Combined Experimental and Computational Study of TpRu{P(pyr)$_3$}(NCMe)Me (pyr = *N*-pyrrolyl): Inter- and Intramolecular Activation of C−H Bonds and the Impact of Sterics on Catalytic Hydroarylation of Olefins

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Complexes of the type TpRu{P(pyr)$_3$}(L)R {L = PPh_3 or NCMe; R = Cl, OTf (OTf = trifluoromethanesulfonate), Me, or Ph; Tp = hydridotris(pyrazolyl)borate; pyr = *N*-pyrrolyl} and TpRu{κ^2-*P*,*C*-P(pyr)$_2$(NC_4H_3)}NCMe have been synthesized and isolated. TpRu{P(pyr)$_3$}(NCMe)Me initiates intermolecular C−H activation of benzene to form TpRu{P(pyr)$_3$}(NCMe)Ph and, in the absence of benzene, intramolecular C−H activation of a pyrrolyl ring to form the cyclometalated species TpRu{κ^2-*P*,*C*-P(pyr)$_2$(NC_4H_3)}NCMe. TpRu{P(pyr)$_3$}(NCMe)Ph catalyzes the hydrophenylation of ethylene in benzene to produce ethylbenzene in low yields. Experimental and computational analyses of the hydrophenylation of ethylene by TpRu{P(pyr)$_3$}(NCMe)Ph suggest that inefficient catalysis is not due to difficulty in the C−H activation of benzene by the active catalyst species, but rather likely arises from the steric bulk of the tris-*N*-pyrrolyl phosphine ligand, which inhibits coordination of ethylene and thus thwarts C−C bond formation.

Introduction

The use of transition metal catalysts to activate carbon−hydrogen bonds is a potentially attractive tool for the functionalization of aliphatic and aromatic compounds.[1−9] A diversity of transition metal systems that direct stoichiometric C−H activation reactions are now known; however, the development of catalytic C−H functionalizations remains a challenge.[2,5,10] Currently, catalytic Suzuki, Heck, Sonogashira, Stille, Negishi, and related reactions provide powerful methods for C−C bond formation with aromatic substrates;[11−17] yet these methodologies suffer from the required incorporation of carbon−halide bonds into the aromatic precursor. Alternatively, the direct addition of aromatic C−H bonds across olefin C=C bonds (i.e., olefin hydroarylation) provides an atom-economical method for the formation of C−C bonds (Scheme 1).[18−39] Olefin hydroarylation

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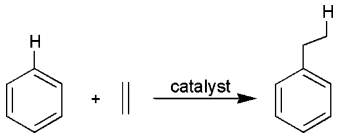
Scheme 1. Depiction of Olefin Hydroarylation Using Benzene and Ethylene as Substrates



offers the potential to improve reaction efficiency for synthetic organic chemistry as well as commodity chemical processes such as the preparation of ethylbenzene, cumene, and long-chain alkyl benzenes. Currently, alkyl arenes are produced on a multi-billion-pound scale predominantly by acid-catalyzed reactions that suffer from several limitations (e.g., poor selectivity and high energy input).[40,41]

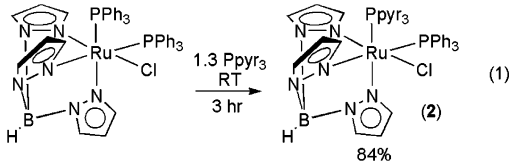
Our group has been investigating the use of $TpRu^{II}$ {Tp = hydridotris(pyrazolyl)borate} complexes as homogeneous catalysts for the hydroarylation of olefins.[42−48] For example, TpRu(CO)(NCMe)Ph catalytically produces alkyl arenes from ethylene or simple α-olefins and arenes and is, to our knowledge, the most active homogeneous catalyst for the hydrophenylation of ethylene that proceeds through a metal-mediated C−H activation pathway.[42−44] In order to better understand the factors that control the catalysis and in an effort to access improved systems, we have sought to synthesize analogues of TpRu(CO)(NCMe)Ph by formally substituting CO with alternative neutral two-electron-donating ligands.

For TpRu(CO)(NCMe)Ph-catalyzed hydroarylation of olefins, mechanistic studies are consistent with a catalytic cycle that involves initial NCMe/olefin ligand exchange to form TpRu(L)(η^2-olefin)Ph, olefin insertion into the Ru−Ph bond to produce an unsaturated Ru−alkyl complex, and coordination of benzene followed by Ru-mediated C−H activation to release alkyl benzene.[43] We have recently disclosed benzene C−H activation and catalytic hydroarylation and hydrovinylation using $TpRu(PMe_3)(NCMe)R$ (R = Me or Ph).[49] These studies suggest that more electron-deficient systems {i.e., similar to TpRu(CO)(NCMe)R} are likely to be optimal for successful olefin hydroarylation. Along these lines, we now disclose the synthesis of $TpRu\{P(pyr)_3\}(NCMe)R$ (pyr = *N*-pyrrolyl; R = Me or Ph), which is electronically similar to TpRu(CO)(NCMe)R, including studies of stoichiometric C−H activation and catalytic hydroarylation of ethylene.

Results and Discussion

The ligand tris-*N*-pyrrolyl phosphine has been reported to have an overall donating ability similar to CO.[50] Thus, the tris-*N*-pyrrolyl phosphine ligand was targeted as a replacement for the CO ligand of TpRu(CO)(NCMe)R systems in order to render a complex electronically similar to TpRu(CO)(NCMe)R but with an enhanced steric profile to potentially control the regioselectivity of α-olefin insertion and, hence, control the regioselectivity of hydroarylation of α-olefins (i.e., linear to branched ratios of alkyl arenes).

The previously reported complex $TpRu(PPh_3)_2Cl$ reacts with tris-*N*-pyrrolyl phosphine at room temperature to produce $TpRu\{P(pyr)_3\}(PPh_3)Cl$ (**2**) in 84% isolated yield (eq 1). At room temperature, the ^1H NMR spectrum of $TpRu\{P(pyr)_3\}(PPh_3)Cl$ (**2**) exhibits broadening of the resonances due to the triphenylphosphine (7.48, 7.24, and 7.09 ppm) and tris-*N*-pyrrolyl phosphine ligands. At room temperature in the ^1H NMR spectrum of **2**, the hydrogen atoms of the coordinated $P(pyr)_3$ appear as a single broad resonance at 6.04 ppm spanning a window of approximately 480 Hz (300 MHz spectrometer). The ^{31}P NMR spectrum of **2** shows two doublets ($^2J_{PP}$ = 40 Hz) at 37.8 and 123.0 ppm due to the PPh_3 and $P(pyr)_3$ ligands, respectively.



The reaction of **2** in a mixture of refluxing THF and acetonitrile produces $TpRu\{P(pyr)_3\}(NCMe)Cl$ (**3**) in 92% isolated yield (eq 2). The combination of **3** and AgOTf (OTf = trifluoromethanesulfonate) at room temperature yields the product of chloride/triflate metathesis $TpRu\{P(pyr)_3\}(NCMe)OTf$ (**4**) (eq 3). Complex **4** has not been isolated pure (NMR spectroscopy reveals minor amounts of impurities) and is taken to the next step and purified after methylation. The addition of 1 equiv of Me_2Mg to **4** at room temperature gives $TpRu\{P(pyr)_3\}(NCMe)Me$ (**1**) in 79% isolated yield (eq 4). Consistent with asymmetric systems, complexes **3**, **4**, and **1** reveal nine unique Tp resonances in both ^1H and ^{13}C NMR spectra. Additionally, complex **4** exhibits a singlet in the ^{19}F NMR spectrum, and complex **1** exhibits an upfield doublet ($^3J_{HP}$ = 2 Hz) for the methyl ligand at 1.08 ppm in the ^1H NMR spectrum. Cyclic voltammetry of **1** shows a reversible Ru(III/II) oxidation at $E_{1/2}$ = 0.76 V (vs NHE), which suggests that complex **1** is slightly more electron-rich than TpRu(CO)(NCMe)Me {Ru(III/

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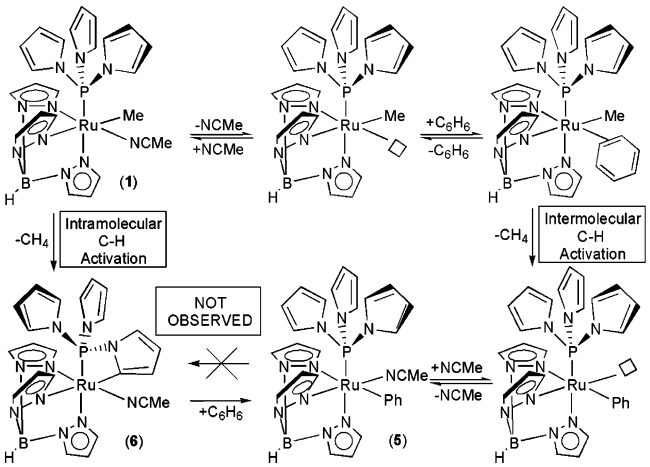
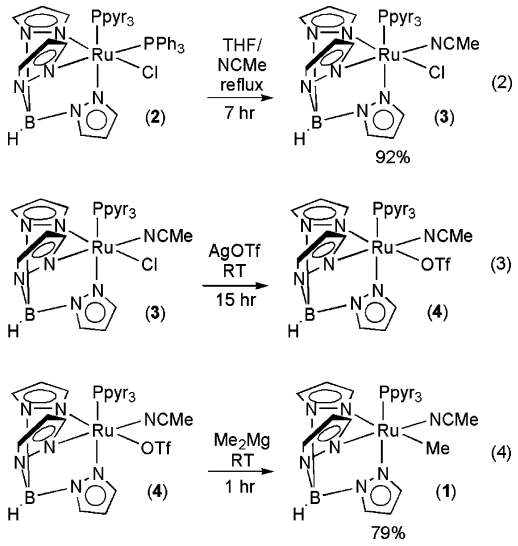
Scheme 2. Schematic Representation of the Conversion of TpRu{P(pyr)$_3$}(NCMe)Me (1) to TpRu{P(pyr)$_3$}(NCMe)Ph (5) via Intermolecular C−H Activation of C_6H_6 and TpRu{κ^2-*P,C*-P(pyr)$_2$(NC$_4$H$_3$)}NCMe (6) via Intramolecular C−H Activation of a Pyrrolyl Moiety[a]

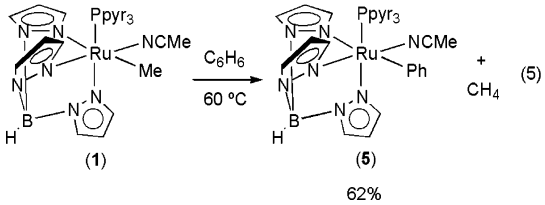


[a] Square indicates vacant coordination site.

II) $E_{1/2} = 0.95$ V}[42] yet significantly less electron-rich than TpRu(PMe$_3$)(NCMe)Me {Ru(III/II) $E_{1/2} = 0.10$ V}.[49]



Heating **1** to 60 °C in C_6H_6 results in intermolecular C−H activation of benzene to form TpRu{P(pyr)$_3$}(NCMe)Ph (**5**) (eq 5). In addition to complex **5**, a brown product that is NMR silent and presumably paramagnetic is isolated from this reaction. Monitoring the conversion of **1** and C_6D_6 to **5**-d_5 in sealed NMR tubes reveals that **5**-d_5 is reproducibly formed in approximately 60% to 65% yield. In the reaction in C_6D_6 to form **5**-d_5, complex **1** is consumed at a rate of $1.15(1) \times 10^{-4}$ s^{-1} at 60 °C. Additionally, both CH_3D (1:1:1 triplet at 0.14 ppm) and CH_4 (singlet at 0.16 ppm) (∼2:1 molar ratio by integration of resonances in the ^{1}H NMR spectrum) production are observed by ^{1}H NMR spectroscopy for reactions performed in sealed NMR tubes. The formation of CH_3D is consistent with intermolecular C−H(D) activation of benzene by complex **1** (see Scheme 2 above). The formation of CH_4 is suggestive of either an intramolecular C−H activation or intermolecular C−H activation between two molecules of **1**, thus liberating the methyl ligand as CH_4 and rendering a species that presumably decomposes to the uncharacterized brown precipitate.



Complex **5** has been isolated pure in 62% yield and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and a single-crystal X-ray diffraction study (Figure 1 and Table 1). The ORTEP of **5** reveals a Ru−P distance of 2.1894(7) Å, which is shorter than the Ru−PMe$_3$ bond of TpRu(PMe$_3$)(NCMe)Ph {Ru−P = 2.279(1) Å}.[51] The decreased Ru−P bond distance to the P(pyr)$_3$ ligand of **5** compared to the corresponding bond distance of TpRu(PMe$_3$)(NCMe)Ph is likely a result of Ru-to-phosphine π-back-bonding for the π-acidic tris-*N*-pyrrolyl phosphine ligand. Additionally, the crystal structure of **5** reveals that the NCMe and phenyl ligands are canted slightly toward each other with a C10−Ru1−N7 bond

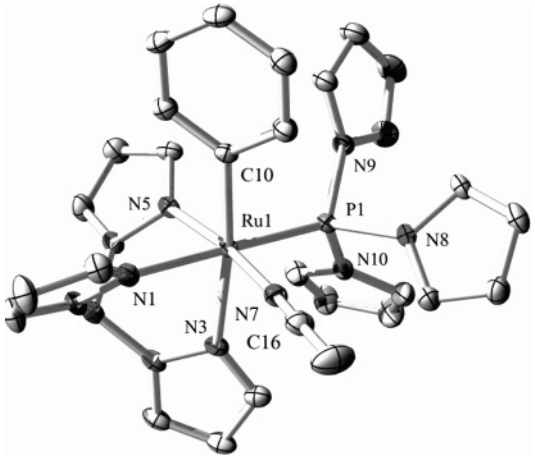


Figure 1. ORTEP of TpRu{P(pyr)$_3$}(NCMe)Ph (**5**) (50% probability with hydrogen atoms omitted). Selected bond lengths (Å): Ru1−N7, 2.015(2); Ru1−C10, 2.071(3); Ru1−P1, 2.1894(7); Ru1−N1, 2.130(2); Ru1−N3, 2.190(2); Ru1−N5, 2.086(2); N7−C16, 1.144(4); P1−N8, 1.722(2); P1−N9, 1.730(2), P1−N10, 1.723(2). Selected bond angles (deg): N7−Ru1−C10, 87.1(1); N7−Ru1−P1, 94.38(7); C10−Ru1−P1, 93.40(8).

Table 1. Selected Crystallographic Data for [TpRu{P(pyr)$_3$}(NCMe)Ph (5)·CH_2Cl_2]and [TpRu{κ^2-*P,C*-P(pyr)$_2$(NC$_4$H$_3$)}NCMe (6)·0.5C_6H_6]

	complex **5**	complex **6**
empirical formula	$C_{30}H_{32}BCl_2N_{10}PRu$	$C_{26}H_{27}BN_{10}PRu$
fw	746.41	622.43
cryst syst	orthorhombic	monoclinic
space group	$Pca2_1$	$P2_1/c$
a, Å	14.2295(4)	8.6486(4)
b, Å	13.3202(4)	15.4071(7)
c, Å	17.0744(4)	21.9014(1)
β, deg		100.399(1)
V, Å^3	3236.3(2)	2870.4(2)
Z	4	4
D_{calcd}, g/cm^3	1.532	1.440
cryst size (mm)	0.44 × 0.22 × 0.04	0.10 × 0.16 × 0.50
R_1, wR_2 {$I > 2(I)$}	0.0306, 0.0717	0.0364, 0.0920
GOF	1.081	1.031

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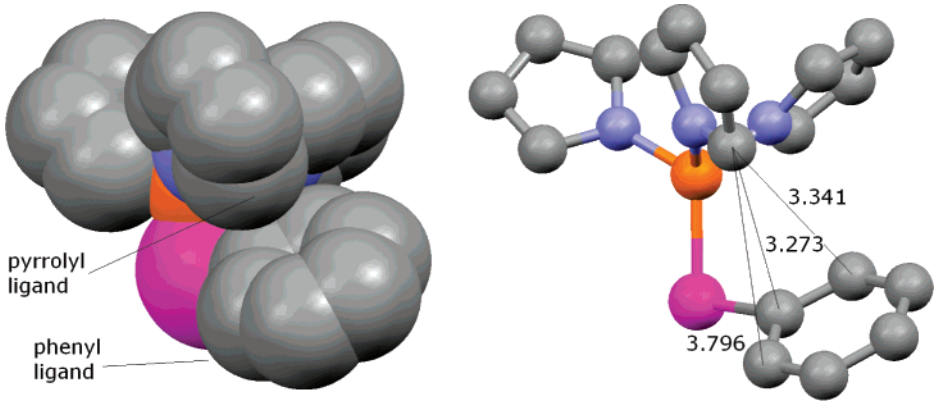


Figure 2. Cutaway views of Ru{P(pyr)$_3$}Ph fragment of TpRu{P(pyr)$_3$}(NCMe)Ph (**5**). Shown are the space-filling model (left view) and ball-and-stick diagram (right view) with distances (Å) from the nearest pyrrolyl 2-position carbon to ipso and meta carbons of the phenyl ring (hydrogen atoms omitted for clarity; Ru = pink, C = gray, N = blue, P = orange).

angle of 87.1(1)°. The P1−Ru1−N7 bond angle is 94.38(7)°, while the P1−Ru1−C10 bond angle is 93.40(8)°. The increase in the P1−Ru1−C10 and P1−Ru1−N7 bond angles to greater than 90° and the decrease of the angle between the phenyl and NCMe ligands to less than 90° are likely the result of the steric influence of the phosphine ligand, though the deformations from the ideal 90° of octahedral geometry are not substantial (perhaps due to the counterbalance of sterics by the bulky Tp ligand).

^{1}H NMR spectroscopy of **5** at room temperature reveals broad resonances due to the pyrrolyl and phenyl fragments (6.88, 6.50, 6.09, and 6.00 ppm), while the Tp and NCMe resonances are well-resolved. The observation of broad resonances suggests hindered rotation of the phenyl and tris-*N*-pyrrolyl phosphine ligands on the ^{1}H NMR time scale, which is likely due to steric hindrance between the two ligands and is similar to the broadening observed with TpRu{P(pyr)$_3$}(PPh$_3$)Cl (see above). Figure 2 illustrates both a space-filling model and a ball-and-stick diagram obtained from crystallographic data of TpRu{P(pyr)$_3$}(NCMe)Ph (**5**). The models highlight the close contacts between a pyrrolyl ring of P(pyr)$_3$ and the phenyl ligand, providing a possible cause for steric perturbations implicated by the broadening of both the phenyl and P(pyr)$_3$ resonances in the ^{1}H NMR spectrum.

Variable-temperature NMR studies of **5** were conducted from 110 to −80 °C. At low temperatures in CD_2Cl_2 multiple decoalescence points were observed. At −80 °C at least 10 new identifiable resonances emerge; however, the slow exchange regime was not accessed at −80 °C and specific assignment of resonances could not be made due to the broad nature of most resonances. At elevated temperatures in toluene-d_8, ^{1}H NMR spectroscopy revealed a decrease in line width of resonances. At 110 °C, two resonances due to the pyrrolyl groups (6.24 and 6.05 ppm) are observed with the resonance at 6.24 ppm (2,5-pyrrolyl positions) only slightly broadened relative to those upfield (3,4-pyrrolyl positions). The observation of two resonances (^{1}H NMR, 100 °C) due to the P(pyr)$_3$ ligand is consistent with rapid Ru−P and P−N$_{pyr}$ bond rotation relative to the ^{1}H NMR time scale. Unfortunately, the phenyl resonances overlap with the toluene-d_8 resonances and cannot be fully elucidated; however, their sharpening relative to room-temperature spectra is evident. In addition, the improved resolution due to the increased ligand rotational frequency allows for full identification of all Tp resonances that were previously overlapping with broadened phenyl and P(pyr)$_3$ resonances.

The addition of 5 equiv of acetonitrile to the reaction of **1** and C_6D_6 suppresses the decomposition to the brown NMR-silent materials, but also slows the rate of formation of **5** at 60 °C. Under these conditions, after 17 h only 6% conversion to **5** is observed (compared with complete consumption of complex **1** and ~63% conversion to **5** in 7.5 h in the absence of NCMe); however, 12% conversion to a new complex identified as TpRu{κ^2-*P*,*C*-P(pyr)$_2$(NC$_4$H$_3$)}NCMe (**6**), the product of intramolecular C−H activation of a pyrrolyl 2-position, was observed by ^{1}H NMR spectroscopy. We presume that the presence of free acetonitrile suppresses benzene/NCMe ligand exchange to form TpRu{P(pyr)$_3$}(C$_6$H$_6$)Me, which is likely the precursor to benzene C−H activation to form **5**. As a result, in the presence of free NCMe, intramolecular C−H activation of a pyrrolyl group competes with intermolecular C−H activation of benzene. At this point, we are uncertain why the addition of free NCMe does not equally suppress the intramolecular C−H activation.

Heating **1** to 100 °C in neat acetonitrile results in the formation of the cyclometalated species **6** in 62% isolated yield (eq 6). In the ^{31}P NMR spectrum, the resonance of the phosphine ligand of **6** appears at 74.2 ppm, which is shifted substantially upfield of the corresponding resonance for **1** at 124.1 ppm. The room-temperature ^{1}H NMR spectrum of **6** shows the loss of symmetry of the phosphine ligand with 11 resonances due to the tris-*N*-pyrrolyl phosphine ligand. The ^{13}C NMR spectrum of **6** is also consistent with an asymmetric tris-*N*-pyrrolyl phosphine ligand and reveals a downfield doublet at 148.8 ppm with a large $^2J_{CP}$ coupling of 29 Hz due to the cyclometalated carbon. A single-crystal X-ray diffraction study (Figure 3 and Table 1) confirmed the formation of **6** bearing a four-membered cyclometalated ring formed from a pyrrolyl moiety. To our knowledge, the only other example of a structurally characterized cyclometalated P(pyr)$_3$ ligand is that reported by Poë et al. for a hexarhodium-carbonyl cluster that bears a five-membered dimeric cyclic structure in which the pyrrolyl fragment bridges two metal centers.[52] A search of the Cambridge Structural Database reveals no four-membered organometallic cyclometalated phosphine pyrrolyl structures. Geometric details of **6** reveal the anticipated strain as a result of the four-membered Ru−P−N−C ring (Figure 4), particularly at the C(12)−Ru(1)−P(1) fragment with a bond angle of 66.67(7)°. The ring strain is likely relieved through a degree of bond lengthening. For example, the N(8)−C(12) bond of the ring is slightly longer {1.417(3) Å} compared to the non-cyclometalated N−C bonds {e.g., N(9)−C(19), 1.375(4) Å; N(10)−C(23), 1.381(4) Å} of

(52) Babij, C.; Browning, C. S.; Farrar, D. H.; Koshevoy, I. O.; Podkorytov, I. S.; Poe, A. J.; Tunik, S. P. *J. Am. Chem. Soc.* **2002**, *124*, 8922−8931.

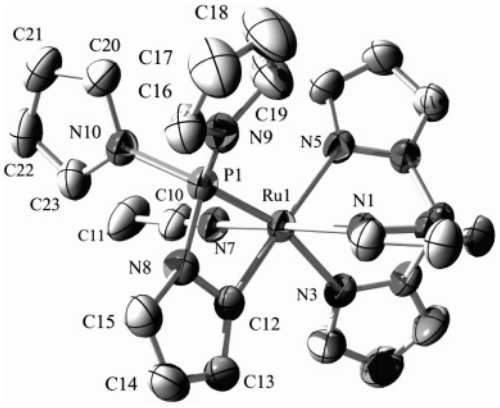


Figure 3. ORTEP of TpRu{κ^2-*P*,*C*-P(pyr)$_2$(NC$_4$H$_3$)}NCMe (**6**) (30% probability with hydrogen atoms omitted). Selected bond lengths (Å): Ru1−N7, 2.027(2); Ru1−C12, 2.064(3); Ru1−P1, 2.2119(7); Ru1−N1, 2.075(2); Ru1−N3, 2.105(2); Ru1−N5, 2.162-(2); N7−C10, 1.133(3); P1−N8, 1.674(2); P1−N9, 1.698(2), P1−N10, 1.725(2); N(8)−C(12), 1.417(3); N(9)−C(19), 1.375(4); N(10)−C(23), 1.381(4); C(12)−C(13), 1.370(4); C(22)−C(23), 1.353(4); C(18)−C(19), 1.350(5). Selected bond angles (deg): N(7)−Ru(1)−C(12), 93.18(9); N7−Ru1−P1, 90.69(7); N(9)−P(1)−Ru(1), 124.24(8); N(10)−P(1)−Ru(1), 129.07(9); N(8)−P(1)−Ru(1), 90.15(8); C12−Ru1−P1, 66.67(7); C(12)−N(8)−P(1), 98.8(2); N(8)−C(12)−Ru(1), 104.3(2).

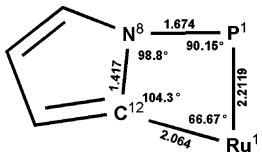
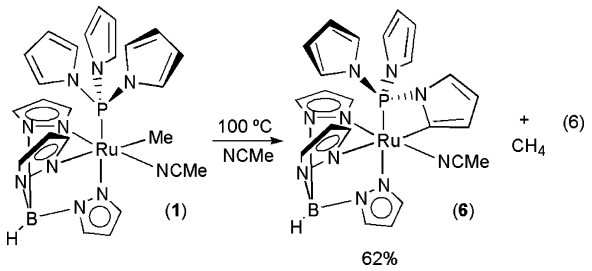


Figure 4. Pictorial representation of bond angles (deg) and bond lengths (Å) for the four-membered ring of TpRu{κ^2-*P*,*C*-P(pyr)$_2$-(NC$_4$H$_3$)}NCMe (**6**).

the tris-*N*-pyrrolyl phosphine ligand. Likewise, the Ru−P bond {2.2119(7) Å} is also longer than that of complex **5** {2.1894-(7) Å}.



The formation of **6** from **1** results from intramolecular C−H activation of a 2-position pyrrolyl C−H bond and elimination of methane. Heating **1** in NCCD$_3$ at 100 °C yields quantitative conversion to TpRu{κ^2-*P*,*C*-P(pyr)$_2$(NC$_4$H$_3$)}NCCD$_3$ (**6**-d_3) and free CH$_4$ in approximately 3 days. Thus, under these conditions the intramolecular C−H activation to produce **6** is *substantially slower* than the intermolecular benzene C−H activation, which is complete after 7.5 h at 60 °C in C$_6$H$_6$. The slow intramolecular C−H activation (relative to intermolecular C−H activation of benzene) may be a result of the formation of a strained four-membered metallacycle for the intramolecular event.

In contrast to the methyl complex **1**, heating the phenyl complex TpRu{P(pyr)$_3$}(NCMe)Ph (**5**) in NCCD$_3$ at 120 °C for 24 h gives no visible sign of intramolecular C−H activation by ^{1}H NMR spectroscopy (Scheme 2). The acetonitrile ligand of **5** readily undergoes degenerate exchange with NCCD$_3$ at 60 °C with $t_{1/2} \approx 80$ min (by ^{1}H NMR spectroscopy), and, thus, the coordinated NCMe is likely to be sufficiently labile at 120 °C to provide an open coordination site (if necessary). Additionally, the lability of the NCMe ligand of TpRu{P(pyr)$_3$}-(NCMe)Me (**1**) was verified by following the degenerate exchange of the NCMe ligand in NCCD$_3$ at 60 °C with $k_{obs} = 1.47(2) \times 10^{-4}$ s^{-1}. The inability of the phenyl ligand to undergo intramolecular C−H activation with a pyrrolyl fragment at 120 °C suggests that elimination of benzene from **5** via intramolecular C−H activation is thermodynamically unfavorable. Consistent with this suggestion, heating complex **6** for 22 h at 80 °C in C$_6$D$_6$ in a NMR tube forms the phenyl complex **5** in 50% yield by NMR (decomposition to NMR-silent products accompanies the formation of **5**). The lack of cyclometalation of the TpRu{P(pyr)$_3$}Ph fragment suggests that **5** might be a viable catalyst for the hydroarylation of olefins as previously studied for analogous TpRu(L)(NCMe)Ph (L = CO and PMe$_3$) complexes.[42−44,49]

Table 2. Hydrophenylation of Ethylene by TpRu{P(pyr)$_3$}(NCMe)Ph (5)

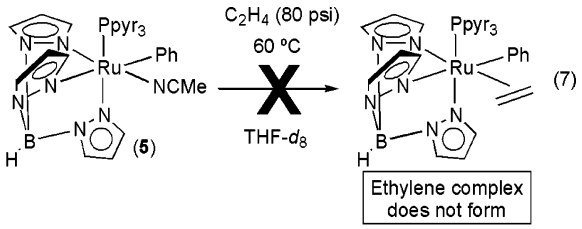
ethylene (psi)	temp (C)	time (h)	ethylbenzene[a]	styrene[a]
25	90	11	none	none
300	90	11	none	none
80	120	11	0.2	none
250	120	11	<0.1	0.2
15	150	11	none	none
25	150	11	trace	none
50	150	17	0.7	0.1
50	150	5 days	0.9	0.1
100	150	11	0.1	trace
300	150	11	0.1	0.2
500	150	16	0.1	0.1
700	150	16	0.1	0.3
100	180	10	0.9	0.2
300	180	10	0.3	0.2
500	180	16	1.2	0.7
700	180	16	1.2	0.7

[a] Moles of product per mole of catalyst

Hydrophenylation of Ethylene. TpRu{P(pyr)$_3$}(NCMe)Ph (**5**) is an electronically similar analogue and structural variant of the previously reported olefin hydroarylation catalyst TpRu(CO)(NCMe)Ph.[42−44] Given that **1** reacts with benzene to initiate relatively facile C−H activation, we probed the efficacy of **5** as a catalyst for the hydroarylation of ethylene. In pressure reactors, conditions were explored from 90 to 180 °C and 25 to 700 psi of ethylene in benzene, as shown in Table 2.

The formation of ethylbenzene was not observed until 80 psi and 120 °C. Increasing the temperature resulted in a slight increase in the formation of ethylbenzene but was also accompanied by the formation of styrene, likely resulting from a β-hydride elimination pathway. At 150 °C, increasing the pressure of ethylene beyond 50 psi resulted in decreased formation of ethylbenzene. Comparatively, results for the hydrophenylation of ethylene (25 psi) using TpRu(CO)(NCMe)-Ph as catalyst yielded 51 turnovers in 4 h at 90 °C.[43] The most successful production of ethylbenzene using **5** was nearly 1 turnover at 180 °C and 100 psi ethylene in 10 h. In all cases, the catalyst solutions remained homogeneous; however, ^{1}H NMR spectral analysis of residual materials (nonvolatiles) from catalysis failed to reveal the observation of **5** or any other intermediates in the proposed catalytic cycle for hydrophenylation of ethylene {i.e., TpRu{P(pyr)$_3$}(η^2-C$_2$H$_4$)R}. Presumably, **5** decomposes to NMR-silent materials. Although complex **5** is stable for prolonged periods of time at temperatures up to 60 °C, at temperatures ≥90 °C, including conditions for attempted catalysis, complex **5** undergoes decomposition.

Since **1** activates the C−H bonds of benzene and the electron density of Ru of TpRu{P(pyr)$_3$}(NCMe)Ph (**5**) is quite similar to TpRu(CO)(NCMe)Ph (see above), the relatively poor catalyst performance of **5** {compared to TpRu(CO)(NCMe)Ph} is possibly due to steric encumbrance as a result of the bulky tris-*N*-pyrrolyl phosphine ligand. For catalytic hydrophenylation of ethylene using TpRu(L)(NCMe)Ph (L = CO or PMe$_3$) systems, we have obtained evidence for the formation of TpRu(L)(η^2-C$_2$H$_4$)Ph complexes as key intermediates in catalytic sequences.[49] In contrast, heating **5** to 60 °C under ethylene pressure (80 psi) in THF-d_8 for 5.5 days does not result in the formation of TpRu{P(pyr)$_3$}(η^2-C$_2$H$_4$)Ph (eq 7). Rather, after 5.5 days of heating, complex **5** is observed to decompose (25% loss of **5** versus internal standard) to NMR-silent species, while no new diamagnetic Tp complexes or organics are formed by ^{1}H NMR spectroscopy. Thus, it is likely that the catalyst is unable to form the species TpRu{P(pyr)$_3$}(η^2-C$_2$H$_4$)(Ph), which would likely precede the C−C bond forming olefin insertion step in the ethylene hydrophenylation catalytic cycle.

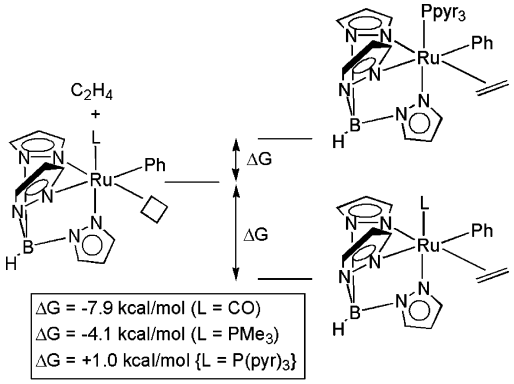


Computational Studies. Computational studies employing density functional theory and effective core potential methods were carried out to address several issues pertinent to the catalytic hydroarylation chemistry of P(pyr)$_3$-ligated TpRu complexes including (1) thermodynamics of ethylene binding to TpRu{P(pyr)$_3$}Ph, (2) thermodynamics of cyclometalation of the pyrrolyl substituent in the 2-position, in particular the relative competence of the TpRu{P(pyr)$_3$}Ph and TpRu{P(pyr)$_3$}-Me complexes for effecting this transformation, and (3) kinetics and thermodynamics of C−H activation of benzene by the putative 16-electron active species TpRu{P(pyr)$_3$}Me.

Ethylene Binding to TpRu{P(pyr)$_3$}Ph. Previous experimental and computational studies have indicated that a key step in the hydroarylation chemistry of TpRu-based catalysts is the coordination of ethylene to the 16-electron phenyl system TpRu(L)Ph. In previous research, L = CO and PMe$_3$ were investigated for the catalytic hydrophenylation of ethylene for model complexes.[43] Herein, we have compared the ethylene binding energetics of these Ru catalysts to the tris-*N*-pyrrolyl phosphine complex under current investigation using the full Tp ligand. The calculated binding enthalpies (free energies) in kcal/mol using the B3LYP/CEP-31G(d) level of theory are as follows: TpRu(PMe$_3$)(Ph)(η^2-C$_2$H$_4$) = −18.8 (−4.1); TpRu(CO)(Ph)-(η^2-C$_2$H$_4$) = −21.3 (−7.9); TpRu{P(pyr)$_3$}(Ph)(η^2-C$_2$H$_4$) = −14.3 (+1.0) (Scheme 3). Thus, coordination of ethylene to TpRu{P(pyr)$_3$}Ph is calculated to be less favorable by 8.9 kcal/mol (ΔG) relative to coordination to TpRu(CO)Ph and less favorable by 5.1 kcal/mol relative to coordination to TpRu-(PMe$_3$)Ph.

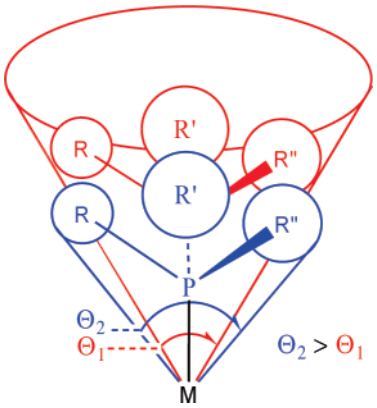
Several points in regard to the calculated ethylene binding energetics are germane in the present context. First, it can be seen by comparing the binding energies of the PMe$_3$ complex with its more electron-deficient derivative, TpRu(CO)(Ph)(η^2-C$_2$H$_4$), that a more π-acidic L group enhances ethylene binding. This enhancement is, of course, in the absence of significant steric factors, which previous research[49] has shown to play a

Scheme 3. Comparison of Calculated Gibbs Free Energy Changes upon Coordination of Ethylene to TpRu(L)(Ph) {L = CO, PMe$_3$, or P(pyr)$_3$} Fragments to Give TpRu(L)(Ph)(η^2-C$_2$H$_4$)[a]



[a] Square indicates vacant coordination site.

Scheme 4. Schematic Depiction of the Effect of Shortened M−P Distance on Cone Angle (Θ)

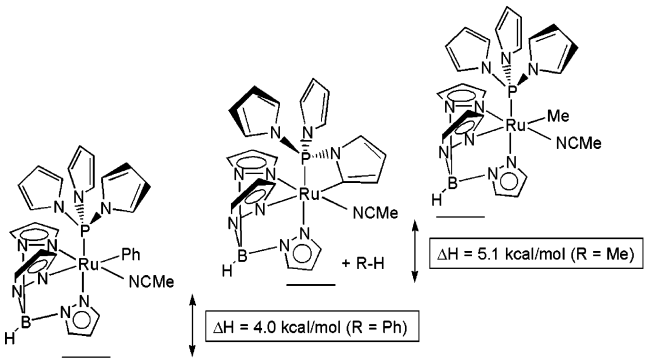


significant role in TpRu hydroarylation catalysis. Second, the P(pyr)$_3$ complex, which has been described[50] as being electronically similar to CO in its π-acidity, has a calculated ethylene binding enthalpy (free energy) that is significantly higher than the values for the carbonyl complex by +7.0 (+8.9) kcal/mol. Hence, the steric impact of P(pyr)$_3$ is prodigious, being ca. 9 kcal/mol (ΔG) with respect to ethylene binding. Not only is the greater steric impact of P(pyr)$_3$ versus CO attributed to the obviously larger cone angle arising from a tetrahedral phosphorus versus a linear CO moiety, but also P(pyr)$_3$ will have a greater steric impact versus typical P(hydrocarbyl)$_3$ phosphines due to the shorter M−P bond distance (ca. 0.1 Å for P(pyr)$_3$ versus PMe$_3$ congeners in both solid-state and calculated structures). The cone angle is measured in the classic Tolman recipe[53] on the assumption of a fixed metal−phosphorus bond distance. Simple geometric considerations imply that shortening the M−P distance will increase the solid angle subtended by the cone (Scheme 4).

P(pyr)$_3$ Cyclometalation. Although cyclometalation reactions are well-known in the literature of triarylphosphines,[54−56] examples for the P(pyr)$_3$ ligand are rare. An inspection of the Cambridge Structural Database (Version 1.9 with updates through May 2007)[57] yields only one example of a cyclometalated P(pyr)$_3$ complex, a hexarhodium-carbonyl cluster in which

(53) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
(54) Mohr, F.; Priver, S. H.; Bhargava, S. K.; Bennett, M. A. *Coord. Chem. Rev.* **2006**, *250*, 1851−1888.
(55) Crabtree, R. H. *J. Organomet. Chem.* **2005**, *690*, 5451−5457.
(56) Werner, H. *Dalton Trans.* **2003**, 3829−3837.

Scheme 5. Comparison of Calculated ΔH for Intramolecular Cyclometalation of P(pyr)$_3$ from TpRu{P(pyr)$_3$}(NCMe)R for R = Me vs Ph



the pyrrolyl group spans two Rh centers.[52] What is particularly interesting in the present study is that cyclometalation is seen when the hydrocarbyl ligand is a methyl but not a phenyl. To probe the possible causes of this reactivity dichotomy, we calculated the thermodynamics of cyclometalation of one pyrrolyl ring of P(pyr)$_3$ at the 2-position for TpRu{P(pyr)$_3$}(NCMe)R (R = Me and Ph). While the cyclometalation is calculated to be *exothermic* for R = Me (ΔH = −5.1 kcal/mol), the analogous reaction is *endothermic* for R = Ph (ΔH = +4.0 kcal/mol; Scheme 5). The extrusion of an equivalent of RH (methane or benzene) provides an entropic enhancement (in the gas phase) and makes both reactions exergonic, but again there is an obvious thermodynamic advantage for cyclometalation of the methyl (ΔG = −15.7 kcal/mol) as compared to the phenyl (ΔG = −10.1 kcal/mol) complex. The calculated thermodynamics for the cyclometalation by the phenyl and methyl complexes are commensurate with the difference in C−H bond energies of benzene (113 kcal/mol) and methane (105 kcal/mol).

Benzene C−H Activation by TpRu{P(pyr)$_3$}Me. Experimental mechanistic studies, augmented by computations, indicate that the catalytic cycle of olefin hydrophenylation by TpRu(L)(NCMe)R systems is initiated by the dissociation of NCMe and the coordination of a benzene to the resultant 16-electron TpRu(L)R active species.[43] The ligation mode of the benzene has been found to be either η^2-C=C or η^2-C−H, the latter being a hallmark of steric congestion about the ruthenium coordination sphere.[49] The benzene adduct of TpRu{P(pyr)$_3$}Me is calculated to be ligated to ruthenium in an η^2-C−H fashion, Figure 5, supporting previous conclusions about the significant steric impact of P(pyr)$_3$ (see above).

For TpRu{P(pyr)$_3$}(η^2-C-H-C$_6$H$_6$)Me, the activation enthalpies (free energies) for the benzene C−H activation transition state are 11.4 (13.8) kcal/mol calculated relative to the benzene adduct. These barriers are competitive with calculated values for TpRu(CO)(η^2-C-H-C$_6$H$_6$)Me and TpRu(PMe$_3$)(η^2-C-H-C$_6$H$_6$)Me, which are 14.3 (14.9) and 10.6 (10.9) kcal/mol, respectively, relative to their corresponding benzene adducts (Scheme 6). Note that both the benzene adducts for the carbonyl and trimethylphosphine complexes are calculated to be η^2-C=C, again reflecting the greater steric impact of the P(pyr)$_3$, although it must be pointed out that η^2-C=C and η^2-C−H structures are expected to be both energetically very similar and separated by small kinetic barriers. The calculations thus suggest

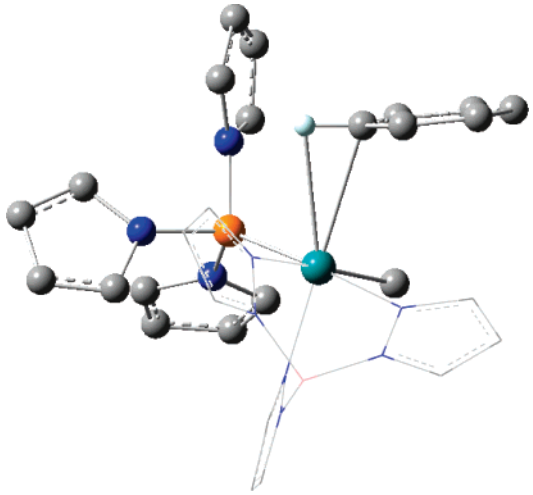
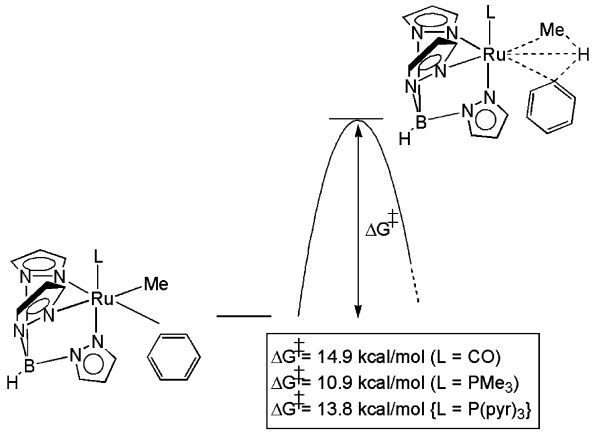


Figure 5. Calculated benzene adduct geometry for the intermediate TpRu{P(pyr)$_3$}(Me)(η^2-*CH*-C$_6$H$_6$). Hydrogen atoms are omitted for clarity except for the agostic hydrogen of benzene. The Tp ligand is shown in a wire frame.

Scheme 6. Comparison of Calculated $\Delta G^{\ddagger}$ (298 K) for C−H Activation of Benzene by TpRu(L)(Me)(benzene) {L = CO, PMe$_3$, or P(pyr)$_3$} Systems



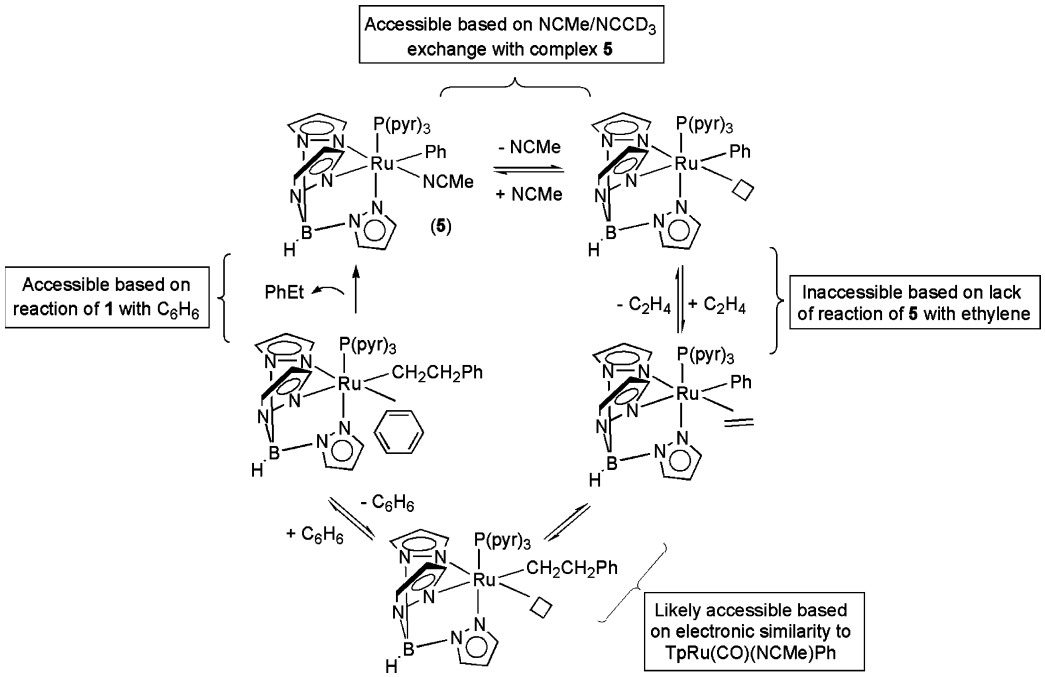
that the hydroarylation catalysis of the tris-*N*-pyrrolyl phosphine complexes is inhibited not by the benzene C−H activation portion of the cycle but rather by the ethylene binding/insertion events.

Summary and Conclusions

The complex TpRu{P(pyr)$_3$}(NCMe)Me (**1**) has been synthesized in an effort to increase our understanding of features that control the catalytic hydroarylation of olefins. Complex **1** stoichiometrically activates benzene to form TpRu{P(pyr)$_3$}(NCMe)Ph (**5**) and, in the absence of benzene, initiates intramolecular C−H activation to yield the cyclometalated species TpRu{κ^2-*P*,*C*-P(pyr)$_2$(NC$_4$H$_3$)}NCMe (**6**). Consistent with the steric encroachment of the P(pyr)$_3$ ligand on the octahedral face, attempted observation of a TpRu{P(pyr)$_3$}(η^2-C$_2$H$_4$)Ph intermediate by ^{1}H NMR spectroscopy under conditions where TpRu(L)(η^2-C$_2$H$_4$)Ph (L = CO or PMe$_3$) systems form resulted in no evidence for ethylene coordination. Using TpRu{P(pyr)$_3$}(NCMe)Ph (**5**) as catalyst, high temperatures and pressures are required to observe ethylene hydrophenylation, and then only in near stoichiometric amounts. It is our conclusion on the basis of experimental mechanistic studies and computational chemistry analyses of the reaction coordinate that

(57) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187−204.

Scheme 7. Analysis of Likely Catalytic Cycle for Hydrophenylation of Ethylene Catalyzed by TpRu{P(pyr)$_3$}(NCMe)Ph (5) Based on Experimental and Computational Studies[a]



[a] Square indicates vacant coordination site.

overall catalytic hydroarylation is impaired by the steric bulk of the P(pyr)$_3$ ligand. Moreover, in terms of catalytic hydroarylation, the P(pyr)$_3$ has minimal effect on the benzene C−H activation portion of the cycle, but its steric bulk prevents facile coordination of ethylene and thus thwarts the C−C bond formation that is needed to make alkyl benzenes directly from benzene and olefins (Scheme 7). Thus, comparative studies of catalytic hydrophenylation of olefins by TpRu(L)(NCMe)R systems {L = CO, PMe$_3$ or P(pyr)$_3$} suggest that in each case substitution of the ligand CO with either PMe$_3$ or P(pyr)$_3$ has a more dramatic impact on the olefin coordination/insertion step of the catalytic cycle than on the aromatic C−H activation reaction.[49] For catalytic cycles that involve the activation of C−H bonds, the C−H activation step is often considered the reaction that is most difficult and receives substantial attention. In contrast, for the case of olefin hydroarylation by TpRu(L)(NCMe)R systems (those studied thus far), the more mundane olefin insertion step appears to dictate whether catalytic olefin hydroarylation is accessible.

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 {O_2(g) < 15 ppm for all reactions}. Benzene and tetrahydrofuran were dried by distillation from sodium/benzophenone. Pentane was distilled over sodium. Acetonitrile and methanol were dried by distillation from CaH_2. Hexanes were purified by passage through a column of activated alumina. Tetrahydrofuran-d_8, benzene-d_6, acetonitrile-d_3, methylene chloride-d_2, toluene-d_8, and chloroform-d_1 were degassed with three freeze−pump−thaw cycles and stored under a dinitrogen atmosphere over 4 Å molecular sieves. ^{1}H NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer and ^{13}C NMR (operating frequency 75 MHz) spectra on a Varian Mercury 300 MHz spectrometer. All ^{1}H and ^{13}C NMR spectra are referenced against residual proton signals (^{1}H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). ^{19}F NMR spectra were obtained on a Varian 300 MHz spectrometer (operating frequency 282 MHz) and referenced against an external standard of hexafluorobenzene ($\delta = -164.9$). ^{31}P NMR spectra were obtained on a Varian 400 MHz spectrometer and referenced against an external standard of H_3PO_4 ($\delta = 0$). Resonances due to the Tp ligand in ^{1}H NMR spectra are listed by chemical shift and multiplicity only (all coupling constants for the Tp ligand are ∼2 Hz). GC-MS was performed using a HP GCD EI system with a 30 m × 0.25 mm HP-5 column with 0.25 mm film thickness. Electron ionizing (EI) mass spectrometry was carried out using a JEOL (Tokyo, Japan) HX110HF high-resolution mass spectrometer at the North Carolina State University Mass Spectrometry Laboratory using perfluorokerosene ions as a reference standard. Ethylene (99.5%) was received in a gas cylinder from MWSC High-Purity Gases and used as received. The preparation, isolation, and characterization of TpRu(PPh$_3$)$_2$Cl,[58] tris-*N*-pyrrolyl phosphine,[59] and Me$_2$Mg[60] have been previously reported. All other reagents were used as purchased from commercial sources. Elemental analyses were performed by Atlantic Microlabs, Inc.

TpRu{P(pyr)$_3$}(PPh$_3$)Cl (2). TpRu(PPh$_3$)$_2$Cl (1.562 g, 1.787 mmol) and tris-*N*-pyrrolyl phosphine (0.532 g, 2.323 mmol) were added to benzene (50 mL) to form a yellow heterogeneous mixture, and the mixture was stirred at room temperature for 3 h, during which time it became homogeneous. The volume of the homogeneous solution was reduced under vacuum to approximately 5 mL, and a solid was precipitated upon addition of MeOH. The light yellow solid was collected over a medium-porosity frit, washed with 10 mL of MeOH, and dried in vacuo (1.265 g, 1.505 mmol, 84%). ^{1}H NMR (CDCl$_3$, δ): 7.67, 7.64 (each 1H, each a d, Tp 3 or 5 positions), 7.48 (7H, br m, triphenylphosphine ortho or meta positions and overlapping Tp 3 or 5 position), 7.39 (1H, d, Tp 3 or

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5 position), 7.24 (3H, br m, triphenylphosphine para positions), 7.09 (6H, m, triphenylphosphine ortho or meta positions), 6.49 (1H, d, Tp 3 or 5 position), 6.04 (12H, very br m, overlapping pyrrolyl positions), 5.85 (1H, d, Tp 3 or 5 position), 5.79 (1H, m, Tp 4 position), 5.42 (1H, t, Tp 4 position), 4.83 (1H, m, Tp 4 position). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 146.9, 145.4, 143.9, 136.4, 136.3, 134.5 (Tp 3 and 5 positions), 134.9 (d, $J_{CP} = 9$ Hz, ortho or meta of triphenylphosphine), 133.7 (d, $^1J_{CP} = 38$ Hz, ipso of triphenylphosphine), 129.4 (unresolved br d, $^4J_{CP} < 1$ Hz, para of triphenylphosphine), 127.9 (d, $J_{CP} = 10$ Hz, ortho or meta of triphenylphosphine), 123.9 (br d, pyrrolyl 2,5-positions), 112.1 (d, $^3J_{CP} = 6$ Hz, pyrrolyl 3,4-positions) 106.5, 106.4, 105.1 (Tp 4 positions). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 123.0 {d, $^2J_{PP} = 40$ Hz, *P*(pyr)$_3$}, 37.8 {d, $^2J_{PP} = 40$ Hz, *P*(Ph)$_3$}. Anal. Calcd for $C_{39}H_{37}BN_9P_2ClRu$: C, 55.69; H, 4.43; N, 14.99. Found: C, 55.40; H, 4.48; N, 14.95.

TpRu{P(pyr)$_3$}(NCMe)Cl (3). TpRu{P(pyr)$_3$}(PPh$_3$)Cl (**2**) (1.193 g, 1.420 mmol) was dissolved in a 1:1.5 (v/v) mixture of acetonitrile (10 mL) and tetrahydrofuran (15 mL) and heated to reflux for 7 h. The reaction mixture was reduced under vacuum to approximately 5 mL, and a solid was precipitated upon addition of hexanes. The light yellow solid was collected over a medium-porosity frit, washed with 10 mL of pentane, and dried in vacuo (0.818 g, 1.30 mmol, 92%). ^{1}H NMR ($CDCl_3$, δ): 8.17 (1H, d, Tp 3 or 5 position), 7.71 (2H, overlapping Tp 3 or 5 positions), 7.68, 6.95, 6.68 (each 1H, each a d, Tp 3 or 5 position), 6.36 (6H, m, overlapping Tp 4 position and pyrrolyl), 6.33 (1H, overlapping with pyrrolyl, Tp 4 position), 6.20 (6H, m, pyrrolyl), 6.00, 5.97 (each 1H, each a t, Tp 4 positions), 2.35 (3H, s, NCC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 145.4, 144.5, 141.8, 134.6 (Tp 3 and 5 positions), 136.2 (2C, overlapping Tp 3 and 5 positions), 123.8 (d, $^2J_{CP} = 6$ Hz, pyrrolyl 2,5 positions), 123.0 (N*C*CH$_3$), 112.1 (d, $^3J_{CP} = 6$ Hz, pyrrolyl 3,4 positions) 106.8, 106.7, 106.0 (Tp 4 positions), 4.7 (NC*C*H$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 123.3 {*P*(pyr)$_3$}.

TpRu{P(pyr)$_3$}(NCMe)OTf (4). To a solution of TpRu{P(pyr)$_3$}(NCMe)Cl (**3**) (0.700 g, 1.117 mmol) dissolved in tetrahydrofuran (50 mL) was added AgOTf (silver triflate) (0.301 g, 1.117 mmol). The round-bottom flask was covered with aluminum foil, and the solution was stirred at room temperature for 15 h. The volume of the resultant heterogeneous mixture was reduced to approximately 20 mL under vacuum and filtered through a plug of Celite on a fine-porosity frit (to remove a light purple solid). The volume of the yellow filtrate was reduced under vacuum, and a solid was precipitated upon addition of hexanes. The light yellow solid was collected over a medium-porosity frit and dried in vacuo (0.849 g, contains free THF that could not be fully removed in vacuo). NMR spectroscopy of **4** reveals *minor* amounts of impurities. This complex was not purified and was taken to the next step (i.e., methylation to form **1**) with the minor impurities. ^{1}H NMR (C_6D_6, δ): 9.15, 7.43, 7.34, 7.30, 6.96, 6.78 (each 1H, each a d, Tp 3 or 5 position), 6.53, 6.17 (each 6H, each a m, pyrrolyl positions), 6.12 (1H, dt, $^3J_{HH} = 2$, $^5J_{HP} = 2$ Hz, Tp 4 position trans to phosphine), 5.63 (2H, overlapping triplets due to Tp 4 positions), 1.09 (3H, s, NCC*H*$_3$). ^{19}F{^{1}H} NMR (C_6D_6, δ): -76.5 (C*F*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, δ): 146.6, 145.6, 144.9, 137.3, 137.2, 135.3 (Tp 3 and 5 positions), 124.2 (d, $^2J_{CP} = 6$ Hz, pyrrolyl 2,5 positions), 121.2 (N*C*CH$_3$), 113.3 (d, $^3J_{CP} = 6$ Hz, pyrrolyl 3,4 positions) 118.3 (q, $^1J_{CF} = 318.8$ Hz, Ru$-$O$_3$S*C*F$_3$), 107.9, 107.7, 106.9 (Tp 4 positions), 2.8 (NC*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 125.2 {*P*(pyr)$_3$}. EI-MS: *m*/*z* (%) $M_{theoretical}$ 734.0658, $M_{sample} = 734.0634$ ($\sigma = 3.3$ ppm), [M$^+$].

TpRu{P(pyr)$_3$}(NCMe)Me (1). TpRu{P(pyr)$_3$}(NCMe)OTf (**4**) (1.285 g, 1.750 mmol) was added to benzene (80 mL) to form a heterogeneous yellow mixture. After addition of Me_2Mg (0.100 g, 1.837 mmol), the solution was stirred for 1 h at room temperature. The volume of the resulting black heterogeneous mixture was reduced to approximately 40 mL and filtered through a plug of Celite on a fine-porosity frit. The volume of the yellow filtrate was reduced under vacuum, and a solid was precipitated upon addition of hexanes. The light yellow solid was collected over a medium-porosity frit and dried in vacuo (0.838 g, 1.38 mmol, 79%). ^{1}H NMR (C_6D_6, δ): 7.81, 7.58, 7.51, 7.45, 7.21, 7.06 (each 1H, each a d, Tp 3 or 5 positions), 6.51, 6.19 (each 6H, each a m, pyrrolyl positions) 6.08 (1H, dt, $^3J_{HH} = 2$ Hz, $^5J_{HP} = 2$ Hz, Tp 4 position trans to phosphine) 5.95, 5.69 (each 1H, each a t, Tp 4 positions), 1.08 (3H, d, $^3J_{HP} = 2$ Hz, Ru$-$C*H*$_3$), 0.64 (3H, s, NCC*H*$_3$). ^{13}C-{^{1}H} NMR (C_6D_6, δ): 144.8, 143.0, 140.2, 136.1, 135.2, 134.8 (Tp 3 and 5 positions), 124.1 (d, $^2J_{CP} = 5$ Hz, pyrrolyl 2,5 positions), 122.2 (N*C*CH$_3$), 111.8 (d, $^3J_{CP} = 5$ Hz, pyrrolyl 3,4 positions) 106.8, 106.2, 105.9 (Tp 4 positions), 2.6 (NC*C*H$_3$), -2.5 (d, $^2J_{CP} = 15$ Hz, Ru$-$*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 124.1 {*P*(pyr)$_3$}. CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2} = 0.76$ V {Ru(III/II)}. Anal. Calcd for $C_{24}H_{28}BN_{10}PRu$: C, 48.09; H, 4.71; N, 23.37. Found: C, 48.46; H, 4.89; N, 23.13.

TpRu{P(pyr)$_3$}(NCMe)Ph (5). TpRu{P(pyr)$_3$}(NCMe)Me (**1**) (0.194 g, 0.323 mmol) was added to benzene (25 mL), and the solution was heated to reflux for 3 h. The orange-brown solution was filtered through a plug of silica, the filtrate volume was reduced under vacuum, and a solid was precipitated upon addition of hexanes. The off-white solid was collected over a medium-porosity frit and dried in vacuo (0.132 g, 1.38 mmol, 62%). ^{1}H NMR (room temperature, CD_2Cl_2, δ): 7.82, 7.78, 7.31, 7.20, 6.99, 6.38 (each 1H, each a d, Tp 3 or 5 position), 6.84 (3H, br phenyl resonances), 6.25$-$5.60 {overlapping resonances including Tp 4 positions at 6.14 (m) and 6.00 (t) and pyrrolyl and/or phenyl resonances at 6.09 (m) and 5.96 (br s)}, 2.22 (3H, s, NCC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 167.4 ($^2J_{CP} = 17$ Hz, ipso carbon of phenyl), 145.4, 142.6, 142.3, 136.3, 134.8, 134.2 (Tp 3 and 5 positions), 141.8 (phenyl position), 123.7 (br d, $^2J_{CP} = 5$ Hz pyrrolyl 2,5 positions), 121.8 (N*C*CH$_3$), 120.7 (phenyl position), 111.3 (d, $^3J_{CP} = 6$ Hz, pyrrolyl 3,4 positions) 106.3, 105.8, 105.2 (Tp 4 positions), 4.8 (NC*C*H$_3$). (Note: A phenyl resonance in the ^{13}C NMR spectrum is missing due to either line broadening from dynamic processes or coincidental overlap.) ^{31}P{^{1}H} NMR (C_6D_6, δ): 127.8 {*P*(pyr)$_3$}. Anal. Calcd for $C_{29}H_{30}BN_{10}PRu$: C, 52.66; H, 4.57; N, 21.18. Found: C, 52.58; H, 4.65; N, 20.86.

TpRu{κ^2-P,C-P(pyr)$_2$(NC$_4$H$_3$)}NCMe (6). TpRu{P(pyr)$_3$}(NCMe)Me (**1**) (0.081 g, 0.135 mmol) and acetonitrile (40 mL) were combined in a thick-walled pressure tube, sealed with a Teflon cap, and heated at 100 °C for 75 h. The resultant mixture was filtered through a fine frit to remove precipitate, the filtrate was reduced to approximately 1 mL, and a solid was precipitated upon addition of hexanes. The light yellow solid was collected over a medium-porosity frit and dried in vacuo (0.049 g, 0.083 mmol, 62%). ^{1}H NMR (C_6D_6, δ): 8.09, 7.63, 7.58 (4H, 1:1:2 ratio, each a d, Tp 3 or 5 position), 7.40, 7.38, 6.92, 6.83, 6.75, 6.49 (10H total, each a m, pyrrolyl and two Tp 3 or 5 positions) 6.20 (2H, overlapping m, Tp 4 positions) 6.10, 6.08 (3H total, each a m, overlapping pyrrolyl positions), 5.52 (1H, t, Tp 4 position), 0.49 (3H, s, NCC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, δ): 148.8 (d, $^2J_{CP} = 29$ Hz, Ru$-$*C*) 145.2, 144.1, 143.5, 135.7, 135.2, 135.1 (Tp 3 and 5 positions), 124.3 (2C, d, $^2J_{CP} = 9$ Hz, pyrrolyl 2,5 positions), 123.1 (2C, d, $^2J_{CP} = 7$ Hz, pyrrolyl 2,5 positions),122.6 (N*C*CH$_3$), 121.0, 118.1 (d, $J_{CP} = 9$ Hz, cyclometalated pyrrolyl positions) 115.4 (d, $J_{CP} = 10$ Hz, cyclometalated pyrrolyl position), 112.8 (d, $^3J_{CP} = 7$ Hz, pyrrolyl 3,4 positions), 112.1 (d, $^3J_{CP} = 6$ Hz, pyrrolyl 3,4 positions), 106.4, 106.1, 105.9 (Tp 4 positions), 2.5 (NC*C*H$_3$). ^{31}P-{^{1}H} NMR (C_6D_6, δ): 74.2 {*P*(pyr)$_2$pyr}. EI-MS: *m*/*z* (%) $M_{theoretical} = 584.1060$, $M_{sample} = 584.1071$ ($\sigma = 1.9$ ppm), [M$^+$]. Anal. Calcd for $C_{23}H_{24}BN_{10}PRu$: C, 47.35; H, 4.15; N, 24.01. Found: C, 47.97; H, 4.32; N, 23.21. Note: A ^{1}H NMR spectrum of the analysis sample prior to shipping revealed 0.1 equiv of THF and 0.05 equiv of hexane per equivalent of **6**. When the presence of residual solvent is taken into account, the calcd data are: C, 47.85; H, 4.32; N, 23.54. Extend drying (5 days) under dynamic

vacuum did not remove the residual THF and hexane. See Supporting Information for corresponding ^{1}H NMR spectrum.

Conversion of TpRu{P(pyr)$_3$}(NCMe)Me (1) and C_6D_6 to TpRu{P(pyr)$_3$}(NCMe)Ph-d_5 (5-d_5) by ^{1}H NMR Spectroscopy. A solution of **1** (0.039 g, 0.064 mmol) in 2.0 mL of C_6D_6, with a small crystal of hexamethylbenzene as internal standard, was divided among three screw-cap NMR tubes. The triplicate set was heated at 60 °C in a temperature-regulated oil bath, and ^{1}H NMR spectra were periodically acquired through 3 half-lives (using a pulse delay of 5 s). The disappearance of **1** was followed by integration of the decreasing resonance due to the Ru−CH_3 at 1.08 ppm, and the formation of **5** was followed by the increasing resonances due to two Tp 3 or 5 protons at 7.26 and 6.86 ppm relative to the standard hexamethylbenzene.

Kinetic Studies: Rate of Acetonitrile Dissociation for TpRu{P(pyr)$_3$}(NCMe)Me (1). A solution of **1** (0.017 g, 0.058 mmol) in 2.4 mL of $NCCH_3$ (46.0 mmol) with 1.0 μL (0.005 mmol) of hexamethyldisiloxane, as internal standard, was divided among three screw-cap NMR tubes. The triplicate set was heated at 60 °C in a temperature-regulated oil bath, and ^{1}H NMR spectra were periodically acquired through 3 half-lives (using a pulse delay of 5 s). Acetonitrile dissociation was followed by integration of the decreasing resonance due to coordinated $NCCH_3$ at 2.25 ppm relative to the standard hexamethyldisiloxane.

Reaction of TpRu{P(pyr)$_3$}(NCMe)Ph (5) with Ethylene. TpRu{P(pyr)$_3$}(NCMe)Ph (**5**) (0.016 g, 0.03 mmol), with a small crystal of hexamethylbenzene as internal standard, was dissolved in THF-d_8 (0.4 mL), placed in a J-Young NMR tube, pressurized to 80 psi with C_2H_4, and heated to 60 °C. The reaction was regularly analyzed by ^{1}H NMR spectroscopy to analyze for potential C_2H_4 coordination and subsequent TpRu{P(pyr)$_3$}(η^3-C_4H_7) formation. After 5.5 days of heating, the reaction mixture consisted of the starting material **5** (∼75% versus internal standard hexamethylbenzene) and presumably ∼25% NMR-silent and paramagnetic materials.

Computational Methods. As full experimental ligand models were studied, the MOE program[61] and the MMFF94[62] force field were initially used to identify the lowest energy conformations for subsequent refinement of geometries with DFT methods. All quantum calculations employed the Gaussian03 package.[63] The B3LYP functional (Becke's three-parameter hybrid functional[64] using the LYP correlation functional containing both local and nonlocal terms of Lee, Yang, and Parr)[65] and VWN (Slater local exchange functional[66] plus the local correlation functional of Vosko, Wilk, and Nusair)[67] were employed in conjunction with the Stevens (SBK) valence basis sets and effective core potentials for all heavy atoms and the -31G basis set for hydrogen. The SBK valence basis sets are valence triplet-ζ for ruthenium and double-ζ for main group elements. The basis sets of main group elements are augmented with a d-polarization function: $\xi_d = 0.8$ for boron, carbon, nitrogen, and oxygen and $\xi_d = 0.55$ for phosphorus. The SBK scheme utilizes a semicore (46-electron core) approximation for ruthenium and a full core approximation for main group elements. All complexes modeled are closed-shell (diamagnetic) species and were modeled within the restricted Kohn−Sham formalism. All systems were fully optimized without symmetry constraint, and analytic calculations of the energy Hessian were performed to confirm species as minima or transition states and to obtain enthalpies and free energies (using unscaled vibrational frequencies) in the gas phase at 1 atm and 298.15 K.

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Supporting Information Available: ^{1}H NMR spectra of complexes **3** and **6** as well as complete tables of crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for X-ray structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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