmetry structure (C_{2v} -**1**) is predicted by DFT to cause the LUMO energy to decrease by an additional 1.3 eV (Figure 2c). This decrease in LUMO energy is significant because it suggests that the P-acceptor orbital becomes more susceptible to substrate binding upon distortion from nontrigonal C_s to C_{2v} symmetry. To further analyze how these MOs are transformed upon biphilic oxidative addition reactions, a previously unreported σ^5 -P compound (**1**•[H]₂, Figure 1b) with a nearly planar PN_3 framework was synthesized.⁴⁷

By comparison to both **1** and $P(NMePh)_3$, the P K-edge XANES absorption edge for σ^5 -P compound **1**•[H]₂ appeared at much higher energy (2148.4 eV; Figure 2b, *right*). The large energy increase (2.5 eV) for the absorption edge in **1**•[H]₂ relative to **1** is consistent with oxidation of P(III) to P(V), which lowers the energy of the $1s_P$ orbital due to the increased effective nuclear charge (Z_{eff}) at P. Indeed, the calculated $1s_P$ orbital for **1**•[H]₂ is stabilized by 1.2 eV relative to **1**. Equally important, TDDFT spectral simulations and NTO analysis for **1**•[H]₂ revealed that the resulting excited state contains mixtures of orbitals that have appreciable σ^*_{P-H} character (MOs 70 and 73; Figure S9), so the transition is assigned as $1s_P \rightarrow \sigma^*_{P-H}$. These data indicate that the P-based frontier donor/acceptor electronic structure of C_{2v} -**1** is transformed upon formation of the σ^5 -P P–H bonds, evolving into the σ_{P-H} and σ^*_{P-H} MOs of divergent energy (Figure 2c).

The same qualitative electronic features observed for **1** and **1**•[H]₂ are also evident when nontrigonal σ^3 -P complexes are bound to transition metals. For instance, the P K-edge XANES spectrum of **2**•[Ru], in which the nontrigonal σ^3 -P behaves as an L-type donor ligand with respect to the metal, shows three features: a shoulder at 2145.9 eV and two prominent peaks at 2146.8 and 2148.1 eV (Figure 3a). DFT calculations revealed that the phosphorus acceptor orbital on the free ligand **2** mixes with the $4d_{z^2}$ on Ru to form a new MO that has some σ^*_{Ru-P} character but is best defined as the P acceptor orbital (MO 210; Figures 3c and 3d), as reflected in the calculated MO composition (43.3% P 3p and 11.2% Ru 4d; Table S16). For comparison, a complementary σ_{Ru-P} bonding MO was identified at lower energy (MO 151; Figure 3c) with lower 3p_P mixing due to the absence of P acceptor character (9.7% P 3p and 5.4% Ru 4d). The remaining frontier orbitals calculated for **2**•[Ru] have < 5% 3p_P character stemming from **2**, and the HOMO and LUMO are best described as Ru–Cl and Ru–N π^* (Figure S10). TDDFT calculations revealed that the intense transition at 2146.8 eV in the P K-edge XANES spectrum of **2**•[Ru] shown in Figure 3b is assigned to an excited state containing mixtures of MOs 194 – 199, 201, and 210 due to the low molecular

symmetry. However, NTO calculations (Figure S13) reveal that the particle state for this transition is 32.8% $3p_P$ consistent with a large contribution from MO 210 due to its significantly higher $3p_P$ character (43.3%; Table S16) compared to the other MOs (<4.4%). Weaker transitions centered around 2146 eV are associated with unoccupied frontier orbitals containing smaller amounts of $3p_P$ character from PPh_3 , whereas transitions at higher energy (ca. 2148 eV) arise from higher energy MOs that have small amounts of Ru-P π^* consistent with Ru→P backbonding (MOs 212, 215, and 216; Figure S10). However, these MOs also contain significant amounts of diffuse $5p_{Ru}$ character (Table S16) suggestive of valence and Rydberg orbitals.^{49,50}

The P K-edge XANES spectrum of $2\bullet[H][Ru]$ exhibits similar features at 2145.9 and 2148.2 eV, as confirmed by TDDFT calculations, *but the intense peak at 2146.8 eV in $2\bullet[Ru]$ is no longer present* (Figure 3b). Inserting P into the Ru–H bond in $2\bullet[H][Ru]$ yields σ_{Ru-P} and σ^*_{Ru-P} orbitals at similar energies to those calculated for $2\bullet[Ru]$ (MOs 155 and 201; Figure 3c), but the P acceptor character in the unoccupied orbital is extinguished (MO 201 has only 2.5% P 3p compared to 43.3% in $2\bullet[Ru]$). The complementary σ_{Ru-P} orbital in $2\bullet[H][Ru]$ (MO 155) has 8.3% $3p_P$ and 3.4% $4d_{Ru}$ character – slightly less than that observed in $2\bullet[Ru]$. Two new MOs assigned to σ_{P-H} and σ^*_{P-H} (MOs 120 and 224, respectively) were also identified for $2\bullet[H][Ru]$, as expected (Figure S11). Overall, the XANES and TDDFT data for $2\bullet[Ru]$ and $2\bullet[H][Ru]$ mirror observations made for **1** and $1\bullet[H]_2$. The low-lying P acceptor orbital in nontrigonal σ^3 -P compounds is clearly transformed upon biphilic chemical reaction, whether in the absence or presence of a transition metal host.

The results of the forgoing spectroscopic investigations are usefully contextualized by a qualitative molecular orbital diagram tracing the nontrigonal distortion coordinate. In threefold symmetry (Figure 4, *left*), orbital $2a_1$ defines the lone pair and orbitals $2e$ are the doubly degenerate set of phosphorus-substituent antibonding orbitals. Descent to C_s symmetry does not dramatically alter the lone pair energy but lifts the degeneracy of the unfilled orbitals and lowers the frontier energy gap by decreasing destructive overlap of the substituents with respect to p_x . Further transit along this distortion coordinate culminates at a C_{2v} -symmetric T-shaped structure possessing orthogonal frontier orbitals, the precise energetic ordering of which depends on the nature of the substituent and its electronegativity.

Moving beyond discrete structures such as **1** and C_{2v} -**1**, a more general evaluation of the effect of nontrigonal distortion on the frontier orbital energies of σ^3 -P was undertaken. The PN_3 framework of model tricoordinate phosphorous triamide $P(NH_2)_3$ was parameterized within C_s symmetry (Figure 5a) and a relaxed potential energy surface scan was conducted at the B3LYP/6–31G* level for two independent driving coordinates (bond angle θ and dihedral angle ϕ). At this level of theory, the overall electronic energy plot (Figure 5b) describes a minimum for $P(NH_2)_3$ that is nearly trigonal ($\theta=93^\circ$, $\phi=113^\circ$),⁵¹ with electronic energy increasing upon planarization ($\phi\rightarrow180^\circ$) but varying only modestly for excursions of θ from equilibrium. Whereas HOMO (i.e. n_P) energies largely correlate with the total electronic energy (Figure S14) in accord with predictions from Walsh's rules, the plot of E_{LUMO} (Figure 5c) shows a qualitative inversion in energetic ordering with respect to E_{tot} . Specifically, structures close to the trigonal minimum for $P(NH_2)_3$ exhibit the energetically

highest-lying LUMOs while the lowest-lying LUMO energies are found for planarized structures ($\varphi \rightarrow 180^\circ$).

Most decisively for the biphilic hypothesis of nontrigonal σ^3 -P, a plot of the frontier orbital energy gap $E_{HOMO/LUMO}$ is given in Figure 5d. Here, trigonal structures maximize

$E_{HOMO/LUMO}$. In terms of reactivity, this large gap in frontier orbital energies diminishes the propensity for biphilic reactivity, instead accentuating a dominant nucleophilicity from the HOMO lone pair. By complement, nontrigonal structures such as **1** and C_{2v} -**1** decrease energy gaps $E_{HOMO/LUMO}$ consistent with an increased biphilicity for these species relative to compositionally related trigonal phosphorous triamides. The difference in $E_{HOMO/LUMO}$ between **1** and C_{2v} -**1** conforms with the orbital analysis in Figure 2c and suggests an increase in biphilic reactivity of nontrigonal σ^3 -P through planarization. Indeed, given that the barrier to interconversion of **1** and C_{2v} -**1** is known to be low,³² it is plausible the reported biphilic reactivity of **1** is expressed through a preequilibrium deformation to C_{2v} -**1**.

Finally, further inspection of Figure 5d shows that C_{2v} -**1** does not represent the minimum $E_{HOMO/LUMO}$ within the surveyed range. Rather, a planar structure with slightly obtuse bond angles (i.e. $\theta=104^\circ$, $\varphi=180^\circ$) defines the absolute minimum for $E_{HOMO/LUMO}$. Consequently, if one were able to access such a structure (presumably through appropriate molecular constraint), then the biphilicity of the phosphorus center would be predicted to be maximized within this local PN_3 substitution pattern.

We conclude that contracted frontier orbital energy gaps and dense spatial orbital array are an inherent consequence of nontrigonal deformation for σ^3 -P compounds. This electronic feature allows for colocalized electron–donor and –acceptor behavior at a single phosphorus site that manifests the biphilic reactivity underpinning the insertion of σ^3 -P to E–H and M–H bonds. Our spectroscopic and theoretical results represent a rare example where a nontrigonal σ^3 -P compound is evaluated side-by-side with a compositionally-related trigonal analogue, allowing a direct quantitative comparison of their electronic structures in a way that illuminates aspects of their differential reactivity. These insights are now guiding our design of next-generation nontrigonal σ^3 -P ligands and biphilic catalysts.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) An illustration of the biphilic hypothesis of nontrigonal σ^3 -P. (b) $P(N)_3$ compounds investigated in this study.

Figure 2.

(a) P K-edge XANES spectra for P(NMePh)_3 , **1**, and $1\cdot[\text{H}]_2$. (b) Experimental (solid line) and simulated (dashed line) P K-edge XANES spectra for P(NMePh)_3 , **1**, and $1\cdot[\text{H}]_2$. Individual transitions are represented by red bars and indicate relative differences in calculated oscillator strength. The transitions are labeled according to the predominant calculated MOs mixing in the excited states. The labels correspond to those provided in Figure 2c and Table S15. (c) Truncated MO correlation diagram of molecular P(N)_3 complexes. Frontier orbitals relevant to the XAS results and reactivity at phosphorus are highlighted in red and connected by dashed lines to show how they transform across the series. (d) Selected donor-acceptor Kohn-Sham orbitals from DFT calculations of P(NMePh)_3 and **1** (isovalue = 0.0200; hydrogen atoms not shown). Kohn Sham orbitals for the remaining MOs labelled in the MO diagram are included in the SI.

Figure 3.

(a) Comparison of P K-edge XANES spectra for **2•[Ru]** and **2•[H][Ru]**. (b) Comparison of experimental (solid line) and simulated (dashed line) P K-edge XANES spectra for **2•[Ru]** and **2•[H][Ru]**. Individual transitions are represented by red bars and indicate relative differences in calculated oscillator strength. The transitions are labeled with calculated MOs mixing in the excited states. (c) Truncated MO correlation diagram of **1**, **2•[Ru]**, and **2•[H][Ru]**. Frontier orbitals relevant to the XAS results and reactivity at phosphorus are highlighted in red in Figure 3c and connected by dashed lines to show how they transform across the series. (d) Selected donor-acceptor Kohn-Sham orbitals from DFT calculations of **2•[Ru]**, and **2•[H][Ru]** (isovalue = 0.0270; hydrogen atoms not shown). Kohn-Sham orbitals for the remaining MOs labelled in the MO diagram are included in the SI.

Figure 4. Qualitative frontier molecular orbital diagrams depicting the electronic structure arising from nontrigonal perturbation of a model σ^3 -P compound.

Figure 5.

(a) Definition of geometrical parameters used to index the computational structures of $P(NH_2)_3$ within local C_s symmetry. Hydrogens are omitted for clarity. (b), (c), (d) Contour maps depicting the (b) total electronic energy (E_{tot}), (c) LUMO energies (E_{LUMO}), (d) E_{HOMO}/E_{LUMO} for $P(NH_2)_3$ structures with C_s -symmetry ($N=4141$ discrete input structures in the range $80^\circ \leq \theta \leq 120^\circ$ and $80^\circ \leq \phi \leq 180^\circ$ at 1° increments). Energies are shown in

units of Hartrees. Points corresponding to the structures of $\text{P}(\text{NMePh})_3$, **1** and C_{2v} -**1** are superimposed as black points. The red points correspond to the absolute minimum.

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