ORGANOMETALLICS

E-Selective Synthesis and Coordination Chemistry of Pyridine-Phosphaalkenes: Five Ligands Produce Four Distinct Types of Ru(II) Complexes

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S Supporting Information

ABSTRACT: Pyridine-phosphaalkene (PN) ligands 2a-e were prepared in an E-selective fashion using phospha-Wittig methodology. Treatment of these five ligands, varying only in their 6-substituent with $RuCl_2(PPh_3)_3$, produced four distinct types of coordination complexes: pyridine-phosphaalkenederived 3b,d, cyclized 4e, and six-coordinate 5a and 6c. Prolonged heating of 3b,d in THF resulted in C-H activation of the Mes* group and cyclization to give 4b,d featuring a bidentate pyridine-phospholane ligand bound to the metal center. Complex 5a, also possessing a newly formed phospholane ring, contained a different spatial arrangement of donors to Ru(II) with an agostic Ru-H-C interaction serving as the sixth donor to the transition metal center.



Ligands 2b,d,e and Ru(II) complexes 3b, 4b,e and 5a were all characterized by X-ray crystallography. Six-coordinate 6c featured a structure similar to 4b,d,e, but with the CF₃ substituent acting as a weakly bound sixth ligand to the Ru(II) center, as observed by ³¹P{¹H} and ¹⁹F NMR spectroscopy. The calculated structure of **6c** established that the closest Ru- - -F contact was at 2.978 Å.

INTRODUCTION

Phosphaalkene-based ligands featuring low-lying π^* orbitals and large P substituents have emerged as a successful class of pincers for stabilizing low-coordinate and electron-rich metal centers,¹ some in unusual geometries including trigonalmonopyramidal A^2 and T-shaped B (Scheme 1, top).³

The versatility of the P=C unit is remarkable, functioning as a strong π acceptor,⁴ as an electron reservoir,⁵ and as a site for both external nucleophilic attack⁶ and intramolecular C-H activation and cyclization.7 These cyclizations generally afford phospholanes,⁸ and in the case of phosphaalkene-derived PCP pincer C_1^{9} a catalytic amount of $[Pt(PCy_3)_2]$ promotes the formation of bis(phospholane) \mathbf{D} .⁷ Interestingly, the PNP analogue E¹⁰ was far more resistant to double cyclization, requiring forcing conditions (80 °C, 11 days) to produce F (Scheme 1, bottom).¹¹ However, a single cyclization of bis(phosphaalkene) E occurs readily at metal centers,¹² affording square-planar G^{12} and octahedral H^{11} with a modified PNP pincer featuring phospholane, pyridine, and phosphaalkene donors. Akin to the metal complexes reported by Milstein that are supported by neutral, tridentate pincers bearing a central N-heterocyclic donor,¹³ treatment of G and H with base results in deprotonation of the benyzlic arm and

Scheme 1. Unusual Metal Geometries Supported by Phosphaalkene-Based PNP Pincers (Top) and Intramolecular C-H Activation and Cyclization of Phosphaalkenes Catalyzed by $[Pt(PCy_3)_2]$ (Bottom)



subsequent dearomatization of the pyridine functionality and isolation of I and J (Scheme 2).^{11,}

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Scheme 2. Synthesis of Dearomatized Pincer Complexes I and J



Dearomatized I is capable of facilitating the N–H activation of ammonia and other primary amines,^{12,14} while a related analogue of J promotes catalytic N-alkylation of amines with alcohols.¹⁵ In both these cases^{12,14,15} and in the majority of the Milstein-type systems,¹⁶ the third donor of the pincer acts as a spectator, leading us to consider if simpler and largely unexplored bidentate pyridine-phosphaalkene ligands (1) in combination with a third exogenous ligand would behave in a similar fashion. Although it was synthesized concurrently with E in 1992,¹⁰ no reports of cyclization of the Mes* group of parent pyridine-phosphaalkene (PN) **1a** (R' = H) across its P==C double bond have been described (Chart 1).¹⁷ In fact,

Chart 1. Previously Reported PNP Pincer E and PN Ligands 1a-c and Targeted 6-Substituted PN Ligands of Type 2



the coordination chemistry of 1a in general has been scarcely reported with only a few examples, including a poorly characterized Cu(I) species.¹⁰ Other C-functionalized analogues such as 1b (R' = Ph) can support square-planar Pt(II) and Pd(II) complexes, with the latter acting as a catalyst for the Overman-Claisen rearrangement.¹⁸ A recent report by Ozawa also highlighted that 1b could stabilize unusual Ni(I) species and highly distorted square-planar Ni(II) complexes and promote unusual $P-C_{Ar}$ ($C_{Ar} = Mes^*$) bond cleavage events,¹⁹ all of which were hypothesized to originate from the presence of low-lying π^* orbitals on the P=C unit. Here, we report that the P=C double bond of pyridine-phosphaalkenes of type 2, featuring sterically and electronically diverse substituents at the 6-position of the pyridine ring, is susceptible to C-H activation of the Mes* group and cyclization to a phospholane on coordination to Ru(II). Specifically, after preparing five PN ligands (2a-e) in an *E*-selective fashion via a phospha-Wittig methodology,²⁰ we discovered that, remarkably, on exposure to RuCl₂(PPh₃)₃ four distinct types of coordination complexes (3-6) are produced, three of which feature newly formed phospholane rings.

RESULTS AND DISCUSSION

Synthesis of Ligands of Type 2. Treatment of 6-substituted pyridine-2-carboxyaldehyde derivatives²¹ with the phospha-Wittig²⁰ reagent Mes*P=PMe₃ resulted in the

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Scheme 3. E-Selective Synthesis of 2a-e



Their formation was identified by the diagnostic downfield shift of the P==C unit observed by ³¹P{¹H} NMR spectroscopy, with the ¹H NMR spectra confirming that the phosphaalkenes were present in the *E* conformation ($J_{PH} = 25 \text{ Hz}$).²¹ Furthermore, the new PN ligands were characterized by ¹³C{¹H} NMR spectroscopy, mass spectrometry, and elemental analysis. X-ray crystallography unequivocally established the structures of **2b,d,e** (Figures 1–3).



Figure 1. X-ray crystal structure of 2b. Selected bond lengths (Å) and angles (deg) are shown in Table 1.



Figure 2. X-ray crystal structure of 2d. Selected bond lengths (Å) and angles (deg) are shown in Table 1.

Solid-State Structures of 2. The solid-state structures of ligands **2a**,²² and **2b**,**d**,**e** all feature P=C bond lengths (1.66–1.69 Å) within the normal range of other bidentate and pincer-type phosphaalkene-based ligands.^{4a} Although the P-Mes* bond lengths show little variation (1.85–1.87 Å), they are marginally longer than most other phosphaalkene-aryl single bonds,^{23,24} while their C=P-C bond angles are approximately 98°, consistent with a lack of hybridization at P.^{4a} Other bond



Figure 3. X-ray crystal structure of 2e. Selected bond lengths (Å) and angles (deg) are shown in Table 1.

lengths and angles of interest are tallied in Table 1. In addition, the X-ray structures of **2b,d,e** (Figures 1–3) revealed that the *E* configuration of the P=C bond in combination with the two-carbon linker between the pyridine N atom and the P center create a promising binding pocket for a metal center.

Ru(II) Complexes. Treatment of 2a-e with RuCl₂(PPh₃)₃ in benzene resulted in the formation of four distinct type of coordination complexes, pyridine-phosphaalkene-derived 3, cyclized 4, and six-coordinate 5 and 6, all in reasonable yields (Scheme 4). The existence of the four different types of coordination complexes (3-6) was readily identified by NMR spectroscopy. Red solutions of 3b,d showed that the phosphaalkene functionality remained intact, maintaining a significantly downfield shifted ³¹P NMR signal (δ >290 ppm), which was coupled to the bound PPh₃ unit (3b, δ 36.0; 3d, δ 34.0 ppm, J_{PP} = 36 Hz). On the other hand, a green solution of cyclized derivative 4e featured an upfield-shifted ³¹P NMR resonance (δ 90.3 ppm) reminiscent of other Ru-bound phospholanes,²⁵ also displaying coupling to PPh₃ (δ 48.6 ppm, $J_{\rm PP} = 36$ Hz). A comparison of the ${}^{31}P{}^{1}H{}$ NMR spectra of 3b and 4e is shown in Figure 4. Moreover, the formation of the phospholane ring in 4e generated a chiral P center, making the CH₂ protons of the new five-membered ring, the benzylic-type protons linking the pyridine to the phospholane unit, and the methyl groups on the phospholane diastereotopic, resulting in a series of ¹H NMR signals with complex splitting patterns integrating in a 1:1:1:1:3:3 ratio. Interestingly, prolonged heating of uncyclized 3b,d in THF (>80 °C) resulted in smooth conversion to cyclized derivatives 4b,d with the ³¹P{¹H} (phospholane P atoms: 4b, δ 91.1 ppm; 4d, δ 89.9 ppm) and ¹H NMR spectra closely resembling that of 4e. Both phosphaalkene-based 3b,d and phospholane-derived 4b,d,e were further characterized by ${}^{13}C{}^{1}H$ NMR spectroscopy, mass spectrometry, and elemental analysis. Ultimately, the

Scheme 4. Synthesis of Ru(II) Complexes 3-6



solid-state structures of **3b** and **4b**, **e** were determined by X-ray crystallography (Figures 5–7).

Like 4b,d,e, the ${}^{31}P{}^{1}H{}$ NMR spectrum of 5a quickly established that the P=C functionality was no longer present. However, the two ³¹P NMR signals detected were much different from those of cyclized 4b,d,e, resonating at 64.0 and 66.8 ppm (J_{PP} = 39 Hz), suggesting that a different type of coordination complex was generated. Diastereotopic benzylic type protons were observed by ¹H NMR spectroscopy, confirming that C-H activation and cyclization had occurred, but one of the newly formed diastereotopic phospholane protons was drastically shifted upfield to 0.73 ppm. We hypothesized that the sterically diminutive C-H group of ligand 2a created a coordination environment in which the phospholane, pyridine, and PPh₃ donors could all be mutually cis to one another. This would orient the strongly π donating chlorides trans to both the phospholane and pyridine, providing a rationale for the high-field PCH₂ signal and the unusual N-Ar resonance observed at 6.43 ppm. Recrystallization of 5a from a concentrated THF solution exposed to pentane vapors afforded X-ray-quality crystals partially validating our hypothesis, but also establishing that 5a was six-coordinate via an agostic interaction from one of the two remaining t-Bu groups (Figure 8). Evidence of this Ru-H-C interaction in solution, specifically an unusually upfield shifted t-Bu proton signal, was not observed.

Ru(II) complexes featuring agostic interactions are common,²⁶ normally resulting in five- or six-membered chelates. For example, Gusev synthesized Ru(II) dichloride K with one of the P-alkyl groups of the POP pincer utilizing an agostic interaction (Ru- - H = 2.23 Å) to establish a five-membered ring,²⁷ while Shaw showed using azine phosphines in L that agostic interactions could be forced by placing the H atom in close proximity to the Ru center, affording six-membered rings (Figure 9, left).²⁸ Furthermore, Caulton²⁹ and Baratta (Ru- -

Table	1. Select	ted Bond	Lengths	(Å)	and	Angles	(deg) of	' Ligand	ls 2a ²	² and	2b,d,e	e ^a
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	$2a (R = H)^{22}$	2b (R = Me)	2d (R = OMe)	$2\mathbf{e} \ (\mathbf{R} = \mathbf{Ar} \cdot \mathbf{m} \cdot \mathbf{NO}_2)$
P=C	1.663(3)	1.674(2)	1.694(4)	1.669(3)
P-Mes*	1.847(3)	1.8607(19)	1.873(3)	1.851(3)
C-P=C	99.15(14)	98.35(9)	98.27(16)	98.17(13)
$N-C_{Ar}$	1.39(5)	1.351(3)	1.368(4)	1.348(3)
$N-C_{Ar}$	1.31(5)	1.337(2)	1.319(5)	1.334(3)
C-N=C	119(4)	118.26(18)	116.4(3)	118.4(2)
backbone C–C	1.470(4)	1.466(3)	1.444(5)	1.461(4)
C _{Ar} -R	0.950	1.504(3)	1.364(4)	1.494(4)

^aR factor (%): 2a (6.0);²² 2b (4.73); 2d (6.71); 2e (4.50).



Figure 4. ${}^{31}P{}^{1}H$ NMR spectra (202 MHz, CDCl₃) of 3b (left) and 4e (right).



Figure 5. X-ray crystal structure of 3b with the solvent molecule omitted for clarity. Selected bond lengths (Å) and angles (deg) are shown in Table 2.



Figure 6. X-ray crystal structure of 4b. Selected bond lengths (Å) and angles (deg) are shown in Table 2.

H = 2.185 and 2.198 Å)³⁰ demonstrated that double agostic interactions³¹ could be formed by generating coordinatively unsaturated Ru(II) centers via halide abstraction or through the use of bulky phosphine ligands. Here, a seven-membered chelate to the Ru center was formed via a Ru–H contact of 2.069 Å with a Ru–H–C bond angle of 126.67° (Figure 9,



Figure 7. X-ray crystal structure of 4e. Selected bond lengths (Å) and angles (deg) are shown in Table 2.



Figure 8. X-ray crystal structure of 5a. Selected bond lengths (Å) and angles (deg) are shown in Table 2.

right), both indicative of a bona fide agostic interaction $(d(M-H) = 1.8-2.3 \text{ Å}; M-H-C \approx 90-140^{\circ}).^{32}$ A second-order perturbation theory analysis of the Fock matrix using NBO indicated that the three-center, two-electron Ru-H-C bond provided 11 kcal/mol of stabilization energy to **5a**. In all cases, these agostic interactions serve to coordinatively saturate the Ru(II) center, affording 18-electron complexes.



Figure 9. Structures of K and L (left) with trimmed X-ray crystal structure of 5a showing the agostic interaction.

The other six-coordinate complex formed was **6c**, which is supported by CF₃-substituted ligand **2c**. Its NMR spectra closely mirrored **4b**,**d**,**e** with the exception that the ³¹P NMR signal of the phospholane (δ 85.8 ppm) was not a doublet but rather an overlapping doublet of quartets with additional coupling to fluorine (J_{PP} = 40 Hz, J_{PF} = 20 Hz; Figure 10). This



Figure 10. Enlarged ${}^{31}P{}^{1}H$ NMR spectrum (202 MHz, CDCl₃) of 6c highlighting the overlapping doublet of quartets for the phospholane donor.

is due to interaction of the CF₃ unit with the 16-electron Ru center.³³ Shaw reported an analogous interaction in **M** with strikingly similar NMR spectra (structure shown in inset of Figure 10);³⁴ like **6c**, only the functionalized phosphine donor trans to F shows J_{PF} coupling (68 Hz). Interestingly, all three F atoms in **6c** and both F atoms in **M** are interacting with the Ru center on the NMR time scale, indicating that rotation about their sp²-sp³/sp² C-C bonds (shown in magenta in the inset of Figure 10) is facile and the Ru–F interaction is weak.³⁴

In fact, by analogy to agostic (three-center, two-electron) versus anagostic (electrostatic) M-H-C bonds,³² the reduced coupling constant in **6c** may reflect an anagostic/electrostatic $Ru-CF_3$ interaction, while the Ru-F "bond" in **M** is significantly more agostic. Distance is often the determining factor distinguishing agostic M-H-C interactions from anagostic interactions, with agostic interactions falling between 1.8 and 2.3 Å and anagostic interactions ranging from 2.3 to 2.9 Å.³² Plenio has argued that for second- and third-row

transition metals that a "true" M–F interaction must place the metal and fluorine atom within 3.0 Å of each other;³⁵ however, Togni has shown via a combination of NMR spectroscopy and X-ray crystallography that these interactions can persist above 3.0 Å.³⁶ Unfortunately, neither **6c** or **M** has been crystallographically characterized; thus, making an assignment of agostic versus anagostic based on distance is premature. However, the structure of **6c** was calculated at the B3LYP-D3/LACV3P** level, establishing the closest Ru- - F contact at 2.978 Å (Figure 11). Although right on the 3 Å threshold,



Figure 11. Computed structure of **6c** with comparison to **4b** (inset). The labels on the chloride donors were omitted, and the *t*-Bu groups were trimmed for clarity.

NBO calculations revealed that no bonding interaction could be found between the Ru center and the C–F bond or the F lone pairs, begging the question: is the "interaction" merely a geometric constraint? Reexamination of the structure of **4b** featuring the sterically similar methyl group suggests that this may be the case, as the nearest Ru- - -H contact sits at 2.917 Å (see inset, Figure 11). Furthermore, the broadened ³¹P NMR signal of the phospholane in **4b** is likely due to a related dynamic process involving interaction of all three H atoms of the Me unit with the Ru center on the NMR time scale.

Solid-State Structures of Five-Coordinate Ru(II) Complexes. Complexes 3b and 4b,e all have distorted fivecoordinate geometries skewed toward square pyramidal with narrow N-Ru-P bite angles.³⁷ The extremely small bite angle of the PN ligand in 3b (80.23°) is likely the result of an abundance of short backbone bonds including the pyridine N-C bond, an sp^2-sp^2 C-C bond, and an intact P=C double bond, leading to a "tied-back" five-membered ring; a related square-planar Pd(Me)(Cl) complex supported by ligand 1c (see Chart 1 for structure) also featured a N-Ru-P angle of approximately 80°.22 Cyclization of the Mes* arm across the P=C bond in 4b,e generates a new sp³ benzylic-type carbon atom and a P-C single bond, providing more flexibility in the chelate and opening up the bite angle to almost 85°. As the bite angle increases, the phospholane unit shifts to a more "apical" position, and the overall geometries of the cyclized species are significantly closer to square pyramidal than is the case for uncyclized 3b. A comparison of the bite angle and τ

Table 2. Selected Bond Lengths	(Å) and Angles (d	leg) of Ligands 3	b, 4b,e, and 5a and	d Comparison	with a Previously
Reported ²² Pd Complex Support	ed by Ligand 1c (See Chart 1 for	Structure of 1c) ^a		

	$\left[Pd(Me)(Cl)(1c) \right]^{b}$	3b (R = Me)	4b (R = Me)	$4e (R = Ar-m-NO_2)$	5a (R = H)
$N-Ru-P_{P=C}$ (bite angle) ^c	79.45(10)	80.23(5)	84.43(7)	84.69(5)	84.11(14)
$ au^{38}$	N/A	0.38	0.19	0.23	N/A
P-C _{PN-Chelate}	1.674(4)	1.671(3)	1.838(3)	1.853(2)	1.847(7)
P-Mes*	1.808(4)	1.825(2)	1.863(3)	1.860(2)	1.835(7)
$Ru - P_{P=C}^{c}$	2.1744(14)	2.1498(6)	2.1826(9)	2.2007(6)	2.2436(17)
Ru-P _{PPh3}	N/A	2.3382(7)	2.2986(9)	2.3072(6)	2.2447(19)
$C-P=C^{c}$	114.26(19)	116.48(11)	110.42(14), 105.29(14), 92.94(14)	111.30(10), 103.23(11), 92.75(10)	105.8(3), 101.9(3), 91.9(3)
Ru-N _{py}	2.164(4)	2.147(2)	2.145(2)	2.1608(19)	2.103(5)

^{*a*}R factor (%): $[Pd(Me)(Cl)(1c)] (5.14);^{22}$ **3b** (3.93); **4b** (3.75); **4e** (4.12); **5a** (5.78). ^{*b*}The bond lengths and angles given in this column are for a Pd complex, not Ru. ^{*c*}For complexes **4b**,**e** and **5a**, cyclization converted the P=C bond into a P–C bond, and therefore, the P atom indicated is for the newly formed phospholane P.

values³⁸ ($\tau = 1$ = idealized TBP; $\tau = 0$ = idealized square pyramidal) is shown in Table 2.

In addition, the X-ray structure determination of the methyl series, specifically, 2b (see Table 1 for structural data), 3b, and 4b provided valuable insight into the structural changes of the phosphaalkene functionality upon binding and cyclization. At first glance, the most striking observation is that the P=Cbond length does not change on coordination to the Ru(II) center (2b vs 3b). Phosphaalkenes are strong π acceptors;^{4a} thus, the bond is expected to elongate. However, on complexation to metals, the P center undergoes extensive rehybridization from largely unhybridized (high s character in lone pair/high p character in P–C bonds) toward sp^2 , adding s character to the P-C bonds and resulting in their contraction; the two opposing effects cancel each other out, yielding no overall change in the P=C bond length.³⁹ Further evidence to support this rehybridization is observed in the shortening of the P-Mes* bond and widening of the C-P=C bond angle to 116.48(11)°; NBO calculations corroborate these findings (Table 3). Addition of the C–H bond on the Mes* arm across

Table 3. Selected Atom Hybridization of Ligand 2b, Its Cyclized Counterpart (Unbound to a Metal Center), and Ru(II) Complexes 3b and 4b

	2b	free phospholane	3b	4b
P LP or P-Ru bond	sp ^{0.51}	sp ^{0.80}	sp ^{1.51}	sp ^{2.02}
P-C _{Mes*} bond	sp ^{5.95}	sp ^{5.30}	sp ^{2.37}	sp ^{3.16}
$P=C \text{ or } P-CH_2 \text{ linker}$	sp ^{3.86}	sp ^{6.15}	sp ^{2.17}	sp ^{3.68}
Ph ₃ P-Ru bond	N/A	N/A	sp ^{2.04}	sp ^{1.98}

the P=C bond also has profound consequences $(3b \rightarrow 4b, Table 2)$. Most obvious is the drastic elongation of the P-C bond as it is transformed from a three-coordinate, P=C double bond into a four-coordinate, P-C single bond, but the P-Mes* bond also lengthens. Likewise, these observations can be rationalized by invoking hybridization arguments. The P donor in the pyridine-phosphaalkene ligand is \sim sp² (C-P=C bond angle = 116.48°), while the phospholane functionality adopts nearly sp³ hybridization. The added p character in the P-C bonds leads to their elongation, while the P center simultaneously reorganizes to a more tetrahedral geometry (average C-P-C bond angle = 102.9°).⁴⁰ A final more subtle observation is that the Ru-P bond to the new PN ligands are all shorter than that to PPh₃. Again, the sp²-hybridized P atom in the pyridine-phosphaalkene should afford the shortest Ru-P

bond (which it does), but why is the Ru–P bond length to the phospholane shorter than that to PPh₃? Recent reports by Glueck⁴¹ and Higham⁴² have compared phosphine and phosphirane donors, finding that when they are of similar size, phosphiranes feature shorter M-P bonds (M = Pt, Rh, Au) because of increased s character in the P lone pair enforced by the severely acute angles of the three-membered ring. We expected similar arguments could be made for the phospholane donor; however, DFT calculations revealed that Ru-P_{phospholane} and Ru-PPh₃ bonds contained the same amount of s character (33% s, Table 3). Instead, we speculate that the shorter Ru-P_{phospholane} bond is due to the fact that the trans coordination site is vacant. Without a trans ligand, the Ru center and phospholane P maximize their orbital overlap, resulting in a shorter Ru-P bond relative to the PPh3 unit, which has to compete with the pyridine donor for electron density.43,44

Solid-State Structure of Six-Coordinate 5a. Ru(II) complex 5a adopts a distorted-octahedral geometry featuring cis-oriented chlorides in plane with the PN chelate; the PPh₃ ligand is bound in the "apical" position and the agostic Ru– H–C interaction is located trans to it, residing in the sixth coordination site. This is in contrast to 3b and 4b,e, in which the chlorides and PPh₃/pyridine donors are mutually trans to one another with the phosphaalkene-derived P atom occupying the apical site in the square pyramid (Chart 2). This different

Chart 2. Comparison of the Spatial Arrangement of Donor Atoms to the Ru Center in 3b and 4b,e versus 5a



spatial arrangement of ligands at Ru(II) has subtle structural consequences that are a manifestation of the trans influence.⁴³ For example, the Ru–N_{pyridine} bond (Ru–N_{avg} = 2.151 Å) in **3b** and **4b**,**e** is approximately 0.05 Å longer than in **5a** (Ru–N = 2.103(5) Å), and the longest Ru–Cl bond (2.4612(16) Å) by roughly 0.06 Å (Ru–Cl = 2.4016(6) Å in **4e**) is found trans to the phospholane in **5a**; both observations are consistent with the pronounced trans influence of a PR₃ group relative to a chloride or pyridine donor.⁴⁴

On the other hand, the most significant structural effect on going from five-coordinate **3b** and **4b**,**e** to six-coordinate **5a** is the drastic pyramidalization of the phospholane center with the sum of the C–P–C angles totaling less than 300° (Table 2, above).⁴⁵ This may be rooted in geometric constraints involved in the fact that the P atom is incorporated into a few unusual ring structures, including a fused 5,7-system with a Ru/P ring junction and a phosphindoline,⁴⁶ which is formally annulated to a seven-membered ring through formation of the Ru–H–C agostic bond. This agostic interaction may also contribute to the pyramidalization of the phospholane, as the PN chelate is now "tridentate"⁴⁷ and bound in a facial arrangement,⁴⁸ enforcing bite angles at Ru to approach 90°.

Origin of Cyclization of Phosphaalkene to Phospholane at Ru. The presence of an agostic interaction also has mechanistic implications, because substrate binding is the first step in activation at a transition-metal center.⁴⁹ With PN ligands 2a-e, there is a clear electronic component to whether or not the *t*-Bu unit of the Mes* group is activated and added across the P=C bond. Electron-rich ligands 2b,d formed 3b,d (R = Me, OMe), in which the phosphaalkene unit persisted (unless heated in THF), while the more electron poor ligands 2c,e (R = CF₃, Ar-*m*-NO₂) including parent **2a** underwent cyclization affording TM complexes **6c**, **4e**, and **5a** featuring a modified PN ligand containing a new phospholane donor.

Literature Precedent. Two relevant mechanisms resulting in the cyclization of the Mes* group across a P=C unit to give phospholanes have been previously reported (Scheme 5). The

Scheme 5. Previously Proposed Mechanisms of Cyclization of the P-Mes* Group across the P=C Double Bond



first was a Lewis acid catalyzed approach experimentally demonstrated by exposing Mes*P=CH₂ to AlCl₃.⁵⁰ The reaction generated phosphenium (PR₂⁺) intermediate N, which C-H activated the *t*-Bu group of the Mes* arm, affording P-Me phospholane O after proton transfer from zwitterionic P.^{50,51} The second mechanism, based on reactivity observed with C (vide supra) and supported largely by computations (B3PW91 functional with 6-31G* basis set for H, C, and P atoms and LANL2TZ(f) basis set for Pt), involved coordination of the phosphaalkene to a phosphine-ligated Pt(0) catalyst followed by stepwise C-H oxidative addition of the *t*-Bu group, intramolecular P-C bond formation to give η^3 intermediate Q, and C-H reductive elimination of phospholane R.⁷

We envisioned that either mechanism could be operative here. For example, if the Ru(II) center acts purely as a Lewis acid (M^+ , no redox chemistry), complexation of the nitrogen atom to Ru(II) opens up a pathway for dearomatization of the pyridine moiety and generation of reactive phosphenium intermediate **S** (Scheme 6, right). Addition of the C–H bond^{50,51} across the cationic P center in **S** constructs a phospholane ring; subsequent proton transfer and rearomatization results in the formation of the new pyridineScheme 6. Two Potential Mechanisms of Cyclization of the P-Mes* Group across Its P=C Double Bond in Ligands 2a-e on Exposure to a Ru(II) Center



phospholane ligand, which coordinates to the Ru(II) center in a bidentate fashion. On the other hand, initial coordination of the pyridine-phosphaalkene to the Ru(II) center could promote oxidative addition of the *t*-Bu group, giving the 7-coordinate, 18-electron Ru(IV) complex T (Scheme 6, left).⁵² Proton transfer to the phosphaalkene carbon atom will furnish zwitterionic **U**, featuring a cationic phosphorus donor. Intramolecular nucleophilic attack of the alkyl arm on the phosphorus atom will quench the charges on both Ru and P and simultaneously give the phospholane ring. These mechanistic possibilities will be explored from both a computational and experimental standpoint in the future.

CONCLUSIONS AND OUTLOOK

Like their pincer counterparts (C and E), simple, bidentate pyridine-phosphaalkene (PN) ligands $2\mathbf{a}-\mathbf{e}$ are capable of cyclizing at transition-metal centers. Unexpectedly, four distinct types of transition metal complexes (3-6) are produced on exposure of these five ligands ($2\mathbf{a}-\mathbf{e}$), varying only in their 6-substituent to RuCl₂(PPh₃)₃. Complexes 4-6feature a new phospholane donor tethered to a pyridine ring via a CH₂ spacer; future studies will assess if these acidic, benzylic-type protons can be deprotonated to generate dearomatized complexes such as 7 (Scheme 7, shown using





4 as a representative example). Analogous complexes supported by pincer ligands have promoted numerous forms of strong bond activation $(C-H, {}^{53} N-H, {}^{12,54} O-H, {}^{55} etc.)$ and dehydrogenation-based catalytic processes.¹⁶ We will target energy relevant substrates with the secondary goal of developing enantioselective catalytic reactions utilizing the phospholane P as the source of chirality, a monodentate chiral phosphine in place of PPh₃, or a pyridine featuring an asymmetric R group.

EXPERIMENTAL SECTION

General Experimental Details. Unless otherwise specified, all reactions and manipulations were performed under a nitrogen atmosphere in a MBraun glovebox or using standard Schlenk techniques. All glassware was oven-dried overnight (at minimum) at 140 °C prior to use. Anhydrous solvents were purchased directly from chemical suppliers (Aldrich or Acros), pumped directly into the glovebox, and stored over oven-activated 4 or 5 Å molecular sieves (Aldrich). RuCl₂(PPh₃)₃ and Zn dust were purchased from Strem and used as is; PMe3 was also bought from Strem and stored over molecular sieves prior to use. The 6-substituted pyridine-2carboxyaldehyde derivatives were obtained from Sigma-Aldrich, and Mes*PCl₂ was prepared via a literature protocol. 56 NMR spectra were obtained on Varian spectrometers operating at 300, 400, or 500 MHz; all spectra are displayed in the Supporting Information. NMR chemical shifts are reported as ppm relative to tetramethylsilane and are referenced to the residual proton or ¹³C signal of the solvent (¹H CDCl₃, 7.27 ppm; ¹H C₆D₆, 7.16 ppm; ¹³C ČDCl₃, 77.16 ppm; ¹³C C₆D₆, 128.06 ppm). Mass spectroscopic data were collected on an Agilent 6545 Accurate-Mass Q-TOF LC/MS instrument (NSF CHE-1532310). Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-065-456. All X-ray-quality crystals were analyzed at the Small Molecular X-ray Crystallography Facility located at the University of California, San Diego.

Synthesis of Pyridine-Phosphaalkenes of Type 2. Derivative 2a was previously prepared as an E/Z mixture by Geoffroy¹⁰ and selectively (at low temperature) as the *E* isomer by Bickelhaupt²² using a phospha-Peterson methodology.¹⁷ Its full spectroscopic characterization is reported in ref 22. Using a phospha-Wittig methodology, in a manner as described below for 2b, parent 2a was isolated in 83% yield.

E-Selective Synthesis of 2b using a Phospha-Wittig Methodology. $Mes*PCl_2$ (1.00 g, 2.88 mmol) and Zn dust (940 mg, 14.4 mmol, 5 equiv) were combined in a vial, and 4 mL of THF was added. Treatment of the suspension with a room-temperature solution of PMe₃ (560 mg, 7.36 mmol, 2.6 equiv) in THF resulted in a yellow reaction mixture. The reaction mixture was stirred at room temperature for 1 h and filtered through a Celite plug directly into a solution of 6-methylpyridine-2-carboxaldehyde (262 mg, 2.16 mmol, 0.75 equiv) in 3 mL of THF to afford a homogeneous yellow-orange solution. After it was stirred for 10 min, the reaction mixture was concentrated under vacuum. The yellow residue was extracted with 5 mL of pentane and filtered through a Celite plug. The filtrate was concentrated under vacuum and recrystallized from 5 mL of a 50/50 solution of THF and acetonitrile at -35 °C to give a yellow solid (700 mg, 1.84 mmol, 85% yield).

Anal. Calcd for $C_{25}H_{36}NP$: C, 78.70; H, 9.51; N, 3.67. Found: C, 78.42; H, 9.54; N, 3.59. HRMS: m/z calcd for $C_{25}H_{36}NP$ [M]⁺, 381.2585; found, 381.2591. ³¹P{¹H} NMR (CDCl₃): δ 280.4. ¹H NMR (CDCl₃): δ 8.10 (d, J = 25.0 Hz, 1H, P=CH), 7.51 (m, 2H, Ar), 7.43 (s, 2H, Ar), 6.97 (br m, 1H, Ar), 2.53 (s, 3H, Me), 1.52 (s, 18H, t-Bu), 1.35 (s, 9H, t-Bu). ¹³C{¹H} NMR (CDCl₃): δ 175.6 (d, J = 33.8, P=C), 158.2 (Ar), 157.5 (d, J = 15.0 Hz, Ar), 136.4 (Ar), 123.7 (Ar), 121.6 (Ar), 119.4 (Ar), 117.0 (d, J = 20.0 Hz, Ar), 38.2 (CMe₃), 34.0 (t-Bu), 33.9 (t-Bu), 31.8 (CMe₃), 31.6 (CMe₃), 31.4 (t-Bu), 30.9 (Me).

Ligands 2c-e were prepared in an analogous fashion to 2b using a phospha-Wittig methodology. Full experimental details are included in the Supporting Information.

Syntheses of Ru(II) Complexes 3–6. Pyridine-Phosphaalkene Complex 3b. $RuCl_2(PPh_3)_3$ (126 mg, 0.131 mmol) was loaded into a vial and treated with a solution of 2b (50 mg, 0.131 mmol) in 1 mL of benzene at room temperature. The dark reaction mixture was transferred to a J. Young tube and monitored by ${}^{31}P{}^{1}H$ NMR spectroscopy. After it was heated at 60 °C for 120 h, the solution turned dark red, and the ${}^{31}P{}^{1}H$ NMR spectrum showed two doublets at 290.7 and 36.0 ppm. The mixture was subsequently filtered through Celite, and the filtrate was concentrated under vacuum. The crude dark red solid was recrystallized from toluene layered with pentane at -35 °C (83 mg, 0.102 mmol, 78% yield). Crystals suitable for X-ray crystallography were collected by slow diffusion of pentane vapors into a concentrated toluene solution.

Anal. Calcd for $C_{47}H_{59}Cl_2NOP_2Ru [M + THF]$: C, 63.58; H, 6.70; N, 1.58. Found: C, 63.24; H, 6.85; N, 1.46. HRMS: *m/z* calcd for $C_{48}H_{51}N_2O_2P_2Ru [M]^+$, 815.1917; found, 815.2510. ³¹P{¹H} NMR (CDCl₃): δ 290.7 (d, *J* = 36.4, C=P), 36.0 (d, *J* = 36.4, PPh₃). ¹H NMR (CDCl₃): δ 7.56 (t, *J* = 8.0 Hz, 1H, Ar), 7.46–7.39 (m, 8H, Ar), 7.38–7.32 (m, 3H, Ar), 7.26–7.22 (m, 6H, Ar), 6.92 (d, *J* = 7.5 Hz, 1H, Ar), 6.54 (d, *J* = 4.1 Hz, 1H, Ar), 2.85 (s, 3H, Me), 1.33 (s, 9H, *t*-Bu), 1.23 (s, 18H, *t*-Bu).¹³C{¹H} NMR (125 MHz, CDCl₃): δ 163.3 (Ar), 159.5 (Ar), 155.2 (Ar), 153.4 (Ar), 136.0 (Ar), 134.7 (d, *J* = 10.0 Hz, Ar), 133.2 (Ar), 132.9 (Ar), 129.5 (Ar), 127.8 (d, *J* = 10.0 Hz, Ar), 119.2 (d, *J* = 26.0 Hz, Ar), 123.8 (d, *J* = 10.0 Hz, Ar), 119.2 (d, *J* = 26.0 Hz, Ar), 123.8 (CMe₃), 35.2 (CMe₃), 33.9 (*t*-Bu), 31.0 (*t*-Bu), 24.7 (Me).

Due to its similarity to that for **3b**, the synthesis of **3d** is included in the Supporting Information.

Cyclized (Pyridine-Phospholane) Complex 4b. A solution of 3b (15 mg, 0.019 mmol) in 1 mL of THF was heated at 80 °C for 48 h, at which time the phosphaalkene resonance was no longer observed by ³¹P NMR spectroscopy. The cyclized complex (³¹P NMR: δ 91.1, 46.7) was filtered through a pad of Celite, and the filtrate was concentrated under vacuum. The crude solid was recrystallized from a 1/3 solution of THF/pentane at -35 °C to give dark green crystals (12 mg, 0.015 mmol, 80% yield). Crystals suitable for X-ray crystallography were collected by slow diffusion of pentane vapors into a concentrated THF solution.

HRMS: m/z calcd for $C_{45}H_{54}ClN_2P_2Ru [M - (Cl^-) + NCMe]^+$, 821.2494; found, 821.2516. ³¹P{¹H} NMR (202 MHz, CDCl₂): δ 91.1 (br, CH₂P), 48.7 (d, J = 36.4 Hz, PPh₃). ¹H NMR (500 MHz, $CDCl_3$): δ 7.61–7.56 (m, 2H, Ar), 7.40 (t, J = 9.0 Hz, 6H, Ar), 7.31 (t, J = 8.5 Hz, 4H, Ar), 7.21-7.14 (m, 7H, Ar), 6.96 (d, J = 1.5 Hz,1H, Ar), 4.23 (dd, J = 17.0, 11.0 Hz, 1H, benzylic N_{Ar}), 3.99 (dd, J =17.0, 10.0 Hz, 1H, benzylic NAr), 2.80 (s, 3H, Me), 2.17-1.96 (m, 2H, CH₂P), 1.38 (s, 9H, t-Bu), 1.23 (s, 9H, t-Bu), 1.10 (s, 3H, CMe₂), 0.79 (s, 3H, CMe₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 162.1 (Ar), 160.4 (Ar), 157.3 (d, J = 21.3, Ar), 156.7 (d, J = 7.5 Hz, Ar), 153.6 (Ar), 136.2 (Ar), 134.6 (d J = 10.0 Hz, Ar), 133.7 (d, J = 42.5 Hz, Ar), 129.3 (Ar), 129.0 (Ar), 128.3 (d, J = 12.5 Hz, Ar), 127.9 (d, J = 8.8 Hz, Ar), 126.8 (d, J = 10.0 Hz, Ar), 123.8 (Ar), 119.2 (d, J = 10.0 Hz, Ar), 117.9 (d, J = 10.0 Hz, Ar), 50.9 (d, J = 22.5 Hz, benzylic), 47.6 (d, J = 43.8 Hz, PCH₂CMe₂), 43.2 (CMe₂), 37.9 (CMe₃), 35.4 (t-Bu), 35.0 (CMe₃), 34.1 (t-Bu), 31.3 (t-Bu), 28.6 (d, J = 10.0 Hz, CMe_2), 25.0 (Me).

The closely related thermally induced cyclization of **3d** to **4d** can be found in the Supporting Information.

Cyclization of **2e** to **4e**. $\operatorname{RuCl_2(PPh_3)_3}(197 \text{ mg}, 0.205 \text{ mmol})$ was loaded into a vial and treated with a solution of **2e** (100 mg, 0.205 mmol) in 2 mL of benzene at room temperature. The dark reaction mixture was transferred to a J. Young tube and monitored by ³¹P{¹H} NMR spectroscopy. After it was heated at 80 °C for 72 h, the reaction mixture turned dark green, and the ³¹P{¹H} NMR spectrum showed two doublets at 90.3 and 48.6 ppm. The mixture was subsequently filtered through Celite, and the filtrate was concentrated under vacuum. The dark green residue was recrystallized from a 5 mL solution of THF layered with pentane at -35 °C (185 mg, 0.201 mmol, 98% yield). Crystals suitable for X-ray crystallography were collected by slow diffusion of pentane vapors into a concentrated THF solution.

Anal. Calcd for $C_{48}H_{52}Cl_2N_2O_2P_2Ru$ was consistently low (three attempts) in carbon, for example: C, 62.47; H, 5.68; N, 3.04. Found: C, 61.83; H, 5.69; N, 2.69. HRMS: m/z calcd for $C_{48}H_{52}Cl_2N_2O_2P_2Ru$ [M]⁺, 922.1925; found, 922.1906. ³¹P{¹H} NMR (CDCl₃): δ 90.3 (d, J = 36.4 Hz, P-Mes*), 48.6 (d, J = 36.4 Hz, PPh₃). ¹H NMR (CDCl₃): δ 8.57 (s, 1H, Ar), 8.11 (d, J = 7.0 Hz, 1H, Ar), 8.03 (d, J = 9.5 Hz, 1H, Ar), 7.87 (t, J = 8.0 Hz, 1H, Ar), 7.58–7.54 (m, 3H, Ar), 7.27 (m, J = 7.0 Hz, 9H, Ar), 7.08 (t, J = 6.5 Hz, 6H, Ar), 6.95 (s, 1H, Mes*), 6.89 (t, J = 8.0 Hz, 1H, Ar), 4.25

(overlapping m, J = 16.5, 10 Hz, 2H, PCH₂N), 2.34 (dd, J = 16.5, 5.0 Hz, 1H, PCH₂), 1.90–1.81 (m, 1H, PCH₂), 1.35 (s, 9H, *t*-Bu), 1.15 (s, 9H, *t*-Bu), 1.12 (s, 3H, C(Me)₂), 0.78 (s, 3H. C(Me)₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 164.1 (Ar), 160.8 (Ar), 157.5 (d, J = 21.3 Hz, Ar), 156.6 (d, J = 7.5 Hz, Ar), 153.7 (Ar), 148.8 (Ar), 142.6 (Ar), 136.8 (Ar), 134.9 (d, J = 8.8 Hz, Ar), 133.8 (d, J = 42.5 Hz, Ar), 131.4 (Ar), 129.2 (Ar), 127.6 (d, J = 10.0 Hz, Ar), 126.8 (d, J = 10.0 Hz, Ar), 126.4 (Ar), 123.9 (Ar), 123.8 (Ar), 123.2 (Ar), 121.6 (d, J = 10.0 Hz, Ar), 118.1 (d, J = 10.0 Hz, Ar), 50.9 (d, J = 22.5 Hz, benzylic), 45.9 (d, J = 42.5 Hz, Phospholane PCH₂), 42.7 (CMe₂), 37.7 (CMe₃), 35.3 (CMe₂), 35.0 (CMe₃), 34.0 (*t*-Bu), 31.0 (*t*-Bu), 28.8 (d, J = 10 Hz, CMe₂).

Six-Coordinate 5a (C–H Agostic Complex). $RuCl_2(PPh_3)_3$ (55 mg, 0.149 mmol, 1.0 equiv) was loaded into a vial and treated with a solution of 2a (144 mg, 0.149 mmol, 1.0 equiv) in 1 mL of benzene at room temperature. The dark reaction mixture was transferred to a J. Young tube and monitored by ³¹P{¹H} NMR spectroscopy. After it was heated at 80 °C for 72 h, the solution turned dark red, and the ³¹P{¹H} NMR spectrum showed two doublets at 66.8 and 64.0 ppm. The mixture was subsequently filtered through a Celite plug using Et₂O, and the filtrate was concentrated under vacuum. The crude product was recrystallized from a concentrated solution of benzene at 25 °C to give a red solid (50 mg, 0.062 mmol, 42% yield). Crystals suitable for X-ray crystallography were collected by slow diffusion of pentane vapors into a concentrated THF solution.

Anal. Calcd for C42H49Cl2NP2Ru: C, 62.92; H, 6.16; N, 1.75. Found: C, 63.31; H, 6.12; N, 1.37. HRMS: m/z calcd for $C_{42}H_{49}ClNP_2Ru^{\scriptscriptstyle +} \ \ [M \ - \ (Cl^{\scriptscriptstyle -})]^{\scriptscriptstyle +}, \ \ 766.2067; \ \ found, \ \ 766.2077.$ ³¹P{¹H} NMR (202 MHz, CDCl₃): δ 66.8 (d, J = 39.3 Hz, PPh₃), 64.0 (d, J = 39.3 Hz, CH₂P). ¹H NMR (500 MHz, CDCl₃): δ 9.31 (dd, J = 6.1, 1.8 Hz, 1H, Ar), 7.76–7.82 (m, 5H, Ar), 7.42 (dd, J = 4.8, 1.8 Hz, 1H, Ar), 7.27-7.20 (m, 5H, Ar), 7.19-7.13 (m, 6H, Ar), 7.10 (d, J = 1.8 Hz, 1H, Mes*), 7.04 (d, J = 7.1 Hz, 1H, Ar), 6.43 (t, J = 7.1 Hz, 1H, Ar), 3.69 (dd, J = 18.4, 11.4 Hz, 1H, CH₂Ar), 3.44 (dd, J = 18.4, 8.5 Hz, 1H, CH₂Ar), 2.22 (dd, J = 15.3, 7.8 Hz, 1H, PCH₂), 1.30 (s, 9H, t-Bu), 1.26 (s, 3H, Me), 1.25 (s, 3H, Me), 0.86 (d, J = 1.6 Hz, 9H, *t*-Bu), 0.73 (dd, J = 15.2, 2.2 Hz, 1H, PCH₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 164.7 (Ar), 157.0 (Ar), 156.2 (d, J = 14.2 Hz, Ar), 154.2 (Ar), 152.2 (d, J = 10.6 Hz, Ar), 134.8 (d, J = 22.3 Hz, Ar), 134.6 (Ar), 133.9 (d, J = 9.5 Hz, Ar), 129.0 (Ar), 127.6 (d, J = 10.1 Hz, Ar), 124.6 (d, J = 8.2 Hz, Ar), 121.9 (Ar), 121.7 (d, J = 11.4 Hz, Ar), 118.8 (d, J = 8.2 Hz, Ar), 46.8 (d, J = 20.0 Hz, CH₂Ar), 43.6 (d, J = 5.5 Hz, CMe₂), 39.4 (d, J = 31.3 Hz, PCH₂), 35.0 (CMe₃), 30.4 (CMe_3) , 32.8 (t-Bu), 31.7 (d, J = 9.6 Hz, CMe_2), 31.2 (t-Bu), 30.5 (d, $J = 5.3 \text{ Hz}, CMe_2$).

Six-Coordinate 6c ("C–F Agostic" Complex). RuCl₂(PPh₃)₃ (128 mg, 0.130 mmol) was loaded into a vial and treated with a solution of 2c (60 mg, 0.130 mmol) in 2 mL of benzene at room temperature. The dark reaction mixture was transferred to a J. Young tube and monitored by ³¹P{¹H} NMR spectroscopy. After it was heated at 60 °C for 240 h, the solution turned dark green, and the ³¹P{¹H} NMR spectrum showed two doublets at 85.8 and 50.2 ppm. The mixture was subsequently filtered through Celite, and the filtrate was concentrated under vacuum. The crude residue was recrystallized from THF layered with Et₂O at -35 °C to give green crystals (35 mg, 0.039 mmol, 30% yield).

³¹P NMR (CDCl₃): δ 85.8 (overlapping dq, J = 42.8, 21.5 Hz, CH₂P) 50.2 (d, J = 42.8 Hz, PPh₃). ¹H NMR (CDCl₃): δ 7.89 (t, J =7.8 Hz, 1H, Ar), 7.72 (d, J = 7.8 Hz, 1H, Ar), 7.68 (d, J = 7.8 Hz, 1H, Ar), 7.60 (dd, J = 4.6, 2.0 Hz, 1H, Ar), 7.40 (t, J = 7.8 Hz, 4H, Ar), 7.30 (m, 2H, Ar), 7.17 (m, 7H, Ar), 6.97 (d, J = 2.0 Hz, 1H, Ar), 4.33 (dd, J = 16.7, 10.7 Hz, 1H, CH₂Ar), 4.18 (dd, J = 16.7, 9.8 Hz, 1H, CH₂Ar), 2.27 (dd, J = 16.4, 5.1 Hz, 1H, CH₂P), 1.99 (dd, J = 16.4, 10.7 Hz, 1H, CH₂P), 1.38 (s, 9H, *t*-Bu), 1.22 (s, 9H, *t*-Bu), 1.10 (s, 3H, Me), 0.79 (s, 3H, Me). ¹⁹F NMR (CDCl₃): δ -63.4 (d, J = 21.5Hz). ¹³C NMR (125 MHz, CDCl₃): δ 163.9 (Ar), 157.8 (Ar), 156.7 (Ar), 153.8 (Ar), 136.9 (Ar), 134.7 (d, J = 10.0 Hz, Ar), 133.5 (Ar), 133.3 (d, J = 42.8 Hz, Ar), 127.8 (d, J = 9.6 Hz, Ar), 126.8 (Ar), 124.7 (Ar), 122.2 (Ar), 118.1 (Ar), 118.0 (Ar), 52.1 (d, J = 21.5 Hz, PCH₂Ar), 46.5 (d, J = 42.8 Hz, PCH₂), 43.0 (CMe₂), 38.0 (CMe₃), 35.5 (CMe_2), 35.0 (CMe_3), 34.1 (t-Bu), 31.1 (t-Bu), 28.7 (d, J = 10.6 Hz, CMe_2).

DFT Calculations. Full details on the computational methods are provided in the Supporting Information.

X-ray Crystallography. Details for the seven crystal structures are given in the Supporting Information. All data were collected at 100 K (except for 2e, which were collected at 200 K due to an apparent destructive phase change at lower temperatures) on Bruker diffractometers using Mo K α radiation. For 4e, 3b, and 4b, the program SQUEEZE was used to render highly disordered solvent molecules. All specimens of 2d and 5a were found to be rotationally twinned. The structure of 2e contained a disordered *t*-Bu group.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00425.

Complete experimental details supplemented with NMR spectra and specifics on DFT computational methodology (PDF)

Optimized Cartesian coordinates (XYZ)

Accession Codes

CCDC 1936294–1936299 and 1937111 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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