

Probing Hydrogen Atom Transfer at a Phosphorus(V) Oxide Bond Using a "Bulky Hydrogen Atom" Surrogate: Analogies to PCET

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Supporting Information

ABSTRACT: Recent computational studies suggest that the phosphate support in the commercial vanadium phosphate oxide (VPO) catalyst may play a critical role in initiating butane C-H bond activation through a mechanism termed reduction-coupled oxo activation (ROA) similar to proton-coupled electron transfer (PCET); however, no experimental evidence exists to support this mechanism. Herein, we present molecular model compounds, $(Ph_2N)_3V = N - P(O)Ar_2$ (Ar = C_6F_5 (2a), Ph (2b)), which are reactive to both weak H atom donors and a Me₃Si[•] (a "bulky hydrogen atom" surrogate) donor, 1,4-bis(trimethylsilyl)pyrazine. While the former reaction led to product decomposition, the latter resulted in the isolation of the reduced, silvlated complexes $(Ph_2N)_2V-N=P(OSiMe_2)Ar_2$ (3a/b). Detailed analyses of possible reaction pathways, involving the isolation and full characterization of potential stepwise square-scheme intermediates, as well as the determination of minimum experimentally and computationally derived



thermochemical values, are described. We find that stepwise electron transfer (ET) + silvlium transfer (ST) or concerted EST mechanisms are most likely. This study provides the first experimental evidence supporting a ROA mechanism and may inform future studies in homogeneous or heterogeneous C-H activation chemistry, as well as open up a possible new avenue for main group/transition metal cooperative redox reactivity.

INTRODUCTION

Catalyst support systems typically involve unreactive main group oxides, such as silica (SiO_2) , alumina (Al_2O_3) , and phosphate (PO₄³⁻), supporting the catalytically active metal centers. Common supported commercial catalysts include (support in parentheses) the Phillips Cr catalyst for ethylene polymerization (SiO₂); the Haber–Bosch Fe catalysts for N_2 reduction to NH₃ (Al₂O₃ and others); the hydrodesulfurization catalysts for petroleum processing (Al₂O₃); and the vanadium phosphate oxide (VPO) catalyst for the partial oxidation of butane to maleic anhydride (PO₄³⁻).¹⁻⁴ Supports are typically assumed to act as high-surface platforms capable of binding catalytically active centers, while playing little role in the catalytic processes themselves. However, studies have shown that supports may indeed be active in catalysis through various mechanisms, such as spillover effects, strong metalsupport interactions, and more, 5-8 thus requiring a rethinking of the once accepted dogma.

For decades, the mechanism for the conversion of butane to maleic anhydride using the VPO catalyst has been the subject of extensive experimental studies. Key mechanistic steps, including activation of the relatively inert butane C-H bonds, were thought to occur solely at high-valent V-oxo centers. No study invoked the PO4³⁻ support in any reactive step.^{4,9-13} However, recent computational studies by Goddard and coworkers have found that PO_4^{3-} may be involved in the key C-H activation chemistry. They proposed that inert C-H cleavage at butane occurs at a terminal $P^{V}=O$ bond, resulting in its protonation with concurrent reduction of a neighboring V^V (Scheme 1a) as part of a mechanism coined reductioncoupled oxo activation (ROA).¹⁴⁻¹⁶ It is worth noting the similarities between the ROA and well-studied proton-coupled electron transfer (PCET) reactions,^{17–19} particularly in molecules involving well-separated metal and basic sites, which can nonetheless engage in concerted PCET.²⁰⁻²² In contrast to PCET, the proposed ROA mechanism as applied to VPO has yet to be supported by any experimental evidence.

To investigate the proposed noninnocent role of terminal $P^V = O$ bonds in VPO, we have recently reported the synthesis and preliminary reactivity of homogeneous mono- and multimetallic vanadium phosphinate complexes bearing $V^{III} - O - P^V = O$ linkages.^{23,24} These complexes were unreactive to common H atom donors (HADs), perhaps a result of their

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Scheme 1. (a) Proposed ROA (PCET) Mechanism for the C-H Activation of Butane at a P^V =O Bond in VPO; (b) Present Work Highlighting the Reaction of Molecular VPO Analogues (2a, 2b) with H[•] and TMS[•] Donors

a) COMPUTATIONAL STUDIES



relatively low V^{III} oxidation states.¹⁰ Herein, we describe the synthesis of high-valent V^V complexes (**2a**, **2b**) bearing V^V= $N-P^{V}=O$ linkages as molecular VPO models and further probe their reactivity with both HADs and a trimethylsilyl radical (Me₃Si[•] = TMS[•]) donor (Scheme 1b). The latter involved the formation of a reduced product with a silylated P=O bond, following a pathway analogous to ROA (Scheme 1a). As will be outlined, we describe TMS[•] as a "bulky hydrogen atom"—similar to the use of TMS⁺ as a "bulky proton"^{25–27}—and together, these results describe the first direct experimental evidence supporting the proposed ROA mechanism.

RESULTS AND DISCUSSION

The target complexes (2a, 2b) were synthesized by salt metathesis of the reported²⁸ vanadium nitride, $(Ph_2N)_3V(\mu N)Li(THF)_3$ (1), with diaryl phosphinic chlorides, $(C_6F_5)_2P_{(O)}Cl^{29}$ or $Ph_2P(O)Cl$, resulting in the isolation of 2a or 2b, respectively, following purification (Scheme 2).





Both V^V complexes displayed significantly shifted, broadened ⁵¹V NMR resonances at 117 ppm (**2a**) and -6 ppm (**2b**) relative to **1** (-217 ppm), consistent with an increasingly deshielded V center. In contrast, the ³¹P NMR resonances followed the opposite trend, with broad signals (due to coupling to the quadrupolar (I = 7/2) ⁵¹V) at -20 and 19 ppm, respectively, both shifted ~20 ppm upfield relative to the starting materials. Single crystals suitable for X-ray diffraction (XRD)³⁰ studies were grown from pentane/ether (**2a**, Figure 1) or ether (**2b**, Figure S45). Pertinent bond lengths and angles are compiled in Tables S1 and S2. Notable are the elongated V1–N1 bonds in **2a** (1.662(11) Å) and **2b**



Figure 1. Solid state XRD structure of **2a** (*C*, black; N, blue; V, purple; P, orange; O, red; F, violet). Phenyl groups (excluding *ipso* carbons) are omitted for clarity.

(1.661(7) Å) relative to 1 (1.582(3) Å),²⁸ both of which are also nearly identical to the N1–P1 bonds in 2a (1.661(11) Å) and 2b (1.674(7) Å). Combined with the near linear V1–N1–P1 angles (2a: 175.9(7)°; 2b: 173.1(5)°), this suggests a delocalized π manifold.

Exposure of 2a and 2b to common HADs with various element-H bond dissociation free energies (BDFE_{solvent}), such as 2,4,6-tri-tert-butylphenol (O-H BDFE_{MeCN} = 77.1 kcal/ mol), 1,4-cyclohexadiene (C-H BDFE_{tol} = 72.6 kcal/mol), and 2,2,6,6-tetramethylpiperidine-N-hydroxyl (TEMPO-H) (O-H BDFE_{tol} = 65.2 kcal/mol) in benzene resulted in no appreciable reaction as determined by both ¹H NMR and Xband EPR spectroscopies of the reaction solutions.^{17,31} In contrast, exposure of 2a to $Cp(CO)_3Cr-H$ (BDFE_{MeCN} = 57.3 kcal/mol) (Cp = η^5 -C₅H₅)³²⁻³⁴ in C₆D₆ at room temperature resulted in the quantitative appearance of the protonated amide, Ph₂NH, as well as a half-equivalent of the Cr dimer product, $[Cp(CO)_3Cr]_2$, as observed by ¹H NMR spectroscopy (Figure S29).³⁵ The analogous reaction with the deuterium isotopomer, $Cp(CO)_3Cr-D$,^{34,36} resulted in the formation of Ph₂ND as observed by ²H NMR spectroscopy, yet we were unable to quantify the exact amount (Figure \$33). No reaction was observed between any of these HADs and the silanesubstituted complex, (Ph₂N)₃V=NSiMe₃-the precursor to 1^{28} (Scheme 2)—after several days at room temperature. Together, these data may support a possible reaction pathway involving the formal transfer of H^{\bullet} to the terminal $P^{V}=O$ bond with concurrent reduction of V^V to V^{IV} , following a ROA/PCET pathway (Scheme 1).^{14–16} However, the putative PO-H bond would be incompatible with the basic $Ph_2N^$ ligands, resulting in an intramolecular acid-base reaction. While the byproducts of this reaction remain unknown, analysis of the reaction mixture by EPR spectroscopy revealed diagnostic eight-line hyperfine patterns consistent with VIV byproducts (Scheme 1b; Figure S30).

Due to the difficulty in determining the reactive site in 2a with the $Cp(CO)_3Cr-H$ HAD, we explored whether TMS[•] could be used as a "bulky hydrogen atom" surrogate, generating more stable, isolable products. We used the antiaromatic 1,4-bis(trimethylsilyl)pyrazine (TMS₂-pyz) compound as our TMS[•] source.^{37,38} Mashima and co-workers have recently demonstrated the salt-free reduction of transition metal chloride complexes with TMS₂-pyz involving the formal transfer of 2 equiv of TMS[•], reduction of the metal centers, and production of pyrazine and 2 equiv of TMSCl.^{39–41} Exposure of 2 equiv of **2a** or **2b** to an equivalent of TMS₂-pyz

resulted in the formation of pyrazine and the disappearance of the diamagnetic resonances for **2a** and **2b** as observed by multinuclear (⁵¹V, ³¹P, ¹⁹F, ¹H) NMR spectroscopy. Single crystals suitable for XRD studies were grown for both reactions, and the solid state structures confirmed the formation of the reduced, silylated products, $(Ph_2N)_3V^{IV}-N=P(OTMS)Ar_2$ (Scheme 3) (**3a**, Ar = C₆F₅, Figure 2; **3b**, Ar = Ph, Figure S48).

Scheme 3. Reaction of 2a or 2b with TMS_2 -pyz to Generate 3a or 3b



Figure 2. Solid state XRD structure of **3a** (C, black; N, blue; V, purple; P, orange; O, red; F, violet; Si, pink). Phenyl groups (excluding *ipso* carbons) are omitted for clarity.

In contrast to **2a**, **3a** contains a single V1–N1 (1.837(2) Å) bond and a P1–N1 double bond (1.535(2) Å), with a resulting bent V1–N1–P1 angle (145.90(13)°). The P1–O1 bond is also elongated (1.5637(16) Å) relative to **2a** (1.484(8) Å), consistent with more single-bond character.⁴² Similar bond metric differences are observed between **2b** and **3b** (Tables S1 and S2). X-band EPR spectra in tetrahydrofuran (THF) were collected for **3a** and **3b**, and both contain similar spectral features, including expected eight-line splitting patterns at room temperature due to hyperfine coupling of the d¹ electron to the ⁵¹V center (I = 7/2, ~100% abundance). Modeling these, as well as the anisotropic 100 K spectra, suggests that the single unpaired electron is minimally delocalized and rests primarily at the V center (Figures S10–13).^{43,44}

The formal transfer of TMS[•] from TMS₂-pyz to 2 generating 3 represents what we believe is the clearest example yet of reactivity at a terminal P^V =O bond mimicking the proposed ROA/PCET mechanism (Scheme 1). We next wanted to probe the mechanism of this transformation. For PCET processes, distinguishing concerted (ex. H[•] or H⁺/e⁻ transfer)

from stepwise (ex. PT + ET) processes is performed by comparing the thermochemical values of the stepwise ground state free energy changes, $\Delta G^{\circ}_{\rm ET}$ and $\Delta G^{\circ}_{\rm PT}$, to the reaction free energy barrier, ΔG^{\ddagger} . A concerted process is assumed when ΔG^{\ddagger} is lower than both stepwise free energy change values.^{17,45} In order to elucidate the mechanism of the transformation from 2 to 3, we employed a similar strategy of dissecting and studying the individual steps of ET and silylium transfer (ST) as part of a square scheme (Scheme 4).¹⁷





To distinguish a concerted from a stepwise process, the thermodynamic parameters $\Delta G^{\circ}_{ST}(2 \rightarrow 2\text{-}Si^{+})$, $\Delta G^{\circ}_{ET}(2 \rightarrow 2^{-})$, and ΔG^{\ddagger} are required (Scheme 4, eqs 1 and 2).¹⁷ We sought to determine approximate values for these parameters by combining experimental and computational results.

$$\Delta G^{\circ}_{ST} = -RT \ln(K_{rel})$$

= -1.37(kcal·mol⁻¹)×[pK(**2**-**Si**⁺)
- pK(TMS₂-pyz)] (1)

$$\Delta G^{\circ}_{\rm ET} = -FE^{\circ}$$

= -23.06(kcal·mol⁻¹·V⁻¹)×[E^o
(2^{0/-}) - E^o(TMS₂-pyz^{+/0})] (2)

Initial ST was first investigated (Scheme 4). Exposure of 2a and 2b to 1 equiv of [TMS][OTf] resulted in a reaction only with **2b** (OTf = $-OSO_2CF_3$ = triflate).⁴⁶ The new complex (2b-Si⁺) was fully characterized and revealed a significantly downfield shifted ⁵¹V resonance at 229 ppm vs -6 ppm for 2b. A low-resolution solid state XRD structure (Figure S47) revealed a near-linear V1-N1-P1 linkage in 2b-Si⁺ $(174.3(10)^{\circ})$ similar to **2b** $(173.1(5)^{\circ})$, Table S2). The unreactivity of 2a with an equivalent of [TMS][OTf] is likely the result of its poor Lewis basicity (vide infra). However, silvlation was possible using the silvlium cation, [Et₃Si][B- $(C_6F_5)_4$].⁴⁷ The new complex (2a-Si⁺) was fully characterized, including by XRD studies, and revealed the expected PO-SiEt₃ linkage and corresponding $[B(C_6F_5)_4]^-$ counteranion (Figure S44). Bond metrics are also similar to those found in **2a** (Table S1). Both complexes $(2a/b-Si^+)$ could be readily reduced with $CoCp_2$ or $CoCp_2^*$ ($Cp^* = \eta^5 \cdot C_5Me_5$), generating 3a' (where R = Et) or 3b (Scheme 4), respectively, and closing the ST + ET pathways. The formation of both products was confirmed by EPR spectroscopy (Figures S27 and S28).

To obtain estimated ΔG°_{ST} values (eq 1), relative pK values for **2a-Si⁺** and **2b-Si⁺** were needed. We define pK as the extent of TMS⁺ dissociation from the Lewis basic (LB) P==O bonds (eq 3), in analogy to Brønsted acids (K_{rel} is the equilibrium constant relative to an arbitrary LB'). Previously reported K_{rel} values—determined by NMR spectroscopy and set against Nmethylpyridone (NMP) as LB' (eq 3)—for pyridine (pyr), triphenylphosphine oxide (TPPO), and hexamethylphosphoramide (HMPA) were 10, 9.1 × 10⁻², and 1.0 × 10⁻⁴, respectively, in dichloromethane (DCM).⁴⁸ The corresponding pK^{DCM} values for the LB-TMS⁺ cations are -1.0 (pyr), 1.04 (TPPO), and 4.00 (HMPA), consistent with an expected, more highly Lewis basic HMPA vs TPPO and pyr.

$$LB-TMS^{+} + LB' \stackrel{K_{rel}}{\rightleftharpoons} LB + LB'-TMS^{+}$$

$$(2a/b-Si^{+}) \qquad (3)$$

We performed similar competition reactions⁴⁸ and monitored each by NMR spectroscopy (³¹P, ⁵¹V). Exposing 2a or 2b in a 1:1 ratio to [TPPO-TMS][OTf]⁴⁹ in DCM revealed broadened ⁵¹V NMR resonances centered around 2a or 2b-Si⁺, respectively (Figures S35 and S37), with corresponding ³¹P NMR spectra matching these assignments (Figures S36 and S38). Taken together, a relative Lewis basicity of 2a < TPPO <2b can be established. To bracket an upper basicity limit for **2b**, we exposed **2b-Si⁺** to HMPA. The NMR spectra (51 V, 31 P) revealed resonances centered around those for 2b and [HMPA-TMS]⁺ with the latter confirmed by *in situ* generation of [HMPA-TMS][OTf] (Figures S39 and S40). We also note that no reaction occurred between HMPA and TMS₂-pyz, as observed by ¹H and ³¹P NMR spectroscopy. To bracket an upper basicity limit for 2a, we exposed 2a-Si⁺ to an equivalent of pyr. In this case, 2a was regenerated (Figures S41 and S42). Together, an overall basicity trend of 2a < pyr < TPPO < 2b < HMPA < $[TMS-pyz]^-$ is assigned with corresponding experimentally bracketed pK^{DCM} values of 2a-Si⁺ < -1.0 and $1.04 < 2b-Si^{+} < 4.00.^{48}$ A conservative *minimum* experimental $\Delta G^\circ_{\rm ST}$ value of ~7 kcal/mol was extracted based on the bracketed relative pK values of < -1 for 2a-Si⁺ and >4 for TMS_2 -pyz (eq 1). A similar approach could not be used for 2b-Si⁺ due to the possible (yet unlikely) overlapping experimental pK values for $\mathbf{\hat{2}b}$ -Si⁺ (1.04–4.00) and TMS₂-pyz (>4).

We note that the above $\Delta G^{\circ}_{\rm ST}$ is an *extremely* conservative estimate due to very few published $K_{\rm rel}$ values for TMS⁺ equilibria.⁴⁸ In an attempt to extract more precise values, we turned to density functional theory (DFT). Calculations were performed using the uwB97XD method,^{50,51} with Ahlrichs' def2-SVPP basis set,⁵² and with the relativistic effect of V, which was accounted for by the Stuttgart–Dresden effective core potential.⁵³ We also used the polarizable continuum model (PCM) to calculate the systems in DCM.^{54,55} Initial ST involving $2a/b + TMS_2$ -pyz $\rightarrow 2a/b$ -Si⁺ + TMS-pyz⁻ was calculated, and extracted $\Delta G^{\circ}_{\rm ST}$ values were 64.81 kcal/mol (2a, Figure 3, blue) and 52.90 kcal/mol (2b, Figure 3, orange), much higher than the experimental minimum. These results are consistent with the observed increased basicity from 2a to 2b, reflected by a calculated pK difference of ~8.7 units (eq 1) and resulting in a lower $\Delta G^{\circ}_{\rm ST}$. The following ET steps (2a/b-Si⁺ + TMS-pyz⁻ $\rightarrow 3a/b$ + TMS-pyz[•]) were calculated to be



Figure 3. DFT-calculated reaction coordinates for the stepwise conversion of 2a/b to 3a/b via ST + ET or ET + ST pathways. Gibbs free energies are given in kcal/mol relative to the starting materials. For more information, see the Supporting Information.

very downhill at -83.47 kcal/mol (2a) and -74.81 kcal/mol (2b), resulting in overall ΔG°_{rxn} values of -18.66 and -21.91 kcal/mol, respectively (Figure 3). Together, these data suggest that a stepwise mechanism involving initial ST is unlikely (Scheme 4).

The alternative stepwise process involving initial ET was also probed experimentally and computationally (Scheme 4, Figure 3). Both **2a** and **2b** were analyzed by cyclic voltammetry (CV) in DCM, and each revealed quasi-reversible $V^{IV}\!/V^V$ couples at $E_{1/2}$ = -0.99 V and -1.26 V, respectively, versus the ferrocene/ferrocenium (Fc/Fc^+) couple (Figure S49). The more oxidizing 2a is consistent with the enhanced electronwithdrawing ability of the C₆F₅ substituents. Chemical isolation of the reduced forms, $2a^-$ and $2b^-$, was possible using CoCp*₂ ($E_{1/2} = -1.94$ V vs Fc/Fc⁺)⁵⁶ (Scheme 4), and both were structurally characterized (Figures S43 and S46). Bond metrics for 2a⁻ revealed a bent V1-N1-P1 $(145.3(10)^{\circ})$ fragment similar to 3a $(145.90(13)^{\circ};$ Figure 2) and shortened P1-N1 (1.551(14) Å) and P1-O1 (1.455(12) Å) bonds relative to 2a with similar trends observed in $2b^{-}$ (Table S2). Both complexes were analyzed by EPR spectroscopy at room temperature and 100 K. The spectra displayed similar simulation parameters to 3a and 3b (Figures S14-S17). The stepwise ET + ST sequence was closed using [TMS][OTf] (Scheme 4). Treatment of $2a^-$ or $2b^-$ with [TMS][OTf] cleanly generated the product 3a or 3b, respectively, following removal of the [Cp*2Co][OTf] byproduct. We note that, in contrast to 2a, 2a⁻ reacts with [TMS][OTf] (vide supra), consistent with an expected increase in basicity from $2a \rightarrow 2a^-$ upon ET, similar to what is commonly observed in stepwise ET + PT studies.⁴⁵

Next, experimentally derived ΔG°_{ET} values could be determined based on the obtained $E_{1/2}$ values for the $2^{0/-}$ couples (eq 2). However, we noticed a discrepancy in the reported $E_{1/2}$ of the TMS₂-pyz^{+/0} couple ($E_{1/2} = -0.24$ V vs Fc/Fc⁺ in DCM).³⁹ Using analogous conditions, an $E_{1/2} = -0.97$ V vs Fc/Fc⁺ was obtained in our hands (Figure S50). We further corroborated our value using a different reference, Fe(η^{5} -C₅Me₅)₂ (Fc⁺), and obtained an $E_{1/2} = -0.39$ V vs Fc//Fc^{*+} (Figure S51), corresponding to approximately -0.95 V vs

Fc/Fc⁺ (using an $E_{1/2} = -0.56$ V for Fc^{*}/Fc^{*+} vs Fc/Fc⁺ in DCM in our hands (Figure S52)).⁵⁷ Thus, using our $E_{1/2}$ values for **2a** (-0.99 V), **2b** (-1.26 V), and TMS₂-pyz (average of -0.96 V), we calculated experimental $\Delta G^{\circ}_{\rm ET}$ values of 0.7 and 6.9 kcal/mol, respectively, for the stepwise ET steps with **2a** and **2b** (eq 2). The corresponding DFT-calculated values are both slightly exergonic at -4.49 and -1.76 kcal/mol for **2a** and **2b**, respectively (Figure 3). The deviation from experimental values is likely a result of the PCM solvation model, which provides only a dielectric continuum and does not take into account the solvent's molecular interactions with the calculated molecules. Despite this, the DFT results follow the same trends as the experimental values wherein **2a** is more prone to initial ET than **2b**.

As noted earlier, in the PCET literature, concerted PET processes are assumed when the reaction barrier (ΔG^{\ddagger}) is lower than the stepwise ground state free energy changes, ΔG°_{ET} and ΔG°_{PT} (or ΔG°_{ST} in our case).^{17,45} In an analogous fashion, we attempted to obtain kinetic information by UV-vis spectroscopy for the $2 \rightarrow 3$ transformations; however, our efforts were hampered by several factors. First, the reactions appeared to be very fast, even at the concentrations used (10^{-5} M) . Second, while stopped-flow methods were attempted, the absorption spectra of 2a/3a and 2b/3b revealed no distinct isosbestic points amenable to clean kinetic analyses (Figures S55, S58, S59). Moreover, monitoring the reactions over extended periods of time also revealed the emergence of Ph_2NH (Figure S59), which we ascribe to the introduction of adventitious water, further complicating our kinetic analyses. While we are unable to obtain experimental ΔG^{\ddagger} values, our results nonetheless suggest that the stepwise ST + ET mechanism is highly unlikely (Figure 3), whereas both stepwise ET + ST or near barrierless concerted EST pathways are possible for the transformations of $2 \rightarrow 3$ (Scheme 4). The low experimental and computational $\Delta G^{\circ}_{\rm ET}$ values obtained would, however, render it difficult to distinguish between the two.

CONCLUSION

In summary, we have demonstrated a clear example of reactivity at a terminal P^V=O bond mimicking the proposed ROA/PCET mechanism for VPO catalysis (Scheme 1) using a TMS[•] donor (TMS₂-pyz) as a "bulky hydrogen atom" surrogate. With the use of a square scheme and resulting experimentally and computationally derived thermochemical values, we have determined that a stepwise ST + ET mechanism is highly unlikely; however, stepwise ET + ST or concerted EST pathways are viable. Together, this study has provided the first experimental evidence supporting the cooperative metal/main group reactivity of a $V^{V} = N - P^{V} = O$ fragment with a TMS[•] source in direct analogy to overall H[•] transfer proposed in the ROA mechanism (Scheme 1a). These results may benefit future studies in homogeneous or heterogeneous C-H activation chemistry⁵⁸ and serve to highlight the potential for main group/metal cooperative redox reactivity over multiple bonds.²⁰⁻²² This, as well as possible applications of TMS[•] donors as bulky hydrogen atom surrogates, is currently being investigated in our laboratory.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an atmosphere of dry, oxygen-free N_2 or Ar by means of standard Schlenk or glovebox techniques (MBraun UNIlab Pro SP Eco equipped with a -38 °C freezer). Pentane, toluene, benzene, diethyl ether, tetrahydrofuran, and dichloromethane were dried using an MBraun solvent purification system. Benzene- d_6 , bromobenzene d_5 , and tetrahydrofuran- d_8 were purchased from Aldrich and dried over CaH₂ for several days prior to distillation. All solvents were degassed by freeze-pump-thaw and stored on activated 4 Å molecular sieves prior to use. Ph₂NH, ⁿBuLi (1.6 M in hexanes), VCl₃(THF)₃, Me₃SiN₃, ⁱPr₂NH, Ph₂POCl, (C₅Me₅)₂Co, (C₅H₅)₂Co, Me₃SiCl, Me₃SiOTf, Et₃SiH, [Ph₃C][B(C₆F₅)₄], and D₂ were purchased from Aldrich, Strem, or other commercial vendors and were used as received. (C₆F₅)₂POCl,²⁹ 1,4-bis(trimethylsilyl)pyrazine (TMS₂-pyz),³⁹ [Ph₃P(OSiMe₃)][OTf],⁴⁹ CpCrH(CO)₃,³³ [CpCr-(CO)₃]₂,³⁵ and 1²⁸ were prepared according to literature procedures. Elemental analyses (C, N, H) were performed at the University of California, Berkeley, using a PerkinElmer 2400 Series II combustion analyzer.

Spectroscopic Analyses. NMR spectra were obtained on a Varian Unity Inova 500 MHz or Agilent Technologies 400 MHz spectrometer and referenced to residual solvent or externally (¹¹B: BF₃·Et₂O; ¹⁹F: CFCl₃; ⁵¹V: VOCl₃; ³¹P: 85% H₃PO₄). Chemical shifts (δ) are recorded in ppm, and the coupling constants are in Hz. X-band EPR spectra were collected on a Bruker EMX EPR spectrometer equipped with an Oxford ESR 900 liquid helium cryostat. A modulation frequency of 100 kHz was used for all EPR spectra, and the data were plotted using SpinCount. EPR simulations used the program QPOWA by Belford and co-workers, as modified by J. Telser.⁵⁹ UV–vis spectroscopy was performed using a Shimadzu UV-2401PC spectrophotometer with quartz cuvettes equipped with airtight J. Young adaptors.

X-ray Crystallography. Data were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo K α X-ray source (α = 0.710 73 Å). The crystals were mounted on a cryoloop with Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans with 0.5° frame widths. Data collection and cell parameter determination were conducted using the SMART program. Integration of the data frames and final cell parameter refinement were performed using SAINT software. Absorption correction of the data was carried out using SADABS. Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL or OLEX².

Electrochemical Analyses. Cyclic voltammetry was performed on a CH Instruments 630E electrochemical analysis potentiostat, equipped with a 3 mm diameter glassy carbon working electrode, a Ag wire pseudoreference electrode, and a Pt counter electrode with $[Bu_4N][PF_6]$ (0.1 M) supporting electrolyte solution in CH₂Cl₂. The glassy carbon working electrode was cleaned prior to each experiment by polishing with 1, 0.3, and 0.05 mm alumina (CH Instruments) in descending order, followed by sonication in distilled water for 2 min. Background scans were conducted for each experiment in a solution containing only electrolyte and were then subtracted from each experiment. All voltammograms were referenced to the Fc/Fc⁺ redox couple.

Synthesis of $(Ph_2N)_3VNPO(C_6F_5)_2$ **(2a).** In the glovebox, a solution of $(C_6F_5)_2POCl$ (208 mg, 0.5 mmol) in 3 mL of benzene was added dropwise to a solution of complex 1 (415 mg, 0.5 mmol) in 10 mL of benzene and briefly shaken. The resulting black solution stood at room temperature for 1 h. The LiCl precipitate was removed by filtration over Celite using a fine-porosity filter, and the solvent was then removed *in vacuo*. The black residue was washed with cold pentane (2 × 5 mL) to afford a dark brown solid (400 mg, 0.42 mmol, 84% yield). Dark brown crystals suitable for XRD studies were grown by slow vapor diffusion of pentane into a concentrated solution of **2a** in diethyl ether at room temperature. ¹H NMR (400 MHz, C_6D_6 , 25 °C): $\delta = 6.84$ (m, 24H; *o*-ArH and *m*-ArH), 6.69 (m, 6H; *p*-ArH). ¹³C NMR (100 MHz, C_6D_6 , 25 °C): $\delta = 154.1$, 128.9, 126.0, 123.0

 (NPh_2) . The signal-to-noise ratio was too low for properly identifying any C_6F_5 ¹³C resonance. ⁵¹V NMR (105 MHz, C_6D_6 , 25 °C): δ = 117.3 (br). ³¹P NMR (162 MHz, C_6D_6 , 25 °C): δ = -20.0 (br m). ¹⁹F NMR (376 MHz, C_6D_6 , 25 °C): δ = -131.6 (br, 4F; *o*- C_6F_5), -148.2 (br, 2F; *p*- C_6F_5), -160.3 (br, 4F; *m*- C_6F_5). Anal. Calcd for $C_{48}H_{30}F_{10}N_4OPV$: C, 60.64; H, 3.18; N, 5.89. Found: C, 60.64; H, 3.29; N, 5.91.

Svnthesis of (Ph₂N)₃VNPOPh₂ (2b). In the glovebox, a solution of Ph2POCl (82.8 mg, 0.35 mmol) in 3 mL of THF was added dropwise to a solution of complex 1 (290 mg, 0.35 mmol) in 10 mL of THF and briefly shaken. The resulting black solution stood at room temperature for 1 h before the solvent was removed in vacuo. The black residue was extracted into benzene (8 mL) and filtered over a pad of Celite. The filtrate solvent was removed in vacuo, and the residue was recrystallized from ether at -35 °C over 24 h to afford a dark brown solid (260 mg, 0.322 mmol, 92% yield). Dark brown crystals suitable for XRD studies were grown by cooling a concentrated solution of 2b in ether to -35 °C and standing overnight. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ = 7.55 (m, 4H; ArH of Ph₂PO), 7.07–6.97 (m, 6H; ArH of Ph₂PO), 6.94 (d, ${}^{3}J_{HH} = 8.0$ Hz, 12H; o-ArH of NPh₂), 6.89 (t, ${}^{3}J_{HH}$ = 8.0 Hz, 12H; m-ArH of NPh₂), 6.77 (t, ${}^{3}J_{HH} = 7.2$ Hz, 6H; *p*-ArH of NPh₂). ${}^{13}C$ NMR (100 MHz, C_6D_6 , 25 °C): δ = 154.4 ($P\bar{h}_2N$), 135.2 (d, J_{PC} = 124.7 Hz; Ph_2P), 132.3 (s; Ph_2P), 131.7 (d, $J_{PC} = 117.8$ Hz; Ph_2P), 129.1 (Ph_2N), 125.3 (Ph_2N), 123.6 (Ph_2N). ⁵¹V NMR (105 MHz, C_6D_6 , 25 °C): $\delta = -6.1$ (br). ³¹P NMR (162 MHz, C₆D₆, 25 °C): $\delta = 19.9$ (br m). Anal. Calcd for C48H40N4OPV: C, 74.80; H, 5.23; N, 7.27. Found: C, 74.77; H, 5.14; N, 7.28.

Synthesis of (Ph₂N)₃VNP(OSiMe₃)(C₆F₅)₂ (3a). *Method 1.* In the glovebox, a solution of **2a** (82 mg, 0.086 mmol) in cold toluene (3 mL, -35 °C) was added dropwise to a solution of TMS₂-pyz (9.8 mg, 0.043 mmol) in cold toluene (2 mL, -35 °C), and the resulting black solution was kept at -35 °C for 0.5 h. The volatiles were removed *in vacuo* to give a dark brown solid, which was washed with cold pentane (1 mL) to give a dark brown solid (80 mg, 91% yield). Dark red crystals suitable for XRD studies were grown by slow vapor diffusion of pentane into a concentrated solution of **3a** in toluene at -35 °C over several days. Anal. Calcd for C₅₁H₃₉F₁₀OPSiV: C, 59.83; H, 3.84; N, 5.47. Found: C, 59.75; H, 3.66; N, 5.45.

Method 2. In the glovebox, a solution of 2a (47.5 mg, 0.05 mmol) in fluorobenzene (3 mL) was added dropwise to a solution of Cp*₂Co (16.5 mg, 0.05 mmol) in fluorobenzene (1 mL). The resulting dark brown solution was stirred using a magnetic stirbar at ambient temperature for 0.5 h. A separate solution of trimethylsilyl trifluoromethanesulfonate (11.1 mg, 0.05 mmol) in fluorobenzene (1 mL) was added dropwise to the reaction solution. The reaction solution turned dark red and was allowed to stir at ambient temperature for another 0.5 h. The volatiles were removed in vacuo, and the dark brown solid mixture was washed with cold pentane $(2 \times$ 2 mL) to afford a dark brown solid. The product was extracted into benzene $(2 \times 3 \text{ mL})$ and filtered over a pad of Celite, and the solvent was removed in vacuo. The resulting brown solid was washed with cold pentane (2 mL) to give a dark brown powder (44 mg, 0.043 mmol, 86% yield). Anal. Calcd for C51H39F10OPSiV: C, 59.83; H, 3.84; N, 5.47. Found: C, 59.60; H, 4.00; N, 5.44.

Synthesis of $(Ph_2N)_3VNP(OSiMe_3)Ph_2$ (3b). Method 1. A solution of 2b (81 mg, 0.1 mmol) in cold fluorobenzene (3 mL, -35 °C) was mixed with a solution of TMS_2 -pyz (11.3 mg, 0.05 mmol) in cold fluorobenzene (1 mL, -35 °C), and the mixed solution was kept at -35 °C for 0.5 h. The volatiles were removed *in vacuo* to give a dark brown, greasy solid mixture, which was washed with cold pentane (2 × 2 mL) to give a dark brown solid (45 mg, 0.053 mmol, 53% yield). Dark blue crystals suitable for XRD studies were grown from a concentrated solution of 3b in pentane at -35 °C over several days. Satisfactory elemental analysis could not be obtained from this method due to the contamination of pyrazine.

Method 2. In the glovebox, a solution of **2b** (81 mg, 0.1 mmol) in dichloromethane (3 mL) was added dropwise to a solution of $Cp*_2Co$ (33 mg, 0.1 mmol) in dichloromethane (1 mL). The resulting dark brown solution was allowed to stir using a magnetic

stirbar at ambient temperature for 0.5 h. A separate solution of trimethylsilyl trifluoromethanesulfonate (22.2 mg, 0.1 mmol) in dichloromethane (1 mL) was added dropwise to the reaction solution. The resulting dark red solution was again allowed to stir at ambient temperature for another 0.5 h. The volatiles were removed *in vacuo* to give a dark brown residue, which was washed with cold pentane (2 × 2 mL) to afford a dark brown solid. The product was extracted into ether (2 × 3 mL) and filtered over a pad of Celite, and then the solvent was removed *in vacuo*. The resulting brown solid was washed with cold pentane (2 mL) to give a fluffy brown powder (48 mg, 0.057 mmol, 57% yield). Anal. Calcd for $C_{51}H_{49}N_4$ OPSiV: C, 72.58; H, 5.85; N, 6.64. Found: C, 71.47; H, 5.56; N, 6.60. Attempts to obtain satisfactory elemental analysis consistently resulted in reduced carbon percentages likely due to incomplete combustion.⁶⁰

Synthesis of $[(Ph_2N)_3VNPO(C_6F_5)_2][CP*_2Co] (2a⁻). In the glovebox, a solution of Cp*_2Co (25.3 mg, 0.0768 mmol) in 2 mL of fluorobenzene was added dropwise to a solution of complex 2a (73 mg, 0.0768 mmol) in 3 mL of fluorobenzene. The resulting dark red solution stood at room temperature for 4 h, and the volume was reduced to about 0.5 mL$ *in vacuo*. Pentane (2 mL) was slowly added dropwise to the concentrated solution to afford an orange-red precipitate. The precipitate was filtered, washed with pentane (5 mL), and dried*in vacuo* $to afford an orange-red solid (92 mg, 0.0719 mmol, 94% yield). Dark brown needles suitable for XRD studies were grown by slow diffusion of pentane into a concentrated solution of <math>2a^-$ in fluorobenzene at room temperature. Anal. Calcd for $C_{68}H_{60}CoF_{10}N_4OPV$: C, 63.80; H, 4.72; N, 4.38. Found: C, 63.56; H, 4.99; N, 4.13.

Synthesis of $[(Ph_2N)_3VNPO(C_6H_5)_2][CP*_2Co] (2b⁻). In the glovebox, a solution of Cp*_2Co (24.7 mg, 0.075 mmol) in 2 mL of fluorobenzene was added dropwise to a solution of complex 2b (60.6 mg, 0.075 mmol) in 3 mL of fluorobenzene. The resulting dark red solution stood at room temperature for 3 h, and the volume was reduced to about 0.5 mL$ *in vacuo*. Pentane (2 mL) was slowly added dropwise to the concentrated reaction solution to afford an orange-red precipitate. The precipitate was filtered, washed with pentane (5 mL), and dried*in vacuo*to afford an orange-red solid (92 mg, 0.0719 mmol, 94% yield). Dark brown crystals suitable for XRD studies were grown by slow diffusion of pentane into a concentrated solution of 2b⁻ in THF at <math>-35 °C (77 mg, 0.070 mmol, 93% yield). Anal. Calcd for C₆₈H₇₀CoN₄OPV: C, 74.24; H, 6.41; N, 5.09. Found: C, 73.87; H, 6.65; N, 4.94.

Synthesis of $[(Ph_2N)_3VNP(OSiEt_3)(C_6F_5)_2][B(C_6F_5)_4]$ (2a-Si⁺). In the glovebox, neat Et₃SiH (1.5 mL, 9.39 mmol) was mixed with $[Ph_3C][B(C_6F_5)_4]$ (46 mg, 0.05 mmol). The reaction mixture was allowed to stir for 12 h, and a white precipitate crashed out of solution. The excess silane was decanted, and the white solid was washed with pentane $(2 \times 4 \text{ mL})$ and dried in vacuo. A separate solution of 2a (47 mg, 0.05 mmol) in benzene (3 mL) was added dropwise to the white solid, and the resulting dark green solution was stirred under ambient temperature for 0.5 h. The volatiles were removed in vacuo and washed with pentane $(2 \text{ mL} \times 2)$ to afford a green solid (84 mg, 0.048 mmol, 96% yield). Dark green needles suitable for XRD studies were grown by slow diffusion of pentane into a concentrated solution of $2a-Si^+$ in dichloromethane at room temperature. ¹H NMR (400 MHz, C₆D₅Br, 25 °C): δ = 7.14–6.92 (m, 30H; Ph_2 NH), 0.80 (t, ${}^{3}J_{HH} = 7.2$ Hz, 9H; SiCH₂CH₃), 0.58 (q, ${}^{3}J_{HH} = 7.2$ Hz, 6H; SiCH₂CH₃). 51 V NMR (105 MHz, C₆D₅Br, 25 °C): δ = 521.0 (d, J = 172.2 Hz). ³¹P NMR (162 MHz, C₆D₅Br, 25 °C): δ = -21 (br). ¹⁹F NMR (376 MHz, C₆D₅Br, 25 °C): δ = -129.5 $(br, 4F; o-P(C_6F_5)_2), -131.8 (br, 8F; o-B(C_6F_5)_4), -138.9 (br, 2F; p-138.9)$ $P(C_6F_5)_2)$, -155.3 (br, 4F; m- $P(C_6F_5)_2$), -162.5 (br, 4F; p- $B(C_6F_5)_4$), -166.3 (br, 8F; m- $B(C_6F_5)_4$). ¹³C NMR (100 MHz, C_6D_5Br , 25 °C): δ = 153.8, 129.1, 128.6, 121.4 (NPh₂), 6.1, 5.4 (SiEt₃). The signal-to-noise ratio was too low for properly identifying any C₆F₅ ¹³C resonance. Anal. Calcd for C₇₈H₄₅B F₃₀N₄OPSiV: C, 53.69; H, 2.60; N, 3.21. Found: C, 53.46; H, 2.71; N, 3.27.

Synthesis of $[(Ph_2N)_3VNP(OSiMe_3)(C_6H_5)_2][OTf]$ (2b-Si⁺). In the glovebox, a solution of 2b (142 mg, 0.176 mmol) in DCM (4 mL) was added dropwise to a solution of Me₃SiOTf (39 mg, 0.176 mmol)

in DCM (1 mL). The resulting dark brown solution was allowed to stir at ambient temperature for 10 min. The volatiles were removed in *vacuo*, and the brown residue was washed with pentane $(5 \text{ mL} \times 2)$ to afford a dark brown solid (165 mg, 0.166 mmol, 94% yield). Dark brown needles suitable for XRD studies were grown by slow diffusion of pentane into a concentrated solution of 2b-Si⁺ in dichloromethane at room temperature. ¹H NMR (400 MHz, THF- d_8 , 25 °C): δ = 7.71 (t, ${}^{3}J_{HH} = 7.8$ Hz, 2H; p-H of POPh₂), 7.51 (td, ${}^{3}J_{HH} = 7.8$ Hz, ${}^{4}J_{PH} =$ 3.6 Hz, 4H; *m*-H of POPh₂), 7.28 (dd, ${}^{3}J_{PH} = 14.4$ Hz, ${}^{3}J_{HH} = 7.2$ Hz, 4H; o-H of POPh₂), 7.17 (t, ${}^{3}J_{HH} = 7.8$ Hz, 12H; m-H of NPh₂), 7.11 (t, ${}^{3}J_{HH} = 7.8$ Hz, 6H; p-H of NPh₂), 6.70 (d, ${}^{3}J_{HH} = 7.8$ Hz, 12H; o-H of NPh₂), 0.15 (s, 9H; Si Me_3). ¹³C NMR (100 MHz, THF- d_8 , 25 °C): $\delta = 154.5 (Ph_2N), 135.1 (Ph_2P), 132.6 (d, J_{PC} = 12.7 Hz; Ph_2P),$ 130.2 (d, J_{PC} = 14.5 Hz; Ph_2P), 129.7 (Ph_2N), 127.5 (Ph_2N), 122.9 (Ph_2N) , 0.8 (SiMe_3). ⁵¹V NMR (105 MHz, THF- d_{8} , 25 °C): $\delta =$ 229.8 (br). ³¹P NMR (162 MHz, THF- d_8 , 25 °C): δ = 22 (br). Anal. Calcd for C₅₂H₄₉F₃N₄O₄PSSiV: C, 62.89; H, 4.97; N, 5.64. Found: C, 62.79; H, 5.01; N, 5.84.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b09063.

NMR, EPR, UV-vis, DFT, CV, competition results (PDF)

Crystallographic data of 2a (CIF) Crystallographic data of $2a^-$ (CIF) Crystallographic data of $2a-Si^+$ (CIF) Crystallographic data of 2b (CIF) Crystallographic data of $2b^-$ (CIF) Crystallographic data of $2b-Si^+$ (CIF) Crystallographic data of 3a (CIF) Crystallographic data of 3a (CIF)

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Notes

The authors declare no competing financial interest.

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