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C–H Activation of Pyrazolyl Ligands by Ru(II)

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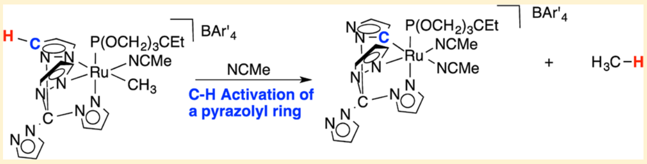
Supporting Information

ABSTRACT: Previously, hydridotris(pyrazolyl)borate (Tp) Ru(II) alkyl and aryl complexes of the type TpRu(L)(NCMe)-R (R = methyl or aryl; L = charge-neutral two-electron donating ligand) were demonstrated to activate aromatic C–H bonds. To determine the impact of replacing the anionic Tp ligand with charge-neutral poly(pyrazolyl)alkane ligands, $[(C(pz)_4)Ru(P(OCH_2)_3CEt)(NCMe)Me][BAr'_4]$ (pz = pyrazolyl, BAr'_4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) was prepared. Heating a C_6D_6 solution of $[(C(pz)_4)Ru(P(OCH_2)_3CEt)(NCMe)Me][BAr'_4]$ with 1 equiv of NCMe resulted in C–H activation of the 5-position of a pyrazolyl ring to yield $[(\kappa^3\text{-}(N,C^5,N)C(pz)_4)Ru(P(OCH_2)_3CEt)(NCMe)_2][BAr'_4]$ and CH_4. Intramolecular C–H activation of the 5-position of a pyrazolyl ring also occurred when $(\eta^6\text{-}p\text{-cymene})Ru(P(OCH_2)_3CEt)(Br)Ph$ was heated in the presence of $C(pz)_4$ to yield $[(\kappa^3\text{-}N,C^5,N)C(pz)_4]Ru(P(OCH_2)_3CEt)(NCMe)Br$ and C_6H_6. Density functional theory calculations revealed that the different reactivities of $TpRu(P(OCH_2)_3CEt)(NCMe)R$ and $[(C(pz)_4)Ru(P(OCH_2)_3CEt)(NCMe)Me][BAr'_4]$ result from the stronger binding of the Tp pyrazolyl rings to Ru(II) compared to that of $C(pz)_4$.



INTRODUCTION

Transition-metal mediated C–H activation has been heavily studied for several decades, and recent advances include many examples of transition-metal catalyzed C–H functionalization.[1−10] An important consideration for the design of catalysts for C–H functionalization is the possibility of intramolecular C–H activation of ligands that can compete with desired C–H activation of substrates. For example, phosphine ligands are often susceptible to cyclometalation.[11−14] Bidentate 2,2′-bipyridines have been reported to undergo "rollover" cyclometalation including reactions of Ir(III), Rh(III), Pd(II), Pt(II), and Au(II) complexes.[15−24] The rollover cyclometalation occurs via rotation of the C–C bond to allow activation of the C(3)–H bond. Poly(pyrazolyl)alkane and poly(pyrazolyl)borate ligands with ≥ three pyrazolyl rings often coordinate to metals in a κ^3-*N,N,N* mode; however, examples of intramolecular C–H activation at the 5-position of the pyrazolyl ring have been reported.[25−29]

Transition-metal catalyzed olefin hydroarylation provides a method for alkylation of aromatic substrates.[7,30−50] Our groups have been studying TpRu(II) complexes of the type TpRu(L)(NCMe)Ph [Tp = hydridotris(pyrazolyl)borate; L = CO, PMe_3, $P(OCH_2)_3CEt$, P(*N*-pyrrolyl)$_3$ and $\mathrm{P(O\overline{CH_2)_2(OC}CH_3)}$] as catalysts for olefin hydroarylation.[11,51−58] Combined experimental and computational studies have found that strongly donating "L" ligands inhibit olefin insertion and allow olefin C–H activation to compete with olefin insertion.[11,51,52,55,56] The activation of the olefin C–H bond ultimately results in the formation of an η^3-allyl complex leading to catalyst deactivation (Scheme 1). These results suggest that octahedral Ru(II) complexes that possess a similar ligand motif to TpRu(L)(NCMe)Ph complexes but with reduced electron density at Ru should provide improvements in catalyst longevity.

For the series of TpRu(L)(NCMe)R complexes, we have used Ru(III/II) potentials obtained from cyclic voltammetry to compare electron density with reactivity (Figure 1).[52,55,56] An advantage of poly(pyrazolyl) ligands is the ability to modulate their donor ability.[59−67] On the basis of previously reported data,[68,69] it was estimated that replacing the anionic Tp ligand of TpRu(L)(NCMe)Ph complexes with charge-neutral poly(pyrazolyl)alkanes should shift the Ru(III/II) redox potentials positive by approximately 0.3 to 0.4 V (Figure 1). Consistent with this prediction, replacing Tp of $TpRu(P(OCH_2)_3CEt)(NCMe)Ph$ with tris(pyrazolyl)ethane on Ru(II) results in a shift in the Ru(III/II) potential to the positive by ~0.37 V.[68] We anticipated that a cationic complex of the type $[(PPA)Ru(P(OCH_2)_3CEt)(NCMe)Ph]^+$ (PPA = κ^3-poly(pyrazolyl)alkane) would provide a longer-lived catalyst for olefin hydroarylation than the previously reported $TpRu(P(OCH_2)_3CEt)(NCMe)Ph$.[52]

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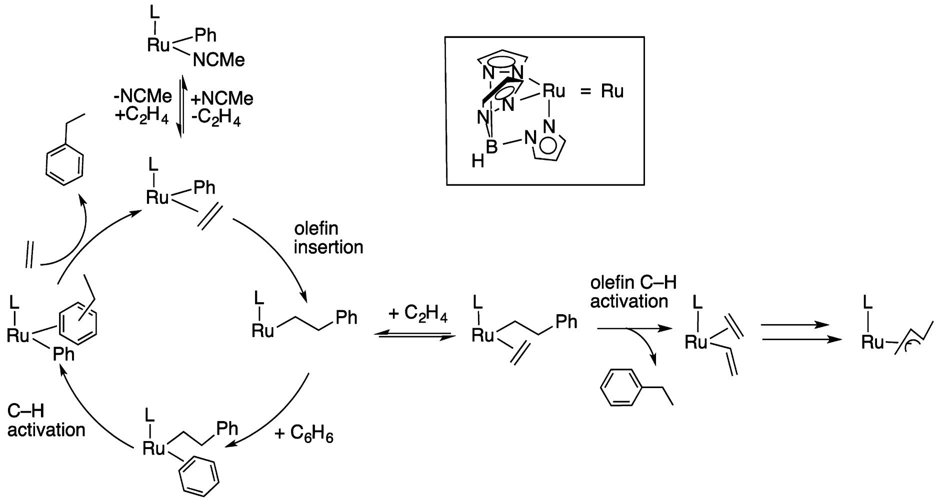
Scheme 1. Catalytic Olefin Hydroarylation and Competing Olefin C–H Activation Reaction



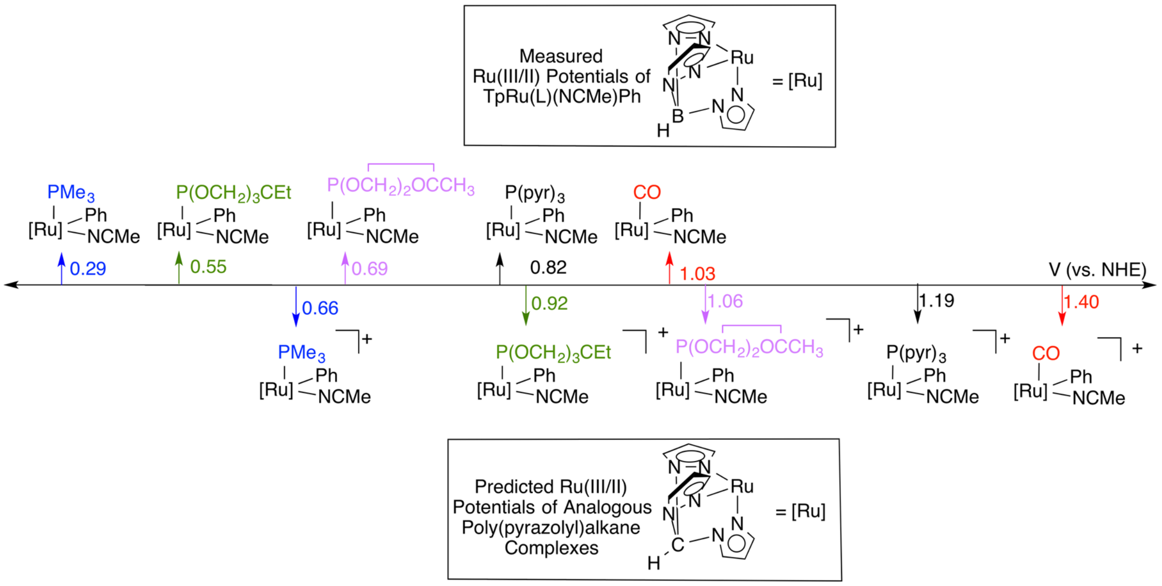
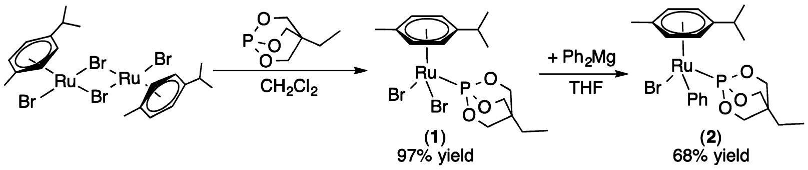


Figure 1. Experimental Ru(III/II) (V vs NHE) potentials for TpRu(L)(NCMe)Ph complexes and predicted Ru(III/II) potentials for putative (HC(pz)$_3$)Ru(L)(NCMe)Ph complexes.

Scheme 2. Synthesis of (η^6-*p*-cymene)Ru(P(OCH$_2$)$_3$CEt)(Ph)Br (2)



Herein, we report the preparation of [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me][BAr′$_4$] (pz = pyrazolyl, BAr′$_4$ = tetrakis[3,5-bis-trifluoromethyl)phenyl]borate) and combined experimental and computational studies that demonstrate intramolecular C–H activation of pyrazolyl ring inhibits successful catalysis.

■ RESULTS AND DISCUSSION

The complexes (η^6-*p*-cymene)Ru(P(OCH$_2$)$_3$CEt)Br$_2$ (**1**) and (η^6-*p*-cymene)Ru(P(OCH$_2$)$_3$CEt)(Br)Ph (**2**) were synthesized using a procedure similar to that previously reported for (η^6-*p*-cymene)Ru[P(OCH$_2$)$_2$(OCCH$_3$)]Br$_2$ and (η^6-*p*-cymene)Ru[P(OCH$_2$)$_2$(OCCH$_3$)](Ph)Br (Scheme 2).[56] Phenylation of **1** in tetrahydrofuran (THF) with Ph$_2$Mg[THF]$_2$ produces **2** (Scheme 2). A single crystal suitable for an X-ray diffraction study was obtained by slow diffusion of Et$_2$O into a THF solution of **2** (Figure 2). The average P–O bond length of complex **2** [1.601(2) Å] is longer than that of the previously reported complex (η^6-C$_6$H$_6$)Ru(P(OMe)$_3$)Cl$_2$ [1.576(3) Å],[70] but shorter than the P–O bond lengths of previously reported complexes such as (η^6-C$_6$H$_6$)Ru(P(OCH$_2$)$_2$(OCCH$_3$))Cl$_2$ [1.613(2) Å] and TpRu(P(OCH$_2$)$_2$(OCCH$_3$))(PPh$_3$)Cl$_2$ [1.627(3) Å].[71]

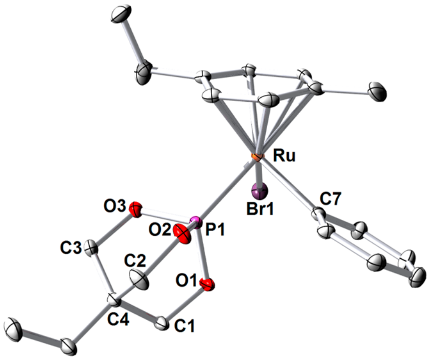
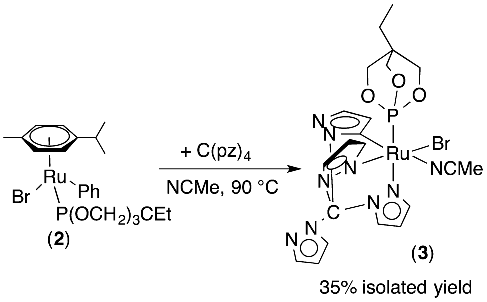


Figure 2. ORTEP of (η^6-*p*-cymene)Ru(P(OCH$_2$)$_3$CEt)(Ph)Br (**2**) (35% probability with hydrogen atoms omitted). Selected bond lengths (Å): Ru−P1, 2.2144(3); P−O1, 1.600(1); P−O2, 1.602(1); P−O3, 1.6029(1). Selected bond angles (deg): O3−P1−O2, 102.31(6); O1−P1−O2, 101.88(6); O1−P1−O3, 101.89(6); O1−P1−Ru, 120.62(4); O2−P1−Ru, 112.98(4); O3−P1−Ru, 114.78(4).

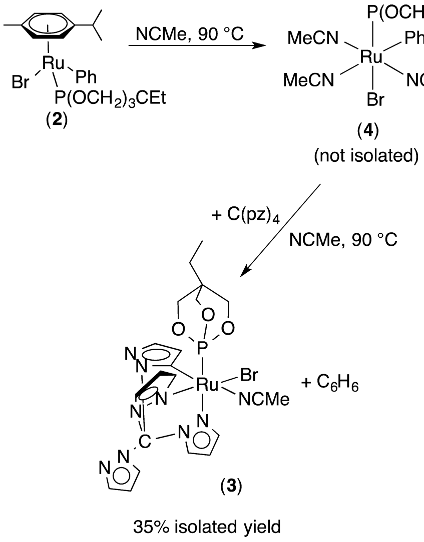
The Ru−P bond length of **2** is 2.2144(3) Å, which is shorter than that for the previously reported complex (η^6-*p*-cymene)Ru(P(OCH$_2$)$_3$CEt)Cl$_2$ (2.2529(4) Å).[71]

To study the effect of a charge-neutral ligand on Ru(II)-catalyzed olefin hydroarylation, we sought to synthesize Ru(II) complexes coordinated by a poly(pyrazolyl)alkane ligand. The acidity of the methane proton of tris(pyrazolyl)methane proved problematic for attempted alkylation and arylation of Ru(II), while Ru(II) complexes (unpublished work) supported by 1,1′,1″-tris(pyrazolyl)ethane showed poor solubility in organic solvents. We observed that Ru complexes of C(pz)$_4$ generally exhibited enhanced solubility in common organic solvents. Complex **2** reacts with C(pz)$_4$ in NCMe (90 °C) to form [(κ^3-*N*,*C*^{5},*N*)C(pz)$_4$]Ru(P(OCH$_2$)$_3$CEt)(NCMe)Br (**3**) (Scheme 3). The formation of benzene (^{1}H NMR) provides evidence of a C−H activation process. The ^{1}H NMR spectrum of **3** shows only 11 resonances for the C(pz)$_4$ ligand, but 12 resonances are observed for the pyrazolyl carbons by ^{13}C{^{1}H} NMR spectroscopy. These data are consistent with intramolecular C−H activation of the 5-position of a pyrazolyl ring leading to benzene and complex **3**. There are at least two previous examples of C−H activation at the 5-position of the pyrazolyl ring of a polydentate ligand. TpIr(PPh$_3$)(C$_2$H$_4$) and [(HC(pz)$_3$)Ir(PPh$_3$)(C$_2$H$_4$)][BF$_4$] each react with PPh$_3$ to yield the cyclometalated species (*N*,*C*^{5},*N*-Tp)Ir(PPh$_3$)$_2$H and (*N*,*C*^{5},*N*-HC(pz)$_3$)Ir(PPh$_3$)$_2$H-[BF$_4$], respectively.[26,72] Complex **3** can also be formed by reaction of C(pz)$_4$ with the putative tris-acetonitrile complex (NCMe)$_3$Ru(P(OCH$_2$)$_3$CEt)(Br)Ph (**4**) (Scheme 4), which is generated *in situ* by heating **2** at 90 °C in NCMe. A similar species (NCMe)$_3$Ru[P(OCH$_2$)$_2$(OCCH$_3$)](Ph)Br has been reported previously.[56] Reactions of **2** or **4** with C(pz)$_4$ at lower temperatures resulted in little or no reactivity.

Scheme 3. Synthesis of [(κ^3-*N*,*C*^{5},*N*)C(pz)$_4$]-Ru(P(OCH$_2$)$_3$CEt)(NCMe)Br (3)



Scheme 4. Stepwise Synthesis of [(κ^3-*N*,*C*^{5},*N*)C(pz)$_4$]-Ru(P(OCH$_2$)$_3$CEt)(NCMe)Br (3)

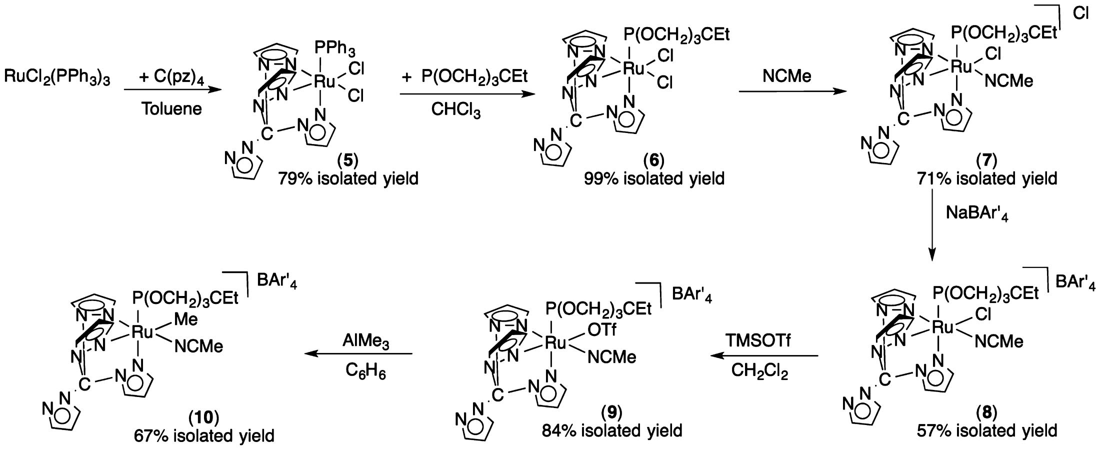


Since the reaction of **2** or **4** with C(pz)$_4$ results in intramolecular C−H activation, we sought an alternative synthetic route to produce (C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)R (R = alkyl or aryl). Refluxing C(pz)$_4$ in toluene in the presence of RuCl$_2$(PPh$_3$)$_3$ produces (C(pz)$_4$)Ru(PPh$_3$)Cl$_2$ (**5**) in 79% isolated yield (Scheme 5). We were unable to obtain satisfactory elemental analysis data for **5**; however, high-resolution mass spectrometry (HR-MS) and NMR data are consistent with the proposed identity. Collection of HR-MS data after dissolving complex **5** in NCMe showed displacement of chloride by acetonitrile to produce the cationic complex [(C(pz)$_4$)Ru(PPh$_3$)(NCMe)Cl]Cl (observed at 720 *m*/*z*).

The phosphite complex (κ^3-C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)Cl$_2$ (**6**) is produced by reaction of **5** with excess P(OCH$_2$)$_3$CEt. The coordination of the P(OCH$_2$)$_3$CEt is apparent by the disappearance of the resonance for coordinated PPh$_3$ at 52 ppm and the appearance of a downfield resonance at 128 ppm (^{31}P NMR). Complex **6** reacts with NCMe to produce [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Cl]Cl (**7**), which is converted to [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Cl][BAr′$_4$] (**8**) upon reaction with NaBAr′$_4$. A single crystal of complex **8** was obtained by diffusion of hexanes into a THF solution of **8** at −30 °C (Figure 3). The O−P−O bond angles of the phosphite ligand of complex **8** are similar to the O−P−O bond angles for complex **2** (see above). The Ru−P bond length of **8** (2.205(2) Å) is slightly shorter than that of complex **2** (2.2144(3) Å). Comparison of the Ru−N$_{\text{pyrazolyl}}$ bond distances shows that the *trans* influence of the phosphite is more pronounced than that of the chloride or acetonitrile ligands. The Ru−N6 bond distance (2.143(5) Å) is longer than both the Ru−N2 (2.028(5) Å) and Ru−N4 (2.046(5) Å) bond distances.

All attempts to alkylate or arylate **8** led to no reaction or decomposition. Therefore, the chloride ligand was replaced with a weakly coordinating triflate group using TMSOTf (TMS = trimethylsilyl; OTf = trifluoromethanesulfonate) in methylene chloride (100 °C) to yield [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)(OTf)][BAr′$_4$] (**9**) (Scheme 5). The singlet at −79 ppm

Scheme 5. Synthesis of [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me][BAr′$_4$] (10)



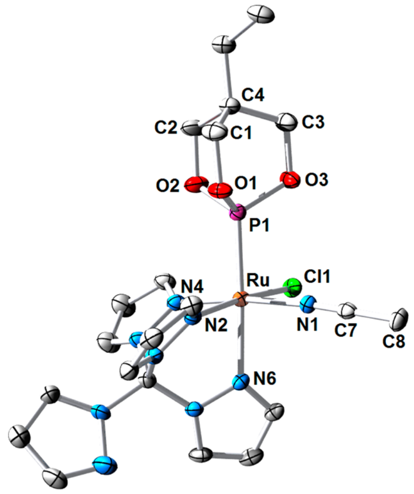
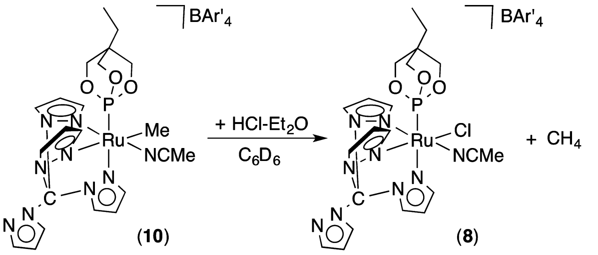


Figure 3. ORTEP of [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Cl][BAr′$_4$] (**8**) (35% probability with hydrogen atoms and BAr′$_4$ omitted.). Selected bond lengths (Å): Ru−P1, 2.205(2); P−O1, 1.594(4); P−O2, 1.599(5); P−O3, 1.595(4); Ru−Cl1, 2.397(2); Ru−N1, 2.023(6), Ru−N2, 2.028(5); Ru−N4, 2.046(5); Ru−N6, 2.143(5). Selected bond angles (deg): O3−P1−O2, 102.2(2); O1−P1−O2, 101.7(2); O1−P1−O3, 101.8(2); O1−P1−Ru, 115.1(2); O2−P1−Ru, 118.3(2); O3−P1−Ru, 115.4(2).

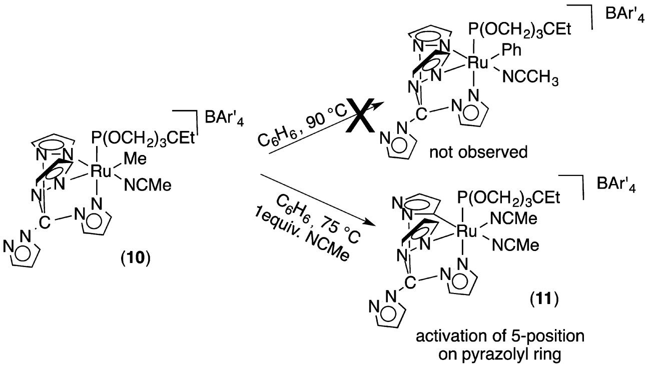
in the ^{19}F NMR spectrum is consistent with coordinated triflate. Methylation of **9** was accomplished upon reaction with 1.5 equiv of AlMe$_3$ to produce [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me][BAr′$_4$] (**10**) in 67% isolated yield. A doublet for the methyl group of **10** is observed at 0.79 ppm with a $^3J_{\text{HP}}$ = 2 Hz. The reaction of complex **10** with 1 equiv of HCl·Et$_2$O to produce **8** and methane (confirmed by ^{1}H NMR spectroscopy and GC-MS) is additional evidence of a Ru−Me bond (eq 1).



(1)

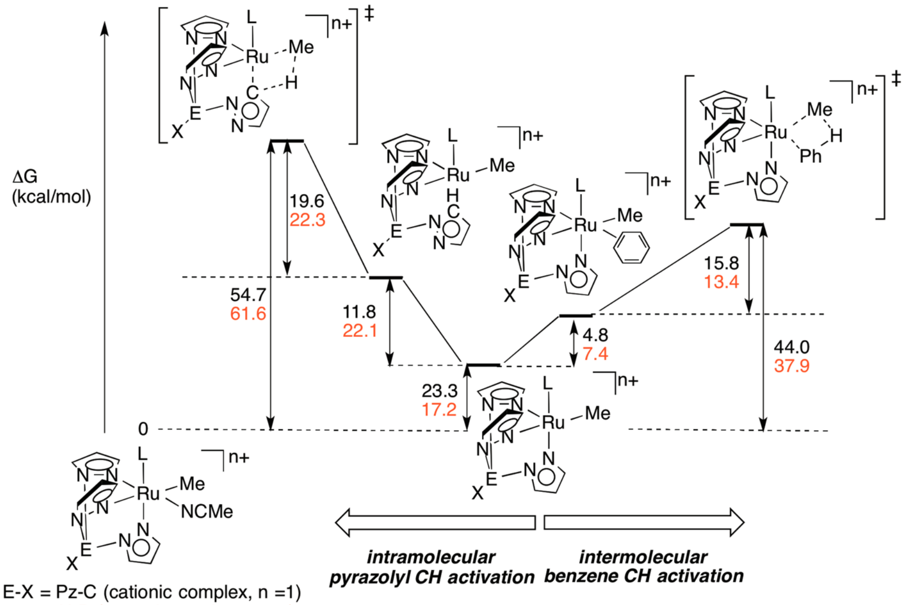
We previously reported that heating TpRu(L)(NCMe)R (R = Me or Ph) complexes in benzene results in benzene C−H activation to yield methane or benzene and TpRu(CO)(NCMe)Ph.[51,53−55] However, heating complex **10** in benzene at 90 °C does not activate the benzene C−H bond. Instead, decomposition to multiple intractable products occurs. The same reaction was attempted with 1 equiv of NCMe since it has been shown that NCMe reduces the extent of decomposition for reactions of TpRu(L)(NCMe)Ph and benzene.[11] When complex **10** is heated to 75 °C in benzene with NCMe, CH$_4$ and {[(*N*,*C*^{5},*N*)C(pz)$_4$]Ru(P(OCH$_2$)$_3$CEt)(NCMe)$_2$}[BAr′$_4$] (**11**) are formed (Scheme 6). The ^{1}H NMR spectrum of **11** shows two inequivalent NCMe groups, which indicates that one NCMe is *trans* to the carbon-bound pyrazolyl ring, while the other NCMe is *trans* to an *N*-bound pyrazolyl ring. The Ru-coordinated carbon resonates as a doublet with a $^3J_{\text{CP}}$ = 20 Hz at 164.9 ppm. There was no evidence of ethylene hydrophenylation using complexes **10** and **11** under a variety of temperatures and ethylene pressures.

Scheme 6. Reactions of Complex [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me][BAr′$_4$] (10) with C$_6$H$_6$



Density functional/pseudopotential theory computations (details in Supporting Information) were used to compare the activation barriers for intermolecular benzene C−H activation ($\Delta G^{\ddagger}_{\text{inter}}$) and intramolecular activation of the 5-position C−H bond of a pyrazolyl arm ($\Delta G^{\ddagger}_{\text{intra}}$) for TpRu(P(OCH$_2$)$_3$CEt)(NCMe)Me and [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me]$^+$ (Scheme 7). As anticipated from previous studies of TpRu(L)(NCMe)R complexes,[55] the calculated activation energy for benzene C−H activation by [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me]$^+$ is greater than that of TpRu(P(OCH$_2$)$_3$CEt)(NCMe)Me ($\Delta G^{\ddagger}_{\text{inter}}$ = 44.0 and 37.9 kcal/mol, respectively). Acetonitrile dissociation is computed to be more endergonic

Scheme 7. Computed Reaction Coordinate for Intermolecular Benzene C−H Activation (($\Delta G^{\ddagger}_{\mathrm{inter}}$) and Intramolecular Pyrazolyl C−H Activation ($\Delta G^{\ddagger}_{\mathrm{intra}}$) by Cationic (EX = C(pyrazolyl); black text) and Neutral (EX = BH, red text) Ru(II) Complexes



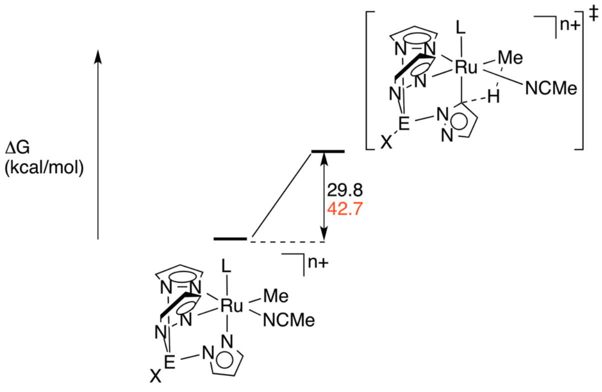
E-X = Pz-C (cationic complex, n =1)
H-B (neutral complex, n = 0)
L = P(OCH$_2$)$_3$CEt

($\Delta\Delta G$ = 6.1 kcal/mol) for cationic [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me]$^+$ than for neutral TpRu(P(OCH$_2$)$_3$CEt)(NCMe)Me; hence, the computed ground state free energy binding difference of 6.1 kcal/mol for NCMe is directly translated into the transition state free energy difference for benzene C−H activation, $\Delta\Delta G^{\ddagger}_{\mathrm{inter}} \approx 6$ kcal/mol, favoring the Tp complex (Scheme 7). From the five-coordinate intermediates that result from NCMe dissociation, namely, [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)Me]$^+$ and TpRu(P(OCH$_2$)$_3$CEt)(NCMe)Me, the calculated activation energies for benzene C−H activation are identical at 20.7 kcal/mol.

Intramolecular pyrazolyl C−H activations were calculated via initial NCMe dissociation; dissociation of a pyrazolyl ring and subsequent pyrazolyl C−H activation were also compared (Scheme 7). The calculated activation barriers for intramolecular C−H activation ($\Delta G^{\ddagger}_{\mathrm{intra}}$) are large for both complexes (54.7 and 61.6 kcal/mol). The results suggest that the main discriminating factors for the $\Delta\Delta G^{\ddagger}_{\mathrm{intra}}$ between the cationic and neutral complexes are more facile NCMe dissociation (cf. 23.3 and 17.2 kcal/mol in Scheme 7) by the neutral Tp complex and the greater free energy to dissociate a pyrazolyl ligand for the neutral TpRu(II) complex (less favorable by 10 kcal/mol for the Tp complex; cf. 11.8 and 22.1 kcal/mol, C(pz)$_4$ and Tp, respectively, in Scheme 7).

The calculated activation barriers for intramolecular pyrazolyl C−H activation by a dissociative pathway are too large for both [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me]$^+$ and TpRu(P(OCH$_2$)$_3$CEt)(NCMe)Me to be competitive with intermolecular benzene C−H activation (Scheme 7). However, a key finding from the simulations is that intramolecular C−H activation of a pyrazolyl ring can occur without dissociation of acetonitrile (Scheme 8). The large $\Delta\Delta G^{\ddagger}_{\mathrm{intra}}$ (12.9 kcal/mol) for intramolecular pyrazolyl C−H activation without NCMe dissociation mirrors the 10 kcal/mol difference in free energy to go from the hypothetical 16-electron κ^3 intermediate to a κ^2 linkage isomer in which the 5-pz C−H bond is agostically ligated to Ru (see Scheme 7). Thus, the calculated energetics for intramolecular C−H activation reflect the expected greater difficulty in dissociating an arm for anionic Tp compared to neutral C(pz)$_4$. The calculations reproduce experimental trends in that the cationic complex [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me]$^+$ is predicted to show a preference for intramolecular pyrazolyl C−H activation ($\Delta G^{\ddagger}_{\mathrm{intra}}$ = 29.8 kcal/mol versus $\Delta G^{\ddagger}_{\mathrm{inter}}$ = 44.0 kcal/mol), while the neutral complex TpRu(P(OCH$_2$)$_3$CEt)(NCMe)Me is predicted to favor intermolecular benzene C−H activation ($\Delta G^{\ddagger}_{\mathrm{intra}}$ = 42.7 versus $\Delta G^{\ddagger}_{\mathrm{inter}}$ = 37.9 kcal/mol).

Scheme 8. Computed Reaction Coordinate for Intramolecular Pyrazolyl C−H Activation without Dissociation of NCMe by Cationic (EX = C(pyrazolyl); black text) and Neutral (EX = BH, red text) Ru(II) Complexes



E-X = Pz-C (cationic complex)
H-B (neutral complex)
L = P(OCH$_2$)$_3$CEt

Summary and Conclusions. The Ru(II) complex **10** undergoes intramolecular C−H activation of the 5-position of a pyrazolyl ring rather than desired intermolecular benzene C−H activation. Computational studies provide a rationalization. Direct intramolecular pyrazolyl C−H activation by [(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me]$^+$ is shown by density functional theory calculations to occur with a smaller $\Delta G^{\ddagger}_{\mathrm{intra}}$ than the complex $\mathrm{TpRu(P(OCH_2)_3CEt)(NCMe)Me}$. We propose that the calculated $\Delta\Delta G^{\ddagger}_{\mathrm{intra}}$ of 12.9 kcal/mol is largely a result of the difference in energy required to dissociate a pyrazolyl ring. The tighter coordination of the pyrazolyl rings of the anionic Tp ligand of the TpRu complex raises the overall activation barrier for intramolecular pyrazolyl C−H activation. Successful catalytic olefin hydroarylation by cationic Ru(II) complexes of the type $\mathrm{[(PPA)Ru(L)(NCMe)Ph]^+}$ (PPA = poly(pyrazolyl)alkane) will require inhibition of the facile intramolecular C−H activation observed for $\mathrm{[(C(pz)_4)Ru(P(OCH_2)_3CEt)(NCMe)Me]^+}$.

■ EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer [$\mathrm{O_2}$ (g) < 15 ppm for all reactions]. THF was dried by distillation from sodium/benzophenone. Pentane was distilled over $\mathrm{P_2O_5}$. Acetonitrile and diethyl ether were dried by distillation from $\mathrm{CaH_2}$. Hexanes, benzene, and methylene chloride were purified by passage through a column of activated alumina. Benzene-d_6, acetonitrile-d_3, methylene chloride-d_2, nitromethane-d_3, and chloroform-d_1 were stored under a $\mathrm{N_2}$ atmosphere over 4 Å molecular sieves. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 300 MHz Spectrometer, a Varian Inova 500 MHz Spectrometer, or a Bruker Avance DRX 600 MHz spectrometer. ^{13}C{^{1}H} NMR spectra were recorded on a Varian Inova 500 MHz Spectrometer (operating frequency 125 MHz) or a Bruker Avance DRX 600 MHz spectrometer (operating frequency 201 MHz). All ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced against residual proton signals (^{1}H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C{^{1}H} NMR). ^{31}P{^{1}H} NMR spectra were obtained on a Varian Mercury Plus 300 MHz (operating frequency 121 MHz) spectrometer and referenced against an external standard of $\mathrm{H_3PO_4}$ (δ = 0 ppm). ^{19}F NMR spectra were obtained on a Varian Mercury Plus 300 MHz (operating frequency 282 MHz) spectrometer and referenced against an external standard of hexafluorobenzene (δ = −164.9 ppm). All X-ray structures were obtained on a Bruker APEX-II CCD apparatus.

Electrochemical experiments were performed under a nitrogen atmosphere using a BAS Epsilon Potentiostat. Cyclic voltammograms were recorded in NCMe using a standard three electrode cell from −1700 to 1700 mV at 100 mV/s with a glassy carbon working electrode and tetrabutylammonium hexafluorophosphate as electrolyte. All potentials are reported versus normal hydrogen electrode (NHE) using ferrocene as the internal standard. Elemental analyses were performed by Atlantic Microlabs, Inc. High-resolution mass spectra were acquired in electrospray ionization (ESI) mode from samples dissolved in a 3:1 acetonitrile/water solution containing sodium trifluoroacetate (NaTFA). Mass spectra are reported for $\mathrm{M^+}$ for monocationic complexes or for $\mathrm{[M + H^+]}$ or $\mathrm{[M + Na^+]}$ for neutral complexes, using $\mathrm{[Na(NaTFA)_{\mathit{x}}]^+}$ clusters as an internal standard. In all cases, observed isotopic envelopes were consistent with the molecular composition reported. Spectra were collected on a Bruker BioTOF-Q, a PerkinElmer Axion2 TOF, a Shimadzu IT-TOF, a Bruker MaXis Impact, an Agilent 6230 TOF, or a Waters Xevo G2Qtof. The preparation, isolation, and characterization of $[(\eta^6\text{-}p\text{-cymene})\mathrm{Ru(Br)}(\mu\text{-Br})]_2$,[73] $\mathrm{NaBAr'_4}$,[74] and $\mathrm{Ph_2Mg[THF]_2}$[14] have been previously reported. $\mathrm{P(OCH_2)_3CEt}$ was obtained from a commercial source and purified by dissolution in hexanes and filtration through Celite. The filtrate was concentrated to dryness to yield a white solid. All other reagents were used as purchased from commercial sources.

Tetrakis(1-pyrazolyl)methane. The synthesis of $\mathrm{C(pz)_4}$ has been previously reported.[75,76] We developed an alternate procedure. Pyrazole (13.437 g, 0.19737 mol) and $\mathrm{[Bu_4N][HSO_4]}$ (2.795 g, 0.008232 mol) were dissolved in $\mathrm{CCl_4}$ (200 mL) and transferred to a 500 mL round-bottom flask. $\mathrm{K_2CO_3}$ (27.90 g, 0.2013 mol) was added in small portions with stirring. KOH flakes (57.810 g, 1.0304 mol) were added to the flask, and the reaction mixture was stirred at reflux (under nitrogen) for 3 d. The reaction mixture was cooled and filtered through Celite (~1/2″). The flask and Celite were washed with methylene chloride, yielding a reddish filtrate. The filtrate was then eluted through approximately 1 inch of silica, and the silica was washed with copious amounts of methylene chloride until the eluate was almost colorless. The yellow eluate was collected and dried under reduced pressure. The yellow oil was dissolved in diethyl ether and dried under reduced pressure. A minimal amount of diethyl ether was added to the flask, and the flask was placed in the freezer. A white solid precipitated. The solid was collected on a fine porosity frit, washed with a minimal amount of cold diethyl ether followed by pentane, and dried under vacuum. A second batch was isolated by reduction of the filtrate to dryness, yielding an oil, which was then dissolved in a minimal amount of fresh ether and allowed to slowly evaporate at room temperature (1.504 g, 11% yield).

(η^6-*p*-Cymene)Ru(P(OCH$_2$)$_3$CEt)Br$_2$ (1). The binuclear complex $[(\eta^6\text{-}p\text{-cymene})\mathrm{Ru(Br)}(\mu\text{-Br})]_2$ (2.726 g, 3.450 mmol) and $\mathrm{P(OCH_2)_3CEt}$ (1.4111 g, 8.692 mmol) were combined in a 1 L round-bottom flask with 400 mL of methylene chloride. The reaction mixture was stirred at room temperature for 2 h. The volume of the solution was reduced *in vacuo* to ~50 mL. Hexanes were added to yield a reddish-orange precipitate. The solid was collected on a fine porosity frit by filtration and dried *in vacuo* to yield a reddish-orange solid (3.7293 g, 97%). ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$) δ 5.62 (d, 2H, $^3J_{\mathrm{HH}}$ = 6 Hz, *p*-cymene H), 5.49 (d, 2H, $^3J_{\mathrm{HH}}$ = 6 Hz, *p*-cymene H), 4.36 (d, 6H, $^3J_{\mathrm{HP}}$ = 5 Hz, $\mathrm{P(OC}\mathit{H}_2\mathrm{)_3CCH_2CH_3}$), 3.00 (sept, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$)), 2.28 (s, 3H, *p*-cymene $\mathrm{C}\mathit{H}_3$), 1.26 (q, 2H, $^3J_{\mathrm{HH}}$ = 8 Hz, $\mathrm{P(OCH_2)_3CC}\mathit{H}_2\mathrm{CH_3}$), 1.22 (d, $^3J_{\mathrm{HH}}$ = 7 Hz, 6H, $\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$), 0.83 (t, $^3J_{\mathrm{HH}}$ = 8 Hz, 3H, $\mathrm{P(OCH_2)_3CCH_2C}\mathit{H}_3$). ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{CDCl_3}$) δ 110.6, 103.8 (each a s, *p*-cymene $\mathrm{C_{Ar}}$), 89.9 (d, $^2J_{\mathrm{CP}}$ = 8 Hz, *p*-cymene $\mathrm{C_{Ar}}$), 89.1 (d, $^2J_{\mathrm{CP}}$ = 6 Hz, *p*-cymene $\mathrm{C_{Ar}}$), 75.7 (d, J_{HP} = 8 Hz, $\mathrm{P(OCH_2)_3CCH_2CH_3}$)), 36.0 (d, J = 32 Hz, $\mathrm{P(OCH_2)_3CCH_2CH_3}$), 30.98 (s, $\mathrm{CH(CH_3)_2}$), 23.4 (s, $\mathrm{P(OCH_2)_3CCH_2CH_3}$), 22.3 (s, $\mathrm{CH(CH_3)_2}$), 19.3 (s, $\mathrm{CH(CH_3)_2}$), 7.3 (s, $\mathrm{P(OCH_2)_3CCH_2CH_3}$). ^{31}P{^{1}H} NMR (121 MHz, $\mathrm{CDCl_3}$) δ 110.5. Anal. Calcd for $\mathrm{C_{16}H_{25}Br_2O_3PRu}$. C, 34.49; H, 4.53; Found C, 34.48; H, 4.57%.

(η^6-*p*-Cymene)Ru(P(OCH$_2$)$_3$CEt)(Br)Ph (2). Complex **1** (0.3551 g, 0.6373 mmol) was placed in THF (20 mL) in a round-bottom flask, yielding a heterogeneous mixture. $\mathrm{Ph_2Mg(THF)_2}$ (0.1641 g, 0.5085 mmol) was dissolved in THF (20 mL). The $\mathrm{Ph_2Mg(THF)_2}$ solution was added to the round-bottom flask containing complex **1**. The reaction mixture was stirred at room temperature for 1 h, and the reaction mixture slowly became bright yellow and homogeneous. The THF was removed *in vacuo*, and 40 mL of benzene was added to the flask. The reaction was stirred for 15 min and then filtered through Celite. The benzene solution was eluted through 1/2 in. of silica followed by THF washes. All solvent was removed, and ~5 mL of methylene chloride was added followed by hexanes to induce precipitation. The precipitate was collected on a fine porosity frit and dried *in vacuo* to yield a bright yellow solid (0.3362 g, 95% yield). ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$) δ 7.66−7.60 (m, 2H, phenyl), 6.93−6.88 (m, 2H, phenyl), 6.88−6.83 (m, 1H, phenyl), 5.45 (dd, 1H, $^3J_{\mathrm{HH}}$ = 6 Hz, $^3J_{\mathrm{HP}}$ = 1 Hz, *p*-cymene H), 5.44 (dd, 1H, $^3J_{\mathrm{HH}}$ = 6 Hz, $^3J_{\mathrm{HP}}$ = 1 Hz, *p*-cymene H), 5.32 (dd, 1H, $^3J_{\mathrm{HH}}$ = 6 Hz, $^3J_{\mathrm{HP}}$ = 1 Hz, *p*-cymene H), 4.98 (dd, 1H, $^3J_{\mathrm{HH}}$ = 6 Hz, $^3J_{\mathrm{HP}}$ = 1 Hz, *p*-cymene H), 4.24−4.17 (m, 6H, $\mathrm{P(OC}\mathit{H}_2\mathrm{)_3CCH_2CH_3}$), 2.73 (sept, 1H, $^2J_{\mathrm{HH}}$ = 7 Hz, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 1.84 (s, 3H, *p*-cymene $\mathrm{C}\mathit{H}_3$), 1.23−1.13 (overlapping multiplets, 8H, coincidental overlap of $\mathrm{P(OCH_2)_3CC}\mathit{H}_2\mathrm{CH_3}$ and $\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$), 0.80 (t, 3H, $^3J_{\mathrm{HH}}$ = 8 Hz, $\mathrm{P(OCH_2)_3CCH_2C}\mathit{H}_3$). ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{CDCl_3}$) δ 154.2 (d, $^2J_{\mathrm{CP}}$ = 30 Hz, ipso of phenyl), 142.9 (d, $^3J_{\mathrm{PC}}$ = 5 Hz, phenyl), 126.6 (s, phenyl), 121.9 (s, phenyl), 117.4 (d, $^3J_{\mathrm{PC}}$ = 5 Hz, ipso of *p*-cymene $\mathrm{C_{Ar}}$), 109.8 (d, $^3J_{\mathrm{PC}}$ = 5 Hz, *ipso* of *p*-cymene $\mathrm{C_{Ar}}$), 93.6 (d, $^2J_{\mathrm{CP}}$ = 4 Hz, *p*-cymene $\mathrm{C_{Ar}}$), 91.0 (d, $^2J_{\mathrm{CP}}$ = 10 Hz, *p*-cymene $\mathrm{C_{Ar}}$), 88.6 (d, $^2J_{\mathrm{CP}}$ = 3 Hz, *p*-cymene $\mathrm{C_{Ar}}$) 88.3 (s, *p*-cymene $\mathrm{C_{Ar}}$), 74.9 (d, $^2J_{\mathrm{CP}}$ = 8 Hz, $\mathrm{P(OCH_2)_3CCH_2CH_3}$), 35.6 (d, $^3J_{\mathrm{CP}}$ = 32 Hz, $\mathrm{P(OCH_2)_3CCH_2CH_3}$), 31.2 (s, $\mathit{CH}\mathrm{(CH_3)_2}$), 23.6, 23.3, 22.2 (all s, $\mathrm{CH(CH_3)_2}$ and $\mathrm{P(OCH_2)_3CCH_2CH_3}$), 18.7 (s, *p*-cymene $\mathrm{CH_3}$), 7.3 (s, $\mathrm{P(OCH_2)_3CCH_2CH_3}$). ^{31}P{^{1}H} NMR (121 MHz, $\mathrm{CDCl_3}$) δ 123.7. Anal. Calcd for $\mathrm{C_{22}H_{30}BrO_3PRu}$. C, 47.66; H, 5.45; Found C, 46.62; H, 5.40%. HR-MS: $\mathrm{[M + Na^+]}$ obsd (%), calcd (%), ppm: 576.0067 (52), 576.0061 (60), 1.1; 577.0058 (92), 577.0053 (94), 0.9; 578.0063 (42), 578.0060 (52.5), 0.5; 579.0054 (100), 579.0048 (100), 1.1.

[(κ^3-*N*,*C*^{5},*N*)C(pz)$_4$]Ru(P(OCH$_2$)$_3$CEt)(NCMe)Br (3). Complex **2** (0.0747 g, 0.134 mmol) and C(pz)$_4$ (0.0394 g, 0.1407 mmol) were dissolved in ~5 mL of NCMe in a pressure tube. The reaction mixture was heated for 19 h at 90 °C. The reaction mixture was brought into the glovebox and allowed to cool to room temperature. The mixture was filtered through Celite, and the yellow filtrate was reduced to dryness. The solid was washed with THF followed by benzene. The remaining solid was dissolved in a minimal amount of methylene chloride, and diethyl ether was added to induce a precipitate. The solid was collected on a fine porosity frit, washed with pentane, and dried under vacuum to yield a yellow solid (0.0321 g, 35% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.27 (d, 1H, $^3J_{HH} = 3$ Hz, C(pz)$_4$), 8.44 (s, 1H, C(pz)$_4$), 8.04 (m, 2H, overlapping C(pz)$_4$), 7.89 (s, 1H, C(pz)$_4$), 7.43 (t, 1H, $^3J_{HH} = 1$ Hz, C(pz)$_4$), 6.72 (s, 1H, C(pz)$_4$), 6.36 (dt, 1H, $^3J_{HH} = 4$ Hz, $^3J_{HH} = 1.6$ Hz, C(pz)$_4$), 6.25 (t, 1H, $^3J_{HH} = 1$ Hz, C(pz)$_4$), 6.08 (t, 1H, $^3J_{HH} = 4$ Hz, C(pz)$_4$), 5.91 (d, 1H, $^3J_{HH} = 4$ Hz, C(pz)$_4$), 4.28 (d, 6H, $^3J_{HP} = 5$ Hz, $P(OC\mathit{H}_2)_3CCH_2CH_3$), 2.29 (s, 3H, $NCC\mathit{H}_3$), 1.23 (q, 2H, $^3J_{HH} = 8$ Hz, $P(OCH_2)_3CC\mathit{H}_2CH_3$), 0.83 (t, 3H, $^3J_{HH} = 8$ Hz, $P(OCH_2)_3CCH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2) δ 170.4 (d, $^2J_{CP} =$ 18 Hz Ru−C(pz)$_4$), 148.5, 146.5, 144.5, 143.5, 141.4, 140.3, 130.7, 121.9, 109.3, 107.2, 107.0, 96.3 (each a s, C(pz)$_4$), 74.6 (d, $^2J_{CP} = 7$ Hz, $P(OCH_2)_3CCH_2CH_3$), 35.6 (d, $^3J_{CP} = 31$ Hz, $P(OCH_2)_3CCH_2CH_3$), 24.0 (s, $P(OCH_2)_3CCH_2CH_3$), 7.5 (s, $P(OCH_2)_3CCH_2CH_3$), 4.8 (s, $NCCH_3$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) δ 133.4. HR-MS: [M − H$^-$] obsd (%), calcd (%), ppm: 660.9983 (54), 660.9969 (61), 2.1; 661.9960 (77), 661.9961 (94), −0.2; 663.0003 (44), 662.9967 (53), 5.5; 663.9978 (100), 663.9956 (100), 3.3.

(C(pz)$_4$)Ru(PPh$_3$)Cl$_2$ (5). C(pz)$_4$ (0.3095 g, 1.104 mmol) and $RuCl_2(PPh_3)_3$ (1.001 g, 1.045 mmol) were combined in a 50 mL round-bottom flask and dissolved in toluene (25 mL). The reaction mixture was heated to reflux overnight. The brown solution gradually turned tan-yellow, and a yellow precipitate formed. The flask was removed from heat and allowed to cool to room temperature. Hexanes (10 mL) were added to complete precipitation. The yellow solid was collected on a fine porosity frit and washed with a small quantity of toluene (5 mL) followed by washing with pentane. The yellow solid was dried *in vacuo* to yield a brownish-yellow powder (0.5883 g, 79% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, 1H, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 3- or 5-position), 8.64 (s, 1H, C(pz)$_4$ 3- or 5-position), 8.28 (d, 1H, $^3J_{HH} = 3$ Hz, C(pz)$_4$ 3- or 5-position), 8.16 (d, 1H, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 3- or 5-position), 7.90−7.79 (m, 6H, PPh$_3$, *ortho* protons), 7.33−7.19 (m, 9H, PPh$_3$, overlapping signals for *meta* and *para* protons), 6.94 (vt, 1H, C(pz)$_4$ 4 position), 6.87 (d, 2H, $^3J_{HH} = 3$ Hz, C(pz)$_4$ 3- or 5-position), 6.76 (m, 2H, C(pz)$_4$ 3- or 5-position), 6.52 (d, 1H, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 4-position), 5.90 (dd, 2H, $^3J_{HH} = 3.0$ Hz, $^3J_{HH} = 2.3$ Hz, C(pz)$_4$ 4-position). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 151.3, 148.3, 144.6, 136.0, 134.8, 134.5, 111.3, 109.6, 109.3 (each a s, C(pz)$_4$), 135.1 (d, $^2J_{CP} = 9$ Hz, *ortho*-PPh$_3$), 132.5 (s, *ipso*-PPh$_3$), 129.0 (s, *para*-PPh$_3$), 127.7 (d, $^3J_{CP} = 9$ Hz, *meta*-PPh$_3$), 94.4 (s, C(pz)$_4$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) δ 52.4. Anal. Calcd for $C_{31}H_{27}Cl_2N_8PRu$. C, 52.11; H, 3.81; N, 15.68; Found C, 52.42; H, 3.94; N, 14.78%. HR-MS [$C_{33}H_{30}N_9PClRu^+$] obsd (%), calcd (%), ppm: 718.1056 (41), 718.1100 (41), −6.1; 719.1069 (58), 719.1102 (61), −4.5; 720.1079 (100), 720.1094 (100), −2.0; 721.1091 (46), 721.1106 (47), −2.0; 722.1070 (71), 722.1091 (75), −2.9. HR-MS [$C_{33}H_{27}N_8O_2F_3PRu^+$] obsd (%), calcd (%), ppm: 754.1002 (33), 754.1002 (34), 0.0; 755.1001 (39), 755.0997 (45), 0.5; 756.1006 (52), 756.1003 (58), 0.4; 757.0985 (100), 757.0993 (100), −1.1; 758.1021 (34), 758.1018 (35), 0.4; 759.1018 (53), 759.1002 (54), 2.2. See above for explanation of HR-MS.

(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)Cl$_2$ (6). Complex **5** (0.457 g, 0.639 mmol) and $P(OCH_2)_3CEt$ (0.415 g, 2.56 mmol) were combined in a round-bottom flask with 20 mL of chloroform. The reaction mixture was heated to reflux overnight. The solution initially turned dark brown, and then upon additional heating, a yellow precipitate formed. The reaction mixture was reduced to ~5 mL, and hexanes were added to induce precipitation. The precipitate was collected on a fine porosity frit and washed with hexanes. The yellow precipitate was placed into a round-bottom flask with 10 mL of chloroform, and the solution was heated to reflux for 6 h. After the solution was cooled to room temperature, the resulting solid was collected on a fine porosity frit and washed with ~5 mL of chloroform and pentane. The yellow solid was dried under vacuum (0.392 g, 99% yield). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.65 (dt, 1H, $^3J_{HH} =$ 2 Hz, $^4J_{HP} = 1$ Hz, C(pz)$_4$ 3- or 5-position), 8.54 (dd, 1H, $^3J_{HH} = 2$ Hz, $^4J_{HP} = 1$ Hz, C(pz)$_4$ 3- or 5-position), 8.32 (d, 1H, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 3- or 5-position), 8.20 (d, 1H, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 3- or 5-position), 8.13 (dd, 2H, $^3J_{HH} = 2$ Hz, $^4J_{HP} = 1$ Hz, C(pz)$_4$ 3 or 5 positions), 7.06 (dd, 2H, $^3J_{HH} = 3$ Hz, $^4J_{HP} = 1$ Hz, C(pz)$_4$ 3- or 5-position), 6.95 (dd, 1H, $^3J_{HH} =$ 3 Hz, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 4-position), 6.62 (dt, 1H, $^3J_{HH} = 3$ Hz, $^3J_{HH} =$ 2 Hz, C(pz)$_4$ 4-position), 6.33 (dd, 2H, $^3J_{HH} = 3$ Hz, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 4-position), 4.38 (d, 6H, $^3J_{HP} = 5$ Hz, $P(OC\mathit{H}_2)_3CCH_2CH_3$,), 1.28 (q, 2H, $^3J_{HH} = 8$ Hz, $P(OCH_2)_3CC\mathit{H}_2CH_3$), 0.86 (t, 3H, $^3J_{HH} = 8$ Hz, $P(OCH_2)_3CCH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2) δ 151.6, 148.3, 145.6, 136.9, 133.9, 133.0, 112.1, 109.6, 109.2 (s, C(pz)$_4$ aromatic C), 94.7 (s, *C*(pz)$_4$), 74.9 (d, $^2J_{CP} = 7$ Hz, $P(OCH_2)_3CCH_2CH_3$), 24.1 (s, $P(OCH_2)_3CCH_2CH_3$), 7.5 (s, $P(OCH_2)_3CCH_2CH_3$). ^{13}C NMR (75 MHz, CD_3NO_2) δ 152.3, 148.9, 146.7, 138.5, 135.6, 134.7, 112.9, 110.0, 109.7, (each a s, C(pz)$_4$ aromatic C), 95.6 (s, C(pz)$_4$), 75.4 (d, $^2J_{CP} = 8$ Hz, $P(OCH_2)_3CCH_2CH_3$), 36.5 (d, $^3J_{CP} = 31$ Hz, $P(OCH_2)_3CCH_2CH_3$), 24.3 (s, $P(OCH_2)_3CC\mathit{H}_2CH_3$), 7.5 (s, $P(OCH_2)_3CCH_2C\mathit{H}_3$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) δ 128.1. HR-MS: [M$^+$ Na$^+$] obsd (%), calcd (%), ppm: 635.9969 (61), 635.9951 (64), 2.9; 636.9961 (100), 636.9942 (100), 2.9; 637.9963 (47), 637.9943 (52), 3.1; 638.9954 (94), 638.9935 (94), 3.0.

[(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Cl]Cl (7). Complex **6** (0.8550 g, 1.391 mmol) was suspended in NCMe (25 mL) to give a yellow heterogeneous mixture. While heating at reflux overnight the reaction mixture became homogeneous, and the color changed to green-yellow, then to brown, and finally back to yellow. The solution was filtered through Celite. The filtrate was reduced *in vacuo* to ~2 mL, and ~2 mL of methylene chloride was added followed by the addition of diethyl ether to induce precipitation. The off-white solid was collected over a fine porosity frit, washed with diethyl ether and pentane, and dried under reduced pressure (0.6486 g, 71% yield). Note: a small amount of a second product is present but is removed in the next step (reaction with NaBAr′$_4$). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.96 (d, 1H, $^3J_{HH} = 3$ Hz, C(pz)$_4$ 3- or 5-position), 8.74, 8.24, 8.01 (each a s, 1H, C(pz)$_4$ 3- or 5-position), 8.34 (s, 1H, C(pz)$_4$ 4-position), 8.11 (d, 1H, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 3- or 5-position), 7.37 (d, 1H, $^3J_{HH} = 3$ Hz, C(pz)$_4$ 3- or 5-position), 7.12 (d, 1H, $^3J_{HH} = 3$ Hz, C(pz)$_4$ 3- or 5-position), 7.08 (s, 1H, C(pz)$_4$ 3- or 5-position), 6.69, 6.55, 6.42 (s, 1H, C(pz)$_4$ 4-position), 4.41 (d, 6H, $^3J_{HP} = 5$ Hz, $P(OC\mathit{H}_2)_3CCH_2CH_3$), 2.43 (s, 3H, $NCC\mathit{H}_3$), 1.32 (q, 2H, $^3J_{HH} = 8$ Hz, $P(OCH_2)_3CC\mathit{H}_2CH_3$), 0.87 (t, 3H, $^3J_{HH} = 8$ Hz, $P(OCH_2)_3CCH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2) δ 151.0, 150.8, 147.3, 146.2, 138.2, 135.8, 134.5, 134.4, 113.1, 110.1, 109.9, 109.5 (each a s, C(pz)$_4$ aromatic C), 124.9 (s, $NCCH_3$), 94.6 (s, C(pz)$_4$), 75.3 (d, $^2J_{CP} = 7$ Hz, $P(OCH_2)_3CCH_2CH_3$), 36.1 (d, $^3J_{CP} = 32$ Hz, $P(OCH_2)_3CCH_2CH_3$), 23.8 (s, $P(OCH_2)_3CCH_2CH_3$), 7.5 (s, $P(OCH_2)_3CCH_2CH_3$) 5.3 (s, $NCCH_3$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) δ 128.1. HR-MS: [M$^+$] obsd (%), calcd (%), ppm: 617.0645 (23), 617.0640 (33.5), 0.8; 618.0636 (29), 618.0630 (38.5), 1; 619.0640 (52), 619.0634 (59.5), 1; 620.0633 (100), 620.0625 (100), 1.3; 621.0640 (27), 621.0634 (36), 1; 622.0631 (70), 622.0623 (75), 1.4.

[(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Cl][BAr′$_4$] (8). NaBAr′$_4$ (0.4783 g, 1.10 mmol) and complex **7** (0.700 g, 1.06 mmol) were combined in THF (15 mL). The reaction mixture was stirred at room temperature for 3 h. The solution was filtered through Celite, and the filtrate was reduced to dryness. The solid was dissolved in diethyl ether and loaded on a plug of neutral alumina. The plug was washed with diethyl ether. The plug was then washed with a 50/50 (v/v) solution of methylene chloride/diethyl ether. The eluate was collected and dried under reduced pressure to yield a yellow oil. The yellow oil was dissolved in a minimal amount of methylene chloride and placed under vacuum to afford a pale-yellow solid (0.8957 g, 57% yield). ^{1}H NMR (800 MHz, CD_2Cl_2) δ 8.78, 8.38 (each a s, 1H, C(pz)$_4$ 3- or 5-positions), 8.26 (d, 1H, $^3J_{HH} = 2$ Hz, C(pz)$_4$ 3- or 5-positions), 8.22, 8.18 (each a s, 1H, C(pz)$_4$ 3- or 5-positions), 7.93 (m, 1H, C(pz)$_4$ 3- or 5-positions), 7.72 (br s, 8H, BAr′$_4$ *ortho* position), 7.55 (br s, 4H, BAr′$_4$ *para* position), 7.37 (d, 1H, $^3J_{HH} = 3$ Hz, C(pz)$_4$ 3- or 5-positions), 6.98 (m, 1H, C(pz)$_4$ 3- or 5-positions), 6.80

(d, 1H, $^{3}J_{HP}$ = 3 Hz, C(pz)$_4$ 4-position), 6.68 (s, 1H, C(pz)$_4$ 4-position), 6.45, 6.36 (each a m, 1H, C(pz)$_4$ 4-position), 4.40 (d, 6H, $^{3}J_{HP}$ = 5 Hz, P(OCH_2)$_3$CCH$_2$CH$_3$), 2.43 (s, 3H, NCCH_3), 1.30 (q, 2H, $^{3}J_{HH}$ = 8 Hz, P(OCH$_2$)$_3$CCH_2CH$_3$), 0.87 (t, 3H, $^{3}J_{HH}$ = 8 Hz, P(OCH$_2$)$_3$-CCH$_2$CH_3). ^{13}C{^{1}H} NMR (201 MHz, CD$_2$Cl$_2$) δ 162.3 (four line pattern, $^{1}J_{CB}$ = 50 Hz, BAr′$_4$), 151.7, 150.5, 147.6, 146.3, 136.8, 135.1, 134.0, 133.6, 112.9, 110.0, 109.9, 109.8 (each a s, C(pz)$_4$) 135.3 (s, BAr′$_4$), 129.4 (q, $^{1}J_{CF}$ = 32 Hz, BAr′$_4$), 125.1 (q, $^{1}J_{CF}$ = 273 Hz, CF$_3$), 124.7 (s, NCCH$_3$), 118.0 (s, BAr′$_4$), 94.7 (s, *C*(pz)$_4$), 75.4 (d, $^{2}J_{CP}$ = 7 Hz, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 36.4 (d, $^{3}J_{CP}$ = 32 Hz, P(OCH$_2$)$_3$-CCH$_2$CH$_3$), 23.9 (s, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 7.5 (s, P(OCH$_2$)$_3$-CCH$_2$CH$_3$), 4.8 (s, NCCH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CD$_2$Cl$_2$) δ 128.3. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$) δ −63.7. Anal. Calcd for $C_{53}H_{38}BClF_{24}N_9O_3PRu$: C, 42.92; H, 2.58; N, 8.50; Found: C, 42.85; H, 2.70; N, 8.30%.

[(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(OTf)(NCMe)][BAr′$_4$] (9). In a thick-walled pressure tube, complex **8** (0.8796 g, 0.5932 mmol) was dissolved in 40 mL of methylene chloride. TMSOTf (1.318 g, 1.07 mL, 5.932 mmol) was added by syringe. The reaction mixture was heated to 100 °C overnight. The reaction vessel was brought back into the glovebox and allowed to cool to room temperature. The reaction mixture was added to 100 mL of hexanes and allowed to stir for 30 min. The desired product oiled out of solution. The hexanes solution was filtered through Celite, and the filtrate was discarded. The Celite was washed with methylene chloride, and the filtrate was placed in the flask with the oil. The methylene chloride was removed *in vacuo* to yield an oil. The oil was dissolved in a minimal amount of methylene chloride and placed in a vial, and the solvent was removed. After removing the solvent *in vacuo*, a minimal amount of diethyl ether was added, followed by removal of the volatiles to yield a low density yellow solid (0.7976 g, 84% yield). ^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ 8.82, 8.43 (m, 1H, C(pz)$_4$ 3- or 5-position), 8.30 (d, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$ 3- or 5-position), 8.26 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$ 3- or 5-position), 8.23 (dd, 1H, $^{3}J_{HH}$ = 2 Hz, $^{4}J_{HP}$ = 1 Hz, C(pz)$_4$ 3- or 5-position), 7.96 (m, 1H, C(pz)$_4$ 3- or 5-position), 7.77 (br s, 8H, BAr′$_4$ *ortho* position), 7.60 (br s, 4H, BAr′$_4$ *para* position), 7.42 (dd, 1H, $^{3}J_{HH}$ = 3 Hz, $^{4}J_{HP}$ = 1 Hz, C(pz)$_4$ 3- or 5-position), 7.02 (dd, 1H, $^{3}J_{HH}$ = 3 Hz, $^{4}J_{HH}$ = 2 Hz, C(pz)$_4$ 3- or 5-position), 6.85 (dd, 1H, $^{3}J_{HH}$ = 3 Hz, $^{4}J_{HP}$ = 1 Hz, C(pz)$_4$ 4-position), 6.72 (dt, 1H, $^{3}J_{HH}$ = 4 Hz, $^{4}J_{HH}$ = 2 Hz, C(pz)$_4$ 4-position) 6.49 (dd, 1H, $^{3}J_{HH}$ = 3 Hz, $^{4}J_{HH}$ = 2 Hz, C(pz)$_4$ 4-position), 6.40 (dd, 1H, $^{3}J_{HH}$ = 3 Hz, $^{4}J_{HH}$ = 2 Hz, C(pz)$_4$ 4-position) 4.45 (d, 6H, $^{3}J_{HP}$ = 5 Hz, P(OCH_2)$_3$CCH$_2$CH$_3$), 2.43 (s, 3H, NCCH_3), 1.34 (q, 2H, $^{3}J_{HH}$ = 8 Hz, P(OCH$_2$)$_3$CCH_2CH$_3$), 0.91 (t, 3H, $^{3}J_{HH}$ = 8 Hz, P(OCH$_2$)$_3$ CCH$_2$CH_3). ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$) δ 162.3 (four line pattern, $^{1}J_{CB}$ = 50 Hz, BAr′$_4$), 152.2, 151.3, 148.7, 146.6, 136.9, 134.9, 134.6, 133.8, 113.2, 110.2 (each a s, C(pz)$_4$, one resonance missing due to coincidental overlap), 129.5 (q, $^{1}J_{CF}$ = 32 Hz, BAr′$_4$), 125.2 (q, $^{1}J_{CF}$ = 273 Hz, CF$_3$), 135.4 (s, BAr′$_4$), 126.7 (s, NCCH$_3$), 118.1 (s, BAr′$_4$), 94.6 (s, *C*(pz)$_4$), 75.7 (d, $^{2}J_{CP}$ = 7 Hz, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 36.7 (d, $^{3}J_{CP}$ = 32 Hz, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 23.8 (s, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 7.5 (s, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 4.5 (s, NCCH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CD$_2$Cl$_2$) δ 127.7. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$) δ −63.2 (BAr′$_4$), −78.9 (OTf). Anal. Calcd for $C_{54}H_{38}BF_{27}N_9O_6PRuS$: C, 40.62 H, 2.40; N, 7.89; Found: C, 39.81; H, 2.62; N, 7.79%. HR-MS: [M$^+$] obsd (%), calcd (%), ppm: 731.0476 (24), 731.0471 (35), 0.6; 732.0469 (32), 732.0463 (42.5), 0.8; 733.0476 (48), 733.0469 (55), 0.9; 734.0467 (100), 734.046 (100), 1.0; 735.0485 (19), 735.0479 (30), 0.9; 736.0472 (48), 736.0465 (55), 1.0.

[(C(pz)$_4$)Ru(P(OCH$_2$)$_3$CEt)(NCMe)Me][BAr′$_4$] (10). In a round-bottom flask, 15 mL of benzene and complex **9** (0.1296 g, 0.08118 mmol) were combined to give a heterogeneous mixture. AlMe$_3$ (0.043 mL, 2 M in toluene, 0.085 mmol) was added by syringe in two portions with 15 min of stirring between each addition, during which time the reaction mixture became bright yellow and homogeneous. The reaction mixture was allowed to stir for 30 min followed by filtration through a plug of Celite. The solvent was removed to yield a yellow low-density solid (0.0801 g, 67% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 8.38 (br s, 8H, BAr′$_4$ *ortho* position), 7.95 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$), 7.92 (d, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 7.88 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$), 7.65 (br s, 4H, BAr′$_4$ *para* position), 7.38 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$), 7.30 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$), 7.00 (d, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 6.57 (d, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 5.90 (dd, 1H, $^{3}J_{HH}$ = 3 Hz, $^{4}J_{HH}$ = 2 Hz, C(pz)$_4$), 5.78 (m, 1H, C(pz)$_4$), 5.74 (d, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 5.44 (m, 1H, C(pz)$_4$), 5.35 (d, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 3.79 (d, 6H, $^{3}J_{HP}$ = 5 Hz, P(OCH_2)$_3$CCH$_2$CH$_3$), 0.98 (s, 3H, NCCH_3), 0.71 (d, 3H, $^{3}J_{HP}$ = 2 Hz, Ru−CH_3), 0.35 (q, 2H, $^{3}J_{HH}$ = 8 Hz, P(OCH$_2$)$_3$CCH_2CH$_3$), 0.17 (t, 3H, $^{3}J_{HH}$ = 8 Hz, P(OCH$_2$)$_3$CCH$_2$CH_3) ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$) δ 162.8 (four line pattern, $^{1}J_{CB}$ = 50 Hz, BAr′$_4$), 148.2, 147.0, 144.6, 144.0, 136.0, 133.8, 131.9, 131.6, 111.0, 108.8, 108.4, 108.1 (each a s, C(pz)$_4$ aromatic C), 135.4 (s, BAr′$_4$), 130.0 (q, $^{1}J_{CF}$ = 32 Hz, BAr′$_4$), 126.3 (s, NCCH$_3$), 118.1 (s, BAr′$_4$), 94.0 (*C*(pz)$_4$), (d, $^{2}J_{CP}$ = 7 Hz, P(OCH$_2$)$_3$ CCH$_2$CH$_3$), 23.0 (s, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 6.7 (s, P(OCH$_2$)$_3$ CCH$_2$CH$_3$), 2.2 (s, NCCH$_3$). Some of the resonances were not observed due to low solubility. ^{31}P{^{1}H} NMR (121 MHz, CD$_2$Cl$_2$) δ 135.1. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$) δ −62.8. HR-MS: [M$^+$] obsd (%), calcd (%), ppm: 597.1183 (40.7), 597.1186 (39.0), −0.5; 598.1175 (47.7), 598.1178 (44.0), −0.4; 599.1183 (58.1), 599.1185 (56), −0.3; 600.1175 (100), 600.11758 (100), 0.0; 601.1190 (32), 601.1199 (27.5), −1.4; 602.1179 (58.1), 602.1183 (55), −0.6.

[{(*N*,*C*^{5},*N*)C(pz)$_4$}Ru(P(OCH$_2$)$_3$CEt)(NCMe)$_2$][BAr′$_4$] (11). In a pressure tube with 3 mL of benzene, complex **10** (0.055 g, 0.5140 mmol) and NCMe (0.00314 g, 0.0766 mmol, 5 μL) were combined. The reaction mixture was heated at 75 °C for 3 h. The solution was filtered through Celite. The filtrate was reduced to yield an oil, to which ~0.5 mL of pentane was added. The solvent was removed *in vacuo* to yield a pale yellow low-density solid (0.0271 g, 53% yield). ^{1}H NMR (600 MHz, C$_6$D$_6$) δ 8.77 (d, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 8.39 (br s, 8H, BAr′$_4$ *ortho* position), 8.06 (d, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 7.75 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$), 7.69 (br s, 4H, BAr′$_4$ *para* position), 7.63 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$), 7.38 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$), 7.35 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$), 6.65 (d, 1H, $^{3}J_{HH}$ = 2 Hz, C(pz)$_4$) 5.96 (dd, 1H, $^{3}J_{HH}$ = 3 Hz, $^{4}J_{HP}$ = 2 Hz, C(pz)$_4$), 5.73 (t, 1H, $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 5.64 (m, 1H, C(pz)$_4$), 5.58 (d, 1H $^{3}J_{HH}$ = 3 Hz, C(pz)$_4$), 3.76 (d, 6H, $^{3}J_{HP}$ = 5 Hz, P(OCH_2)$_3$CCH$_2$CH$_3$), 1.03 (s, 3H, NCCH_3), 0.88 (s, 3H, NCCH_3), 0.33 (q, 2H, $^{3}J_{HH}$ = 8 Hz, P(OCH$_2$)$_3$CCH_2CH$_3$), 0.13 (t, 3H, $^{3}J_{HH}$ = 8 Hz, P(OCH$_2$)$_3$CCH$_2$CH_3). ^{13}C{^{1}H} NMR (201 MHz, C$_6$D$_6$) δ 164.6 (d, $^{2}J_{CP}$ = 20 Hz Ru−*C* pz), 162.5 (four lined pattern, $^{1}J_{CB}$ = 50 Hz, BAr′$_4$), 146.4, 143.2, 142.5, 141.6, 140.3, 135.1, 131.5, 117.4, 108.9, 107.2, 106.7 (each a s, C(pz)$_4$) 135.4 (s, BAr′$_4$), 130.0 (q, $^{1}J_{CF}$ = 32 Hz, BAr′$_4$), 125.8 (s, NCCH$_3$), 124.0 (s, NCCH$_3$), 117.8 (s, BAr′$_4$), 73.9 (d, $^{2}J_{CP}$ = 7 Hz, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 36.4 (d, $^{3}J_{CP}$ = 32 Hz, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 23.9 (s, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 6.19 (s, P(OCH$_2$)$_3$CCH$_2$CH$_3$), 1.40 (s, NCCH$_3$), 0.76 (s, NCCH$_3$). ^{31}P{^{1}H} NMR (121 MHz, CD$_2$Cl$_2$) δ 133.8. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$) δ −62.4. HR-MS: [M$^+$] obsd (%), calcd (%), ppm: 622.1127 (27), 622.1138 (36), −1.8; 623.1119 (36), 623.1130 (44), −1.8; 624.1114 (52), 624.1137 (57), −3.8; 625.1103 (100), 625.1127 (100), −3.9; 626.1147 (28), 626.1151 (27), −0.6; 627.1124 (60), 627.1135 (54), −1.8.

NMR Scale Conversion of Complex 10 to 8. Complex **10** (0.0078 g, 0.0053 mmol) was dissolved in 0.5 mL of C$_6$D$_6$ and added to a screwtop NMR tube. HCl·Et$_2$O (5 μL, 0.0054 mmol) was added to the NMR tube via a syringe. The tube was shaken, and the red-orange solution turned yellow. The headspace of the NMR tube was analyzed by GC-MS, and CH$_4$ was detected. The C$_6$D$_6$ was decanted, and the remaining yellow oil was dissolved in CD$_2$Cl$_2$. Upon acquiring a ^{1}H NMR spectrum complex **8** and CH$_4$ were observed.

NMR Scale Conversion of Complex 10 to 11. Complex **10** (0.0118 g, 0.00807 mmol) and NCMe (42 μL, 0.0081 mmol, 0.19 M) were dissolved in 0.5 mL of C$_6$D$_6$ and added to a J-Young NMR tube. The solution was heated in a 75 °C oil bath and monitored by ^{1}H NMR spectroscopy every hour until complete conversion to complex **11** was observed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, representative NMR spectra and details of computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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