

³¹P NMR Chemical Shift Tensors: Windows into Ruthenium–Phosphinidene Complex Electronic Structures

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Abstract: A series of octamethylcalix[4]pyrrole ruthenium phosphinidene complexes ($\text{Na}_2[\mathbf{1}=\text{PR}]$) can be accessed by phosphinidene transfer from corresponding RPA ($\mathbf{A} = \text{C}_{14}\text{H}_{10}$, anthracene) compounds ($\text{R} = {}^t\text{Bu}$, ${}^i\text{Pr}$, OEt , NH_2 , NMe_2 , NEt_2 , N^iPr_2 , $\mathbf{NA}$, dimethylpiperidino). Isolation of the *tert*-butyl and dimethylamino derivatives allowed comparative studies of their ³¹P nuclear shielding tensors by magic angle-spinning (MAS) solid-state nuclear magnetic resonance (NMR) spectroscopy. Density functional theory (DFT) and natural chemical shielding (NCS) analyses reveal the relationship between the ³¹P chemical shift tensor and the local ruthenium–phosphorus electronic structure. The general trend observed in ³¹P isotropic chemical shifts for the ruthenium phosphinidene complexes was controlled by the degree of deshielding in the δ_{11} principal tensor component, which can be linked to the $\sigma_{\text{RuP}}/\pi_{\text{RuP}}^*$ energy gap. A “ δ_{22} – δ_{33} crossover” effect for $\text{R} = {}^t\text{Bu}$ was also observed, caused by different degrees of deshielding associated with polarizations of the σ_{PR} and σ_{PR}^* natural bond orbitals (NBOs).

Chemical shift tensors inform us about electronic structure through both their magnitudes and anisotropies, a fact readily seen through Ramsey’s classic perturbational treatment of nuclear shielding.¹ This link between solid-state nuclear magnetic resonance (SSNMR) spectroscopy and electronic structure has proven especially useful in investigations of transition metal–ligand multiple bonds,^{2–5} including our own studies of $\text{Pn}\equiv\text{Mo}$ ($\text{Pn} = {}^{15}\text{N}$, ³¹P)^{6,7} centers. Particularly sophisticated have been the studies from the Copéret lab using ¹³C magic-angle spinning (MAS) SSNMR spectroscopy as a central tool in the design and understanding of d^0 olefin metathesis catalysts.^{8–11} While there have been studies of ways ³¹P chemical shifts may inform electronic structure of transition metal complexes,^{12,13} the field remains relatively unexplored. Against this backdrop, we have sought to expand the understanding of metal–phosphinidene bonding through ³¹P MAS SSNMR studies.

Our recent work on phosphinidene transfer from dibenzo-7-phosphanorbornadiene RPA compounds ($\mathbf{A} = \text{C}_{14}\text{H}_{10}$ or anthracene) has positioned us well to explore [RP] unit delivery to a metal center. We now report facile phosphinidene transfer from a series of RPA compounds to a ruthenium(II) calix[4]pyrrole (“porphyrinogen”) complex $\text{Na}_2(\text{DME})_6[\mathbf{1}]$ (Fig. 1).^{14,15} The electronic structure of the resulting $\text{Ru}=\text{P}$ bond is strongly influenced by the substituent, an effect we have characterized through ³¹P MAS SSNMR spectroscopy. The chemical shift tensor is shown to be a direct experimental handle on the $\sigma_{\text{RuP}}/\pi_{\text{RuP}}^*$ energy gap and its orienta-

tion on the nature of the phosphorus–substituent σ_{PR} bond. Density functional theory (DFT) calculations and natural chemical shielding (NCS) analysis were central in uncovering these connections.

First investigated by Floriani et al. in 2001,^{14,15} the ruthenium(II) platform $[\mathbf{1}]^{2-}$ has been reported to support a variety of ruthenium–main group multiple bonds.^{14–16} Our studies began by interrogating the reaction between $\text{Na}_2(\text{DME})_6[\mathbf{1}]$ and ${}^t\text{BuPA}$ by NMR spectroscopy in THF-*d*₈. Although originally reported to have a ¹H NMR spectrum consistent with $[\mathbf{1}]^{2-}$ being a closed-shell complex,¹⁷ we have found THF-*d*₈ solutions of $\text{Na}_2(\text{DME})_6[\mathbf{1}]$ to exhibit a single paramagnetically shifted resonance at ¹H δ –28.3 (s, 8H) ppm, indicating that $[\mathbf{1}]^{2-}$ is likely of intermediate spin $S = 1$, as is typical for square-planar d^6 ruthenium(II) complexes.^{18–20} Monitoring the reaction between $\text{Na}_2(\text{DME})_6[\mathbf{1}]$ and ${}^t\text{BuPA}$ ²¹ over 24 h showed gradual loss of the ¹H δ –28.3 ppm resonance and growth of a new resonance in the ³¹P{¹H} NMR spectrum at δ 1047 ppm, characteristic of a bent phosphinidene.²² This change was accompanied by a dramatic color change from orange-red to purple.

The reaction was relatively slow even at elevated temperatures ($k = 8.7(4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, 80 °C, THF-*d*₈; see SI §S1.7), but could be accelerated by addition of excess ${}^t\text{BuPA}$. Full conversion to this new species was achieved by heating $\text{Na}_2(\text{DME})_6[\mathbf{1}]$ with 3 equiv ${}^t\text{BuPA}$ (80 °C, 18 h, THF), and the product crystallized from hot dioxane solution to yield $\text{Na}_2(\text{dioxane})_5[\mathbf{1}=\text{P}^t\text{Bu}]$ (33% isol.) as deep purple blocks. Characterization by an X-ray diffraction (XRD) study revealed a Ru–P–C angle of 121.57(3)° and a

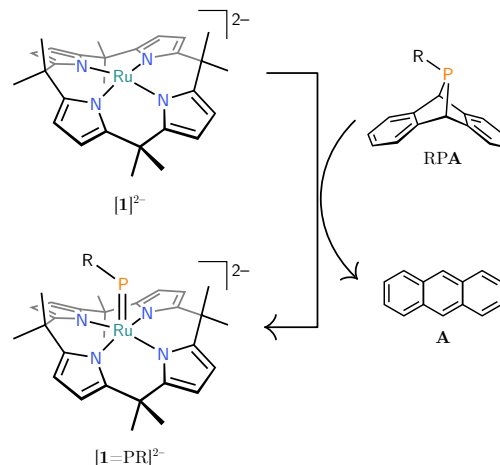


Figure 1. The ruthenium(II) complex $\text{Na}_2(\text{DME})_6[\mathbf{1}]$ accepts phosphinidene fragments from a series of RPA compounds.

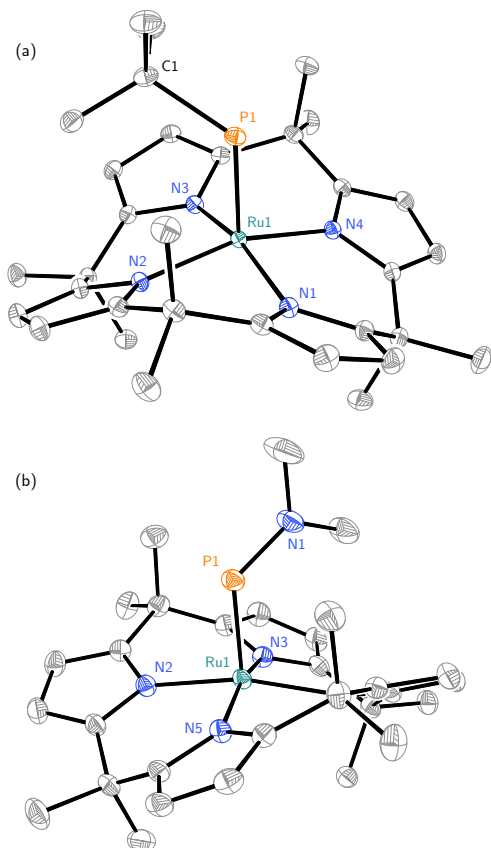


Figure 2. X-ray crystallographic structures (see SI §S2) of (a) $\text{Na}_2(\text{dioxane})_5[\mathbf{1}=\text{P}^t\text{Bu}]$ and (b) $\text{Na}_2(\text{dioxane})_4[\mathbf{1}=\text{PNMe}_2]$ with sodium, dioxane, and hydrogen centers omitted for clarity. (a) Selected interatomic distances (Å) and angles ($^\circ$): average Ru–N 2.0591(8), Ru–P 2.1156(3), P–C 1.8981(11); Ru–P–C 121.57(3). (b) Selected interatomic distances and angles: average Ru–N 2.053(3), Ru–P 2.0829(8), P–N 1.666(3); Ru–P–N 121.05(11).

Ru=P bond length of 2.1156(3) Å (Fig. 2a), shorter than any ruthenium–phosphinidene bond currently catalogued in the Cambridge Structural Database (CSD).²³ It is also slightly shorter than the sum of the two double-bond covalent radii (2.16 Å).²⁴

Similar studies combining Me_2NPA ²⁵ and $\text{Na}_2(\text{DME})_6[\mathbf{1}]$ provided analogous formation of dark purple $[\mathbf{1}=\text{PNMe}_2]^{2-}$ (18 h, 22 $^\circ\text{C}$) by ^{31}P NMR spectroscopy (δ 791 ppm). The product could be isolated as a $\text{Na}_2(\text{dioxane})_4[\mathbf{1}=\text{PNMe}_2]$ salt following recrystallization from hot dioxane (62% isol. yield). Structural parameters from an XRD study (Fig. 2b) are similar to those of $\text{Na}_2(\text{dioxane})_5[\mathbf{1}=\text{P}^t\text{Bu}]$ with a slightly shorter Ru=P bond length of 2.0829(8) Å and a Ru–P–N angle of 121.05(11) $^\circ$.

The ruthenium calix[4]pyrrole platform proved quite versatile in phosphinidene complex formation. Treatment with a medley of RPA compounds showed successful formation of the anticipated $[\mathbf{1}=\text{PR}]^{2-}$ species *in situ* by ^{31}P NMR spectroscopy, resonating over a wide (~ 300 ppm) range of chemical shifts (Fig. 3). The only exceptions were CIPA^{25,26} and HPA,²⁷ which yielded complicated mixtures of products, and $(\text{Me}_3\text{Si})_2\text{NPA}$,²¹ which we presume was too sterically encumbered to react. Additionally, extended heating of $\text{Na}_2(\text{DME})_6[\mathbf{1}]$ with $(^t\text{BuP})_3$ ²⁸ (48 h, 80 $^\circ\text{C}$) did not lead to observation of $[\mathbf{1}=\text{P}^t\text{Bu}]^{2-}$ in the ^{31}P NMR spectrum, indicating that RPA compounds are superior phosphinidene group transfer reagents for this transformation.

The wide range of chemical shifts demonstrated high sensitivity of the resonance to the electronic structure of the Ru=PR center. Collection of ^{31}P MAS SSNMR spectra of $\text{Na}_2(\text{dioxane})_5[\mathbf{1}=\text{P}^t\text{Bu}]$ and $\text{Na}_2(\text{dioxane})_4[\mathbf{1}=\text{PNMe}_2]$ added insight into the nature of the phosphorus chemical shift tensors (Fig. 4a–b). The large spans of the tensors ($\Omega = \delta_{11} - \delta_{33} = 1852$ and 1740, respectively) are characteristic of multiply bonded phosphorus centers,^{7,29} and their highly negative skews ($\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega = -0.82$ and -0.55 , respectively) indicate a single highly-deshielded direction as expected of a double bond.^{30–33} Interestingly, the larger solution ^{31}P chemical shift δ_{sol} of $\text{Na}_2(\text{dioxane})_5[\mathbf{1}=\text{P}^t\text{Bu}]$ than that of $\text{Na}_2(\text{dioxane})_4[\mathbf{1}=\text{PNMe}_2]$ was reflected in all three directions of the chemical shift tensors obtained by simulation of the ^{31}P MAS SSNMR spectra.

Interpretation of these tensors was assisted by density functional theory (DFT) and the natural chemical shielding (NCS)³⁴ analytical subroutine of the natural bond orbital (NBO) program (see SI §S3).³⁵ Nuclear shielding calculations yielded the tensors shown in Fig. 4c–e upon varying the substituent from *tert*-butyl to dimethylamino and methoxy. The axis of strongest deshielding (δ_{11}) uniformly resides in the Ru–P–R plane and is approximately perpendicular to the Ru–P bond, a consequence of the strong paramagnetic deshielding induced by nucleus–orbit coupling between the $\sigma_{\text{Ru}=\text{P}}$ and $\pi_{\text{Ru}=\text{P}}^*$ NBOs. This can be visualized as a 90 $^\circ$ rotation of the σ bond along the δ_{11} principal axis providing significant orbital overlap with the π^* orbital. Such behavior mirrors that of ^{13}C NMR chemical shifts for d^0 olefin metathesis catalysts.⁸ The δ_{11} contributions from the σ/π^* interaction were quantified by NCS analysis to be 1987 ppm (^tBu), 1545 ppm (NMe_2), and 1740 ppm (OMe), giving a trend that matches the solution δ_{iso} values.

Ramsey’s theory of nuclear shielding can be used for a qualitative explanation of this phenomenon. Ramsey’s perturbative treatment relates paramagnetic deshielding to the sum-over-states¹

$$\delta_{uv}^{\text{para}} \propto \sum_{k>0} \frac{\text{Re} [\langle 0 | L_u | k \rangle \langle k | L_{\alpha, v} r_{\alpha}^{-3} | 0 \rangle]}{E_0 - E_k}. \quad (1)$$

Here, α is the nucleus of interest (the phosphorus-31 center), u/v index the Cartesian directions (xyz), $|0\rangle$ is the ground state, $|k\rangle$ indexes all excited states, E_X is the energy of state X , Re indicates the real part of a complex number, L_u is

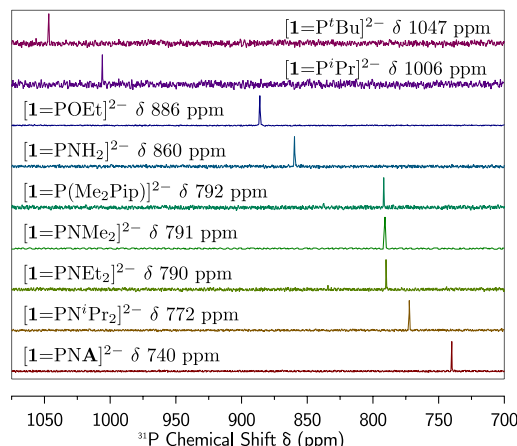


Figure 3. ^{31}P NMR spectra of several phosphinidene complexes $[\mathbf{1}=\text{PR}]^{2-}$ (Me₂Pip = *cis*-2,6-dimethylpiperidino).

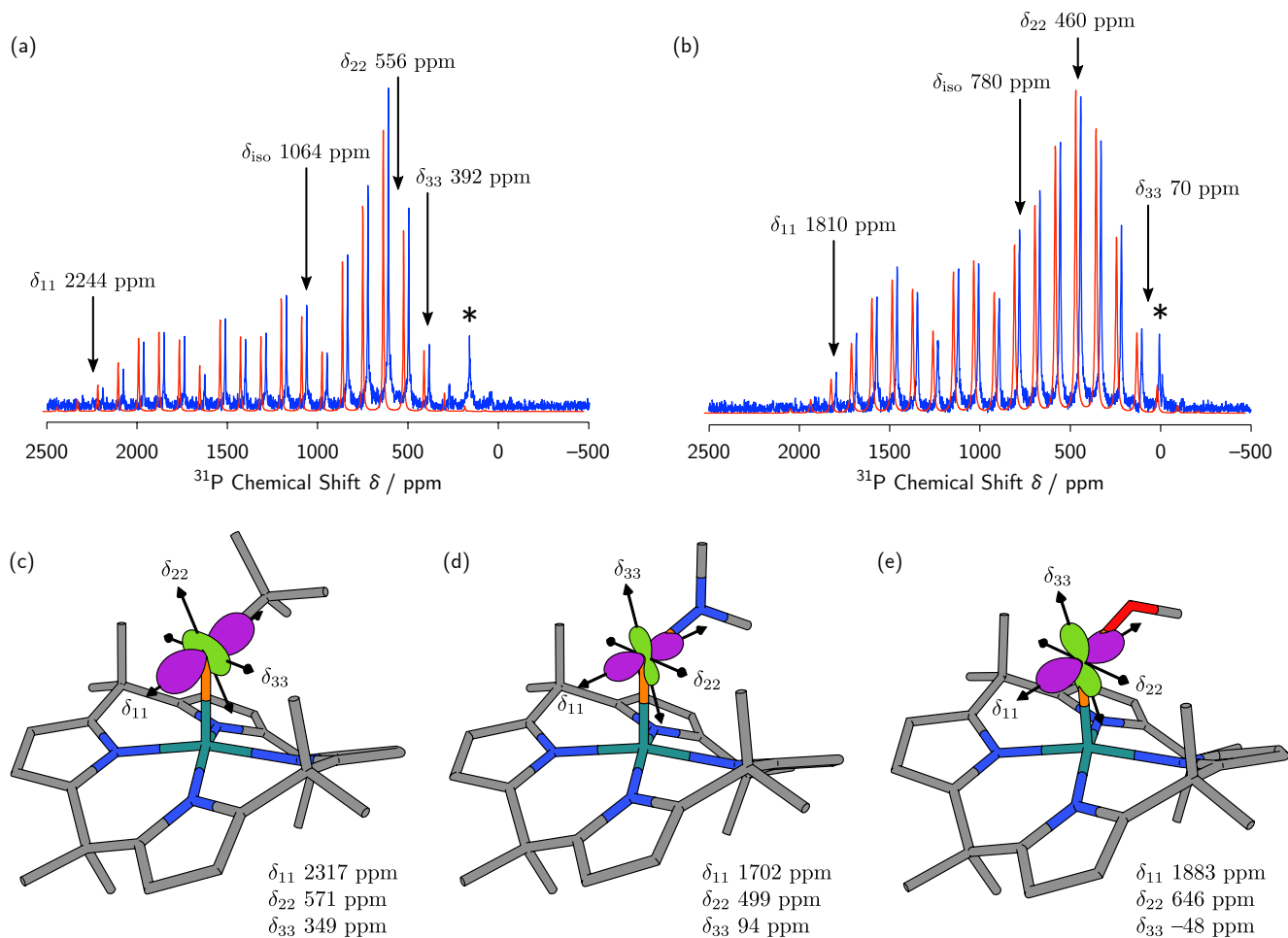


Figure 4. (a, b) Experimental (blue) and simulated (red) ^{31}P MAS SSNMR (16.4 T, 85% aq. H_3PO_4 δ 0 ppm) spectra of (a) $\text{Na}_2(\text{dioxane})_5[\mathbf{1}=\text{P}^t\text{Bu}]$ and (b) $\text{Na}_2(\text{dioxane})_5[\mathbf{1}=\text{PNMe}_2]$. Simulations are deliberately offset downfield for easy visual inspection. Minor impurities are marked with an asterisk (*). (c, d, e) Plots of the anisotropic components of the calculated chemical shift tensors for (c) $\text{Na}_2(\text{OMe}_2)_5[\mathbf{1}=\text{P}^t\text{Bu}]$, (d) $\text{Na}_2(\text{OMe}_2)_5[\mathbf{1}=\text{PNMe}_2]$, and (e) $\text{Na}_2(\text{OMe}_2)_5[\mathbf{1}=\text{POMe}]$ as $\vec{r}(\delta - \frac{1}{3}\text{Tr } \delta)\vec{r}$ for $\vec{r} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. Principal axes are illustrated with arrows; purple lobes indicate downfield shift relative to δ_{iso} and green indicate upfield. Sodium atoms, hydrogen atoms, and molecules of solvation are omitted for clarity. Note the directions of δ_{22}/δ_{33} are inverted in (c) versus (d, e).

the u component of the angular momentum operator, r_α is the distance from nucleus α , and $L_{\alpha,v}$ is the v component of the angular momentum operator relative to nucleus α . The low-lying $\pi_{\text{Ru}=\text{P}}^*$ orbital provides a small $E_0 - E_k$ denominator leading to strong deshielding.³⁶ The δ_{11} shift is thus controlled by the energy of the π^* orbital, which is in turn controlled by the nature of the phosphinidene substituent. Stronger donors should destabilize the $\pi_{\text{Ru}=\text{P}}^*$ orbital, so the δ_{11} shift is a direct experimental readout of π donicity. Indeed, the *tert*-butyl derivative has the most downfield shift of the three, the strong π -donor dimethylamino derivative the most upfield, and the weaker π -donor methoxy derivative is intermediate.

A second interesting difference between the tensors is readily observed in Fig. 4c–e, which shows δ_{22} and δ_{33} are reversed in the *tert*-butyl derivative.^{37,38} NCS calculations clearly reveal that the orientation of the tensor is dictated by a balance of influences from the σ_{RuP} and σ_{PR} NBOs (SI Table S2). The σ_{PR} NBO contributes to deshielding along the Ru–P bond through coupling to the π_{RuP}^* antibonding NBO, and the σ_{RuP} NBO contributes perpendicular to the Ru–P–R plane through coupling to the σ_{RuP}^* antibond. Both influences seem to reflect the polarization of the phosphorus–substituent interaction (Table 1). As the electronegativity

Table 1. Percent Phosphorus Character of NBOs

NBO	Substituent		
	^tBu	NMe_2	OMe
σ_{RuP}	56%	47%	51%
σ_{RuP}^*	44%	53%	49%
π_{RuP}	67%	72%	68%
π_{RuP}^*	33%	28%	32%
σ_{PR}	37%	24%	19%
σ_{PR}^*	63%	76%	81%

of the substituent increases, the phosphorus character of the σ_{PR} NBO decreases and that of σ_{PR}^* correspondingly increases. The ^{31}P deshielding influence of the NBO parallels its phosphorus character, meaning the percent phosphorus character should correlate with the NBO influence. Indeed, this is seen for both the σ_{PR} contribution along the Ru–P bond (^tBu 1166 ppm, σ_{PR} 37% P; NMe_2 497 ppm, σ_{PR} 24% P; OMe 405 ppm, σ_{PR} 19% P) and the σ_{RuP} contribution perpendicular to the Ru–P–R plane (^tBu 434 ppm, σ_{RuP}^* 63% P; NMe_2 559 ppm, σ_{RuP}^* 76% P; OMe 693 ppm, σ_{RuP}^* 81% P). In this way, the orientation of the δ_{22} and δ_{33} axes is an

experimental reflection of the polarization of the P–R bond.

Influences on the ^{31}P chemical shift tensor are undoubtedly multifaceted; however, the wide array of derivatives available from $\text{Na}_2(\text{DME})_6[1]$ has allowed us to map out several of the strongest factors. In this way, ^{31}P MAS SS-NMR spectroscopy makes experimentally accessible the local electronic structure of the $\text{Ru}=\text{PR}$ moiety. Leverage of analogous information in d^0 olefin metathesis catalysts has been a major influence in the design of early transition metal alkylidene catalysts,^{8–11} hinting that ^{31}P MAS SSNMR spectroscopy may be a boon to similar advances in phosphinidene chemistry. Such analogies with metathesis and cyclopropanation catalysts were an early motive in the preparation of the $[\text{1}=\text{PR}]^{2-}$ complexes, as we have recently begun to investigate catalytic “phosphiranation” reactions.³⁹ We plan to use SSNMR to guide the search for further phosphinidene transfer catalysts.

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Notes. The authors declare no competing financial interest.

Supporting Information Available

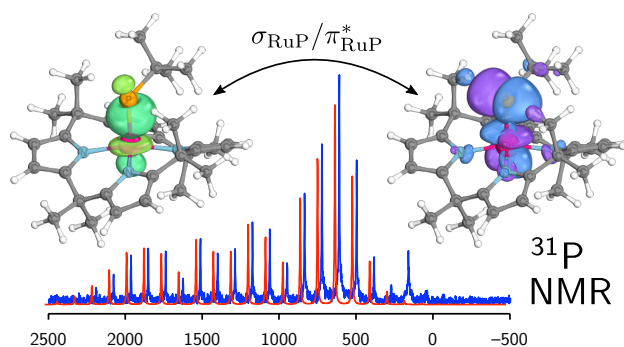
Full synthetic and computational details, including preparative procedures, spectroscopic data, and crystallographic data for characterization of compounds, are in the supplementary materials.

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TOC graphic:



TOC Synopsis Anthracene-based phosphinidene transfer reagents react with a ruthenium calix[4]pyrrole complex to make a series of ruthenium(IV) phosphinidene complexes. Electronic structures of the phosphinidene complexes were interrogated using ^{31}P solid-state nuclear magnetic spectroscopy, which in conjunction with quantum chemical methods is a sensitive probe of metal–phosphorus multiple bonds.