Agostic Isomers

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# Isolation of Two Agostic Isomers of an Organometallic Cation: Different Structures and Colors**

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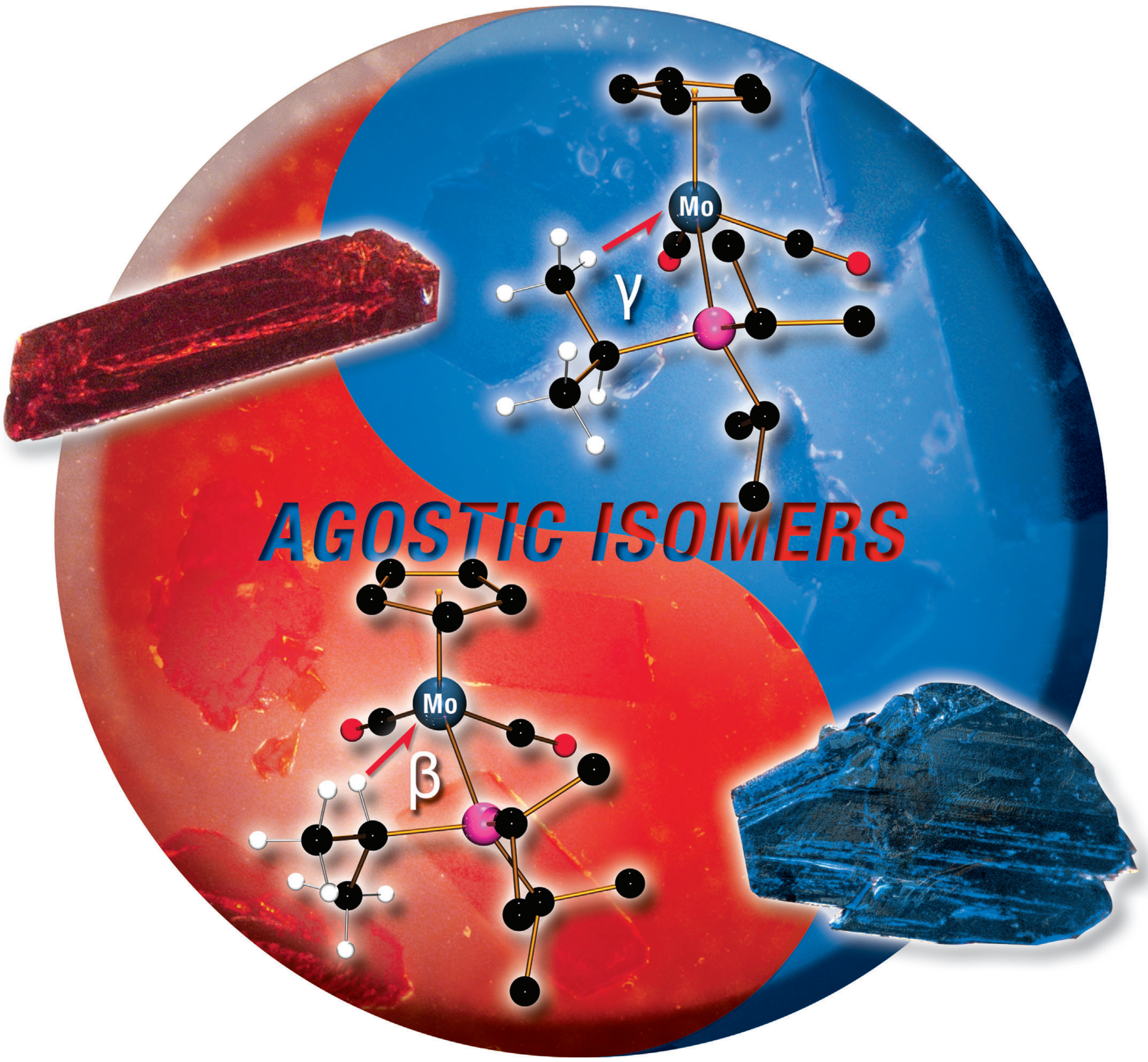
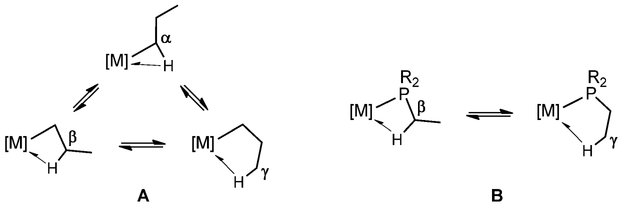


Agostic interactions are of paramount importance in organometallic chemistry and homogeneous catalysis.[1,2] These intramolecular 3-center/2-electron C–H···M interactions can stabilize electronically and coordinatively unsaturated complexes, and are involved in key steps of catalytic processes such as Ziegler–Natta polymerization.[3] Similar C–H···M interactions occur in metal–alkane σ-bond complexes[4]—very reactive intermediates in C–H bond activation[5] that are often modeled by agostic complexes.

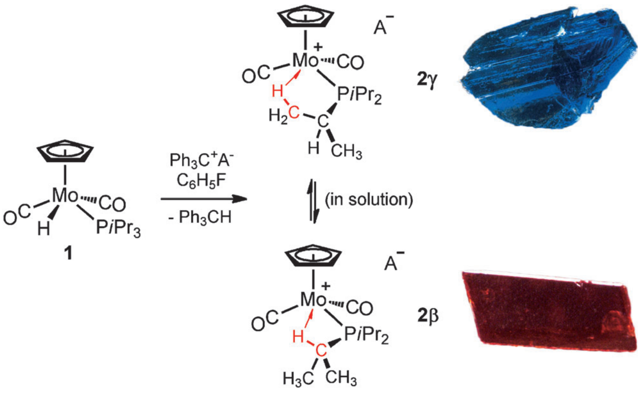
The energetic stabilization associated with an agostic interaction is modest to low ($\leq 15\,\mathrm{kcal\,mol^{-1}}$).[2,6] Consequently, when more than one C–H bond is available for coordination, energetically similar agostic isomers may form (Scheme 1;[7] we call these isomers "agostomers"). In solution, fast interconversion between agostomers often complicates efforts to compare their properties, and for only a handful of Nb and Ta alkyls have agostomers (α and β, cf. A in Scheme 1) been simultaneously characterized using low-temperature NMR spectroscopy.[8,9] Interconversion between agostomers would presumably be hampered in the solid state, but there are no previous reports of complexes for which agostomers have been isolated or characterized as solids. Herein we report crystal structures for β- and γ-agostomers (cf. B in Scheme 1) of a Mo phosphine complex, and we show that these isomers have distinct colors.



***Scheme 1.*** Agostic isomerism in metal alkyl (A) and phosphine (B) complexes. The complexes may be neutral or positively charged.

The chemistry reported herein results from our interest in isolating "16-electron" piano-stool complexes $[\mathrm{CpMo(CO)_2(PR_3)}]^+$ (Cp = η-$C_5H_5$), because of their intermediacy in ionic hydrogenation catalysis.[10] Earlier, we found for R = Ph that the phosphine can act as a four-electron donor by binding in an $\eta^3$ fashion (through P and a phenyl C–C π bond), which emphasizes the tendency of Mo to attain an 18-electron count.[11] We therefore expected the phosphine ligand in trialkylphosphine analogues to behave as a four-electron donor as well, by engaging in an agostic interaction.

Abstraction of hydride from the pale yellow, 18-electron complex **1**[12] (Scheme 2), using $Ph_3C^+\ B(C_6F_5)_4^-$ in fluorobenzene at room temperature,[13] proceeded smoothly to give a violet solution. NMR and IR spectroscopy confirmed the clean production of (diamagnetic) $[\mathrm{CpMo(CO)_2}(P\mathit{i}\mathrm{Pr_3})]^+[\mathrm{B(C_6F_5)_4}]^-$ (**2**). Conclusive support for the occurrence of agostic interactions was not obtained in solution,[12,14] but characterization in the solid state was definitive in this regard. Layering of the fluorobenzene solution of **2** with hexanes provided two types of crystals, growing in the same vessel. Blue/violet crystals formed at the solvent interface, while orange crystals formed near the bottom of the vessel. Under selective crystallization conditions,[12] both forms were also individually obtained as pure materials, each in 80–90% yield. Redissolution of either the blue or orange crystals in fluorobenzene gave violet solutions with identical spectroscopic signatures (and identical to freshly generated **2**), suggesting an isomeric relationship between the two forms, with a low barrier to isomerization in solution.



***Scheme 2.*** Synthesis of the agostomers **2γ** and **2β** ($A^- = B(C_6F_5)_4^-$). Photographs of representative crystals also shown.

Single-crystal X-ray diffraction analyses established the blue and orange forms of **2** to be agostomers **2γ** and **2β**, respectively (Figure 1 and Scheme 2).[15] Short Mo···$C_{ag}$ (ca. 2.7 Å, Table 1) and Mo···$H_{ag}$ (ca. 2.0 Å)[12,16] distances confirm that an agostic interaction occurs in both isomers.[1] The agostic H atoms approximately take the position of the hydride in **1**, thus retaining the four-legged piano-stool geometry around Mo. Severe distortions in the phosphines are also apparent: the Mo-P-C angle involving the agostic *i*Pr

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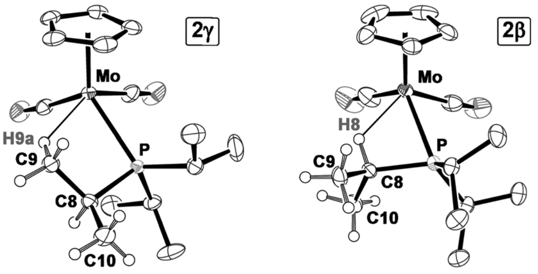


*Figure 1.* Structures of cationic fragments of **2γ** and **2β** · $C_6H_5F$, thermal ellipsoids set at 50% probability. Hydrogen atoms belonging to the agostic isopropyl group are also shown (drawn with arbitrary radius).

*Table 1:* Selected experimental [*theoretical*] bond angles [°] and lengths [Å].

| Parameter | **2γ** | **2β** | **1** |
|---|---|---|---|
| ∡(Mo-P-C8) | 95.3(1) | 74.57(4) | 114.6 |
| | [*94.0*] | [*74.7*] | [*114.4*][a] |
| *d*(Mo-P) | 2.4862(4) | 2.4070(3) | 2.464(1)/2.456(1)[b] |
| | [*2.535*] | [*2.448*] | [*2.483*] |
| *d*(Mo···$C_{ag}$) | 2.737(1) | 2.612(1) | – |
| | [*2.890*] | [*2.662*] | |
| *d*(Mo···$H_{ag}$)[c] | [*2.114*] | [*1.971*] | [*1.724*] (Mo-H) |
| *d*(C-$H_{ag}$)[c,d] | [*1.129*] | [*1.165*] | – |

[a] Average of three Mo-P-C angles. [b] Two independent molecules. [c] Only theoretical values shown; see Ref. [16]. [d] 1.093–1.099 Å for non-agostic $sp^3$ C–H.

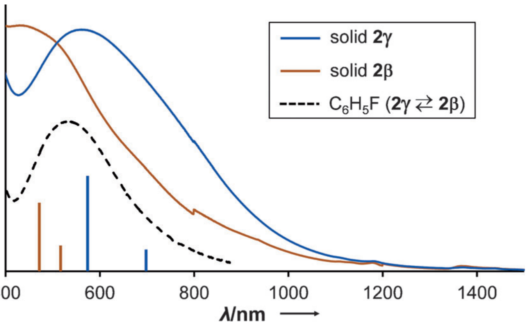


*Figure 2.* Vis/NIR spectra. Artifacts at 800 nm in the solid-state spectra are due to a combined detector and grating changeover. The sticks mark the transitions calculated by TD-DFT; their heights are proportional to the calculated oscillator strengths.

group is 95.3° for **2γ** and only 74.6° for **2β**, while the Mo-P-C angles involving the non-agostic *i*Pr groups fall in the range 117–123° (114–115° for **1**). Notably, the Mo–P distances in **2γ** and **2β** differ by 0.0791(5) Å, being longer and shorter, respectively, than the approximately 2.46 Å in **1**.

For the overwhelming majority of structurally characterized complexes with an agostic alkylphosphine, γ-agostic bonding is found, as in the related $[W(CO)_3(PR_3)_2]$ (R = *i*Pr, Cy)[17] and $[M(CO)_3(PCy_3)_2]^+$ $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$ (M = Mn,[18] Re[19]). We are aware of only one reported precedent for a β-agostic phosphine, as found for $[Rh(PiPr_3)_3]^+$ $B\text{-}(3,5\text{-}(CF_3)_2C_6H_3)_4^-$.[20]

Solid-state IR spectra show carbonyl stretching bands at similar frequencies for both agostomers ($\tilde{\nu}_{CO}$ = 2002 and 1929 $cm^{-1}$ for **2γ**; 2006 and 1942 $cm^{-1}$ for **2β**), with only one set of bands observable in fluorobenzene solution (2006 and 1936 $cm^{-1}$). However, we cannot assign with enough confidence[12] a band to $\nu_{CH}$ of a weakened, agostic C–H bond, in either the solid state or in solution. The electronic spectrum of **2** (Figure 2) in fluorobenzene displays a broad band with $\lambda_{max}$ = 535 nm ($\varepsilon_{max}$ = 370 $M^{-1}cm^{-1}$), while **1** does not significantly absorb in the visible.[12] Although the agostomers are not resolved in solution, the magnitude of the extinction coefficient does inform that a d–d transition is responsible for the absorption. We do observe significantly different spectra when the individually isolated agostomers are measured as solids (measured in total reflectance mode). The absorption maximum shifts from approximately 450 nm for **2β** to about 580 nm for **2γ**, which is in qualitative agreement with the orange versus blue appearance of these isomers.

The availability of isolated samples of both agostomers, obtained under the same conditions, suggests that they are nearly isoenergetic. However, because they are not resolved in solution by either NMR, IR, or Vis spectroscopy, we cannot quantify this experimentally. DFT calculations (see the Experimental Section for details) were employed to provide insights into the energetics involved and the origin of the color difference. Fully optimized geometries of the cationic fragments show good agreement with experiment (Figures 1 and 3, Table 1),[12] and the theoretical energy difference between **2γ** and **2β** is only 0.6 kcal $mol^{-1}$, corroborating the validity of the experimental results. The agostic C–H bonds are longer than the non-agostic ones: the elongation is approximately 0.03 Å for **2γ** and approximately 0.07 Å for **2β**. Additionally, the calculated $\tilde{\nu}_{CH}$ for the agostic C–H bond is 2560 $cm^{-1}$ for **2γ** and 2150 $cm^{-1}$ for **2β** compared to 2960–3050 $cm^{-1}$ for the non-agostic ones.[21] Weakening of the agostic C–H bond clearly occurs in both complexes, its extent being the highest in **2β**.

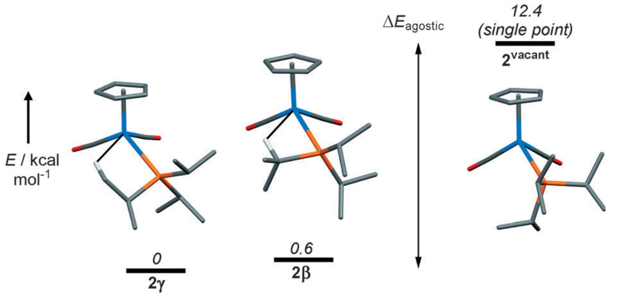


*Figure 3.* Theoretical energy diagram. Mo blue, P orange, C gray, O red, and H white (only agostic H shown; agostic interaction shown as a black line).

The molecular orbital (MO) energy diagram and population analysis[12] show that the compositions and energies of the occupied MOs of both agostomers are quite similar (Figure 4). The HOMO and HOMO−1 are both largely metal-based, harboring the four d-electrons. MOs involved with the agostic interactions (HOMO−12 for **2γ**; HOMO−13

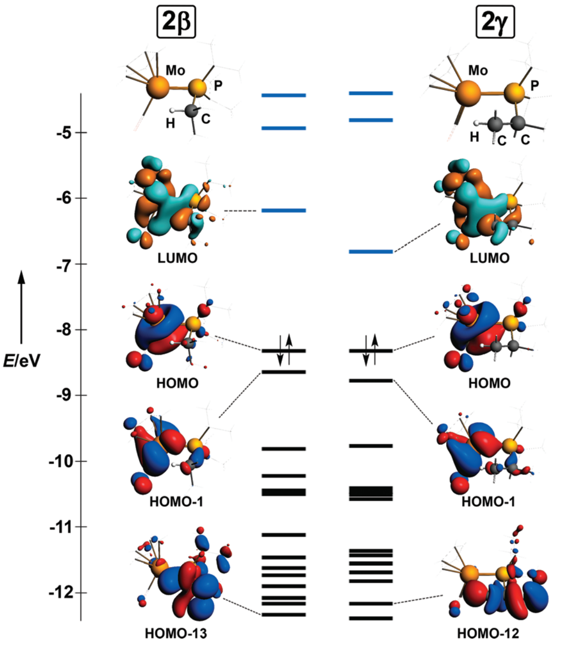


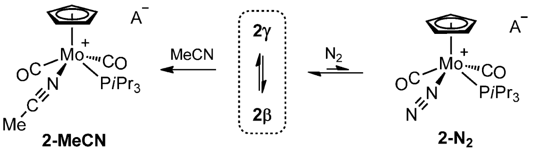
***Figure 4.*** Energy level diagram for **2γ** and **2β**, with selected MOs depicted (isosurface value is 0.03). The double occupancies are only illustrated for the HOMOs. Only the atoms of the agostic Mo-P-C(-C)-H moieties are drawn as balls.

for **2β**) are low in energy and of σ symmetry with respect to the Mo⋯H axis; the contribution from the C–H moiety is more significant (21 % for **2γ**; 25 % for **2β**) than that from Mo (less than 5 %).

An important difference between the agostomers is that the LUMO of **2β** is 0.64 eV higher in energy than that of **2γ**. This is probably caused by a higher contribution from the P atom to the LUMO in **2β** (10 %) than in **2γ** (4 %), owing to the significantly shorter Mo–P bond length in **2β** ($\Delta[d(\text{Mo-P})] = 0.087$ Å, Table 1). The resulting different HOMO–LUMO gaps in **2γ** and **2β** provide the explanation for the different colors observed, as further quantitatively investigated by time-dependent DFT. Two transitions in the visible region were found: HOMO→LUMO (**2γ**: 698 nm; **2β**: 517 nm) and HOMO-1→LUMO (**2γ**: 574 nm; **2β**: 472 nm), drawn as sticks in Figure 2. For both agostomers, the calculated position of the more intense HOMO-1→LUMO transition is in excellent agreement with the maxima obtained in the experimental spectra. Overall, the experimental and theoretical results suggest that the β-agostic bonding mode of the phosphine induces a stronger ligand field than the γ-agostic bonding mode does.

To estimate the total stabilization energy associated with the agostic interactions ($\Delta E_{\text{agostic}}$, Figure 3), hydride **1** was also optimized. Subsequent computational removal of the molybdenum-bound hydride then gives $\mathbf{2}^{\text{vacant}}$ (Figure 3) as a plausible model for a non-agostic structure, having a vacant coordination site at Mo. A single-point calculation on $\mathbf{2}^{\text{vacant}}$, which relaxes to **2γ** when fully optimized, revealed it to be approximately 12 kcal mol$^{-1}$ higher in energy than **2γ** and **2β**. This provides an upper bound for $\Delta E_{\text{agostic}}$; its magnitude is in agreement with estimates of strengths of no more than 15 kcal mol$^{-1}$ for agostic interactions.[2,6]

The weak agostic interactions are readily displaced (Scheme 3). Not surprisingly, **2** binds acetonitrile essentially irreversibly to form orange **2**-MeCN, but it also binds the poorer ligand dinitrogen to give **2**-N$_2$. The extent of N$_2$ coordination, under an atmosphere of N$_2$ in fluorobenzene solution,[22] is only 5–10 % at room temperature.[12] Upon cooling, the equilibrium shifts toward the N$_2$ adduct, and at −40 °C an approximately 2:1 ratio of **2**-N$_2$:**2** is detected by NMR spectroscopy. Warming to room temperature again establishes **2** as the major species, showing that formation of **2**-N$_2$ is reversible. $^{15}$N and $^{31}$P NMR spectra[23] collected for the isotopomer **2**-$^{15}$N$_2$ provide evidence for the end-on coordination of N$_2$. Additional reactivity studies of **2** toward small molecules are currently underway.



***Scheme 3.*** Displacement of the agostic interactions by MeCN and N$_2$.

In summary, we have described the first example of an organometallic complex for which two agostomers have been individually isolated and characterized. These results illustrate the versatility of agostic bonding, and have led to the unanticipated insight that agostomers may be differently colored. Clearly, one crystal structure will not always provide the complete "agostic picture".

## Experimental Section

Synthetic details and characterization data, as well as more complete computational details and atomic coordinates, are given in the Supporting Information. First principles calculations were performed using the DFT-D3(BJ) dispersion-corrected PBE exchange-correlation functional[24] implemented in the Amsterdam Density Functional (ADF 2013.01) program.[25] Scalar relativistic effects were taken into account by the ZORA formalism to the Dirac equation.[26] TZ2P basis sets with small cores were used for geometry optimization; all-electron basis sets were used for property calculations.[27] The time-dependent DFT approach was used to calculate the energies and oscillator strengths of excited states.[28]

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**Keywords:** agostic interactions · density functional calculations · isomers · molybdenum · structure elucidation

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[14] Owing to the highly fluxional behavior of agostic complexes, particularly with agostic P*i*Pr$_3$ or PCy$_3$ groups, NMR spectroscopy is often not definitive in characterizing the agostic interaction (see also Refs. [17–20]).

[15] CCDC 938519 (**1**), 938520 (**2γ**), and 938521 (**2β**·$C_6H_5F$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[21] Calculated $\tilde{\nu}_{\mathrm{CO}}$: 1978 and 1921 cm$^{-1}$ for **2γ**; 1980 and 1924 cm$^{-1}$ for **2β**, in good agreement with the experimental values (given in text).

[22] In the solid state at room temperature, neither **2γ** nor **2β** · $C_6H_5F$ binds $N_2$.

[23] $^{15}$N NMR (233 K, 51 MHz): $\delta = 12.9$ (br, 1N, $N_{\mathrm{distal}}$), −86.1 ppm (dd, $^{2}J_{\mathrm{PN}} = 6$ Hz, $^{1}J_{\mathrm{NN}} \approx 2.5$ Hz, 1N, $N_{\mathrm{proximal}}$). $^{31}$P{$^{1}$H} NMR (233 K, 202 MHz): $\delta = 53.1$ ppm (d, $^{2}J_{\mathrm{PN}} = 6$ Hz).

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