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Reactivity of TpRu(L)(NCMe)R (L = CO, PMe_3; R = Me, Ph) systems with isonitriles: Experimental and computational studies toward the intra- and intermolecular hydroarylation of isonitriles

John P. Lee [a], J. Oscar C. Jimenez-Halla [b], Thomas R. Cundari [b,*], T. Brent Gunnoe [a,*]

[a] Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, United States
[b] Center for Advanced Scientific Computing and Modeling (CASCaM), Department of Chemistry, University of North Texas, Box 305070, Denton, TX 76203-5070, United States

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Abstract

The Ru(II) phenyl complex TpRu(PMe_3)(NCMe)Ph {Tp = hydridotris(pyrazolyl)borate} reacts with isonitriles to form complexes of the type TpRu(PMe_3)(C≡NR)Ph (R = ^{t}Bu, CH_2Ph, CH_2CH_2Ph). Neither thermal nor photolytic reactions of these systems with excess isonitrile and benzene resulted in the production of corresponding imines. DFT studies that probed the energetics of the desired catalytic transformations revealed that (Tab)Ru(PH_3)(C≡NCH_2CH_2Ph)Ph {Tab = tris(azo)borate} is the most stable species in a proposed catalytic cycle. Exclusive of calculated transition states, the highest points on the calculated free energy surface are 34 kcal/mol, for (Tab)-Ru(PH_3)(o,η^2-C,C-CNCH_2CH_2Ph)Ph {relative to the starting material (Tab)Ru(PH_3)(C≡NCH_2CH_2Ph)Ph}, and 27 kcal/mol for the C–H activation product (Tab)Ru(PH_3)(o-$C_6H_4CH_2CH_2NC$) and benzene. The substantial increases in free energy result primarily from the loss of the stable ruthenium–η^1-isonitrile interaction.

Keywords: Ruthenium; Hydroarylation; Isonitrile; Density Functional Theory studies

1. Introduction

Several advances in the catalytic transformations of aromatic carbon–hydrogen bonds have been reported recently [1–6]. Of particular interest, due at least in part to the atom economical nature of the reactions, is the addition of aromatic C–H bonds across multiple bonds (i.e., hydroarylation) [7–12]. For example, the hydroarylation of olefins provides a route for the catalytic formation of C–C bonds [8–29]. Related reactions with unsaturated substrates that possess C–X (X=N or O) multiple bonds would provide methods for hetero-functionalization of C–H bonds. However, insertion reactions involving substrates with C–N or C–O multiple bonds are relatively rare [30–43]. Furthermore, hydroarylation reactions of substrates with C–O or C–N multiple bonds are often thermodynamically unfavorable. For example, the hydroarylation of C≡O results in a change in free energy of approximately +5.4 kcal/mol [44], and it has been established that several transition metals promote the reverse reaction (i.e., decarbonylation of aldehydes) [45–49]. In contrast to the hydroarylation of CO, the hydroarylation of phenylisonitrile is thermodynamically viable (Scheme 1) [44].

Jones and Tanaka have independently studied the hydroarylation of isonitriles using Ru, Fe and Rh catalysts [44,50–54]. The reactions involving intermolecular hydroarylation and hydroalkylation of isonitriles require photolytic conditions. Though these transformations are seminal examples of hydroarylation of carbon-heteroatom multiple bonds, it would be potentially useful to develop reactions

* Corresponding authors. Tel.: +1 919 513 3704; fax: +1 919 515 8909 (T.B. Gunnoe).
E-mail address: brent_gunnoe@ncsu.edu (T.B. Gunnoe).

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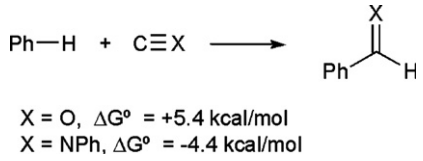


Scheme 1. Thermodynamics of hydrophenylation of carbon monoxide compared with phenylisonitrile.

that occur under thermal conditions. Non-photolytic, *intra*molecular addition of an activated benzylic C–H bond across an isonitrile to produce an indole derivative has been reported by Jones and Kosar [55].

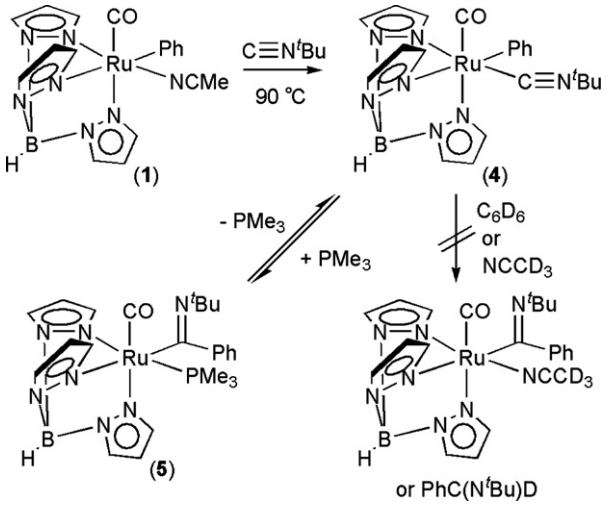
Our group has been pursuing the utilization of Ru(II) complexes as catalysts for the hydroarylation of olefins [56–58]. For example, TpRu(CO)(NCMe)Ph (**1**) {Tp = hydridotris(pyrazolyl)borate} catalyzes the hydroarylation of ethylene and α-olefins, and heteroaryl systems of the type TpRu(CO)(NCMe)Ar (Ar = 2-furyl or 2-thienyl) catalyze the regioselective addition of furan and thiophene 2-position C–H bonds across ethylene [56–58]. Recently, we reported a combined experimental/computational study of the stoichiometric reactivity of complex **1** with various unsaturated substrates that possess carbon-heteroatom multiple bonds [59]. Although net insertions of isonitrile and other substrates with C–X multiple bonds into the Ru–Ph bond of **1** were accessible, catalytic intermolecular hydroarylation was not observed. Herein, we report on attempts to catalyze the addition of aromatic C–H bonds across isonitrile C–N multiple bonds (intra- and intermolecular) using the Ru(II) complexes TpRu(PMe_3)(NCMe)R {R=Ph (**2**) or Me (**3**)} including computational studies that provide insight into the failure to observe catalytic hydroarylation.

2. Results and discussion

2.1. Experimental results

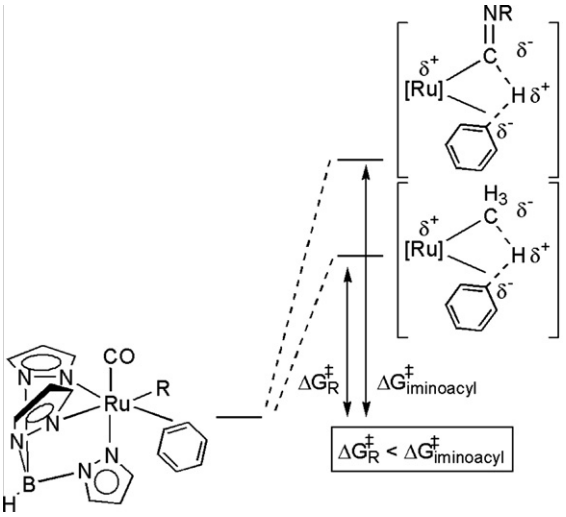
We previously reported that the reaction of TpRu(CO)(NCMe)Ph (**1**) with *t*-butylisonitrile produces TpRu(CO)(CN^{t}Bu)Ph (**4**) (Scheme 2) [59], which undergoes insertion to produce TpRu(CO){*C*(Ph)=N(^{t}Bu)}(PMe_3) (**5**) (in equilibrium with starting substrates) in the presence of PMe_3 (Scheme 2). At 298 K, isonitrile insertion from the model (Tab)Ru(CO)(C≡NH)Ph {Tab = tris(azo)borate} to form (Tab)Ru(CO){*C*(Ph)=NH} was calculated to occur with $\Delta G^{\ddagger} = +17.9$ kcal/mol and a calculated ΔG of +5.0 kcal/mol. Coordination of PH_3 to form (Tab)Ru(CO){*C*(Ph)=NH}(PH_3) was calculated to result in $\Delta G = -7.5$ kcal/mol starting from (Tab)Ru(CO)(C≡NH)Ph and free PH_3. Experimentally, a van't Hoff plot revealed that the ΔH and ΔS values for conversion of **4** and PMe_3 to complex **5** are 9(1) kcal/mol and 20(3) eu, respectively [59].

Although isonitrile insertion is observed with complex **1**, catalytic hydroarylation of the isonitrile (from benzene and excess *t*-butylisonitrile) does not occur. For example,



Scheme 2. Formation of TpRu(CO)(CN^{t}Bu)Ph and isonitrile insertion into the Ru–Ph bond and coordination of PMe_3 to form TpRu(CO){C(Ph)=N(^{t}Bu)}(PMe_3).

attempted catalytic hydrophenylation of *t*-butylisonitrile using either complex **1** or **4** in C_6H_6 does not result in the production of *N*-benzylidene-*t*-butylamine at temperatures up to 120 °C. Given that isonitrile insertion is accessible, the failure to observe production of free imine, which would occur through benzene coordination and C–H activation, is most likely attributable to a substantial kinetic barrier to aromatic C–H activation by the Ru–iminoacyl system. Although complexes of the type TpRu(L)(aromatic)R (R = alkyl or aryl) have been demonstrated to initiate aromatic C–H activation to produce TpRu(L)(aryl) and R–H [57,58,60,61], it is possible that when R = iminoacyl the reduced basicity of the iminoacyl ligand (relative to a simple alkyl or aryl ligand) increases the free energy of activation for the C–H bond cleavage (Scheme 3).



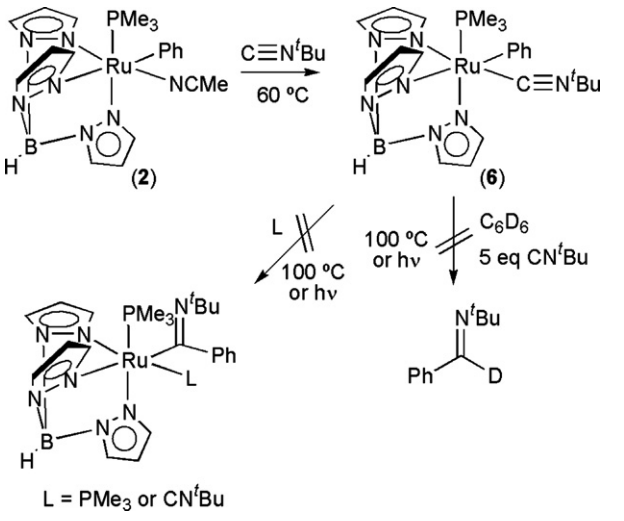
Scheme 3. Gibbs free energy of activation for aromatic C–H activation may be larger for iminoacyl ligand (C=NR) versus alkyl ligand (Me) due to reduced basicity of the former.

Calculations focused on aromatic C–H activation mediated by TpRu(L)R fragments reveal that the transition state is best described as a σ-bond metathesis transformation (i.e., no oxidative addition intermediate is identified) in which a close Ru–H contact (Ru–H distance = 1.61 Å) is calculated (for the hydrogen being activated) [57,62]. This Ru–H interaction suggests the possibility of "oxidative character" for the C–H activation step, and hence, increased electron density at the metal center might facilitate the reaction and therefore potentially render the hydroarylation of isonitriles accessible. Thus, we pursued possible hydroarylation of isonitriles using complexes of the type $TpRu(PMe_3)(C{\equiv}NR)R$ with the strongly donating PMe_3 substituted for CO of complex **1**.

Reaction of $TpRu(PMe_3)(NCMe)Ph$ (**2**) with *t*-butylisonitrile results in the ligand exchange product, $TpRu(PMe_3)(CN^tBu)Ph$ (**6**) (Scheme 4). Neither prolonged heating (100 °C) nor photolysis of **6** in C_6D_6 affords 1,1-insertion of the isonitrile (in the presence of excess CN^tBu or PMe_3) or production of imine (Scheme 4).

The substitution of PMe_3 for CO either renders the isonitrile insertion thermodynamically unfavorable or results in a substantial increase in the activation barrier for isonitrile insertion. Calculations on model complexes support the thermodynamic argument as the calculated $\Delta G^{\ddagger}$s (~ 18 kcal/mol) for isonitrile insertion into the $Ru–C_{ipso}$ bond of (Tab)Ru(L)(Ph)(CNH) {Tab = tris(azo)borate; L = CO or PH_3} are identical whether the coligand "L" is PH_3 or CO (Scheme 5). However, isonitrile insertion and subsequent coordination of PH_3 {(Tab)Ru(L)(Ph)(CNH) + PH_3 → (Tab)Ru(L)(PH_3)(C(=NH)Ph)} is calculated to be overall exergonic for L = CO ($\Delta G_{rxn} = -2.5$ kcal/mol), but endergonic for L = PH_3 ($\Delta G_{rxn} = +1.3$ kcal/mol).

IR spectroscopy reveals that the energy of absorption for the coordinated isonitrile ligands (ν_{CN}) of the PMe_3 complex **6** is 2030 cm^{-1} while that of the CO complex **4** is 2143 cm^{-1}. Furthermore, the Rh(III) complexes

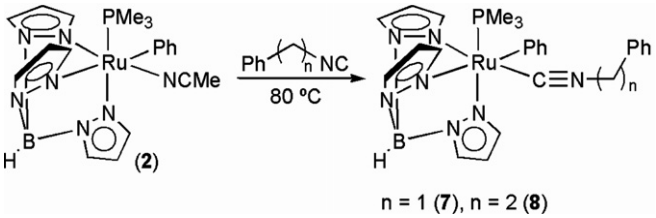


Scheme 4. Formation of $TpRu(PMe_3)(CN^tBu)Ph$ and lack of reactivity toward insertion or hydroarylation of isonitrile.

$Cp^*Rh(X)(p\text{-tolyl})(CNneo\text{-}Pn)$ (Cp^* = pentamethylcyclopentadienyl; X = Cl or Br; CNneo-Pn = neopentyl-isonitrile), which exhibit $\nu_{CN} = 2180$ (Cl) and 2190 (Br) cm^{-1}, were found to undergo facile 1,1-insertion of isonitrile into the Rh-*p*-tolyl bond [44]. Thus, higher energy ν_{CN} may reflect an enhanced propensity toward insertion of isonitrile, which is consistent with isonitrile insertion being dictated, at least in part, by the extent of electron density donated from the metal dπ orbitals to the π* orbitals of the isonitrile. That is, more strongly π-basic metal centers exhibit increased dπ-back-bonding, which serves to strengthen metal-isonitrile coordination and potentially render insertion less favorable thermodynamically.

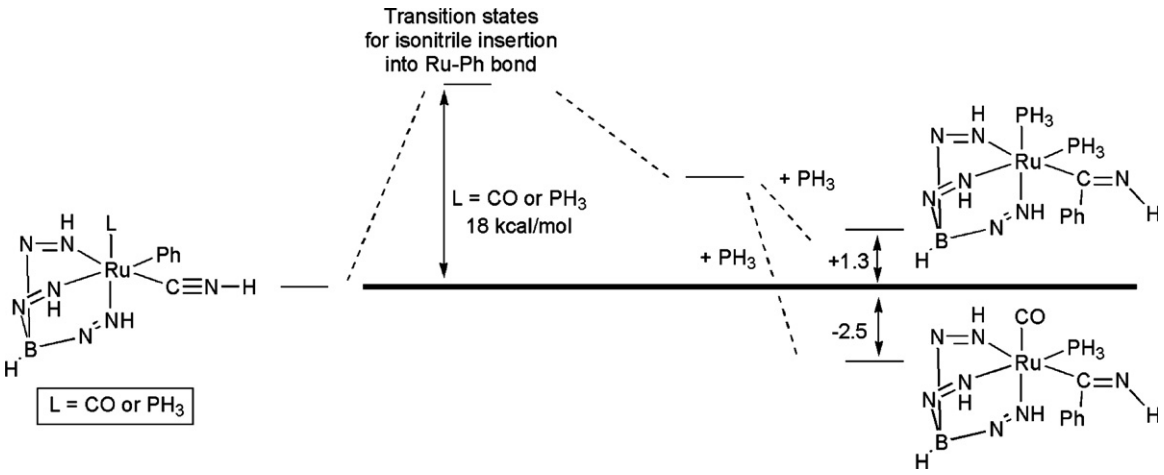
Intramolecular hydroarylation of isonitriles catalyzed by $TpRu(PMe_3)(C{\equiv}NR)Ph$ was attempted. A possible catalytic cycle is depicted in Scheme 6. The key step in this transformation is likely the intramolecular C–H activation of a tethered phenyl ring on a coordinated isonitrile to produce benzene and a metallacycle. If accessible, the cyclometalated complex would possess ring strain and thus may undergo a facile insertion to produce the coordinated cyclic imine. A subsequent intermolecular C–H activation of a second equivalent of isonitrile would release the organic product and complete the catalytic cycle.

Complex **2** reacts with benzylisonitrile and β-phenethylisonitrile to produce $TpRu(PMe_3)(CNCH_2Ph)Ph$ (**7**) and $TpRu(PMe_3)\{CN(CH_2)_2\}Ph$ (**8**), respectively (Eq. (1)). Although produced quantitatively by ^1H NMR spectroscopy, complexes **7** and **8** were isolated in 48% and 32% yield (likely due to high solubility in hydrocarbon solvents and difficulty in separation), respectively, and characterized by ^1H, ^{13}C and ^{31}P NMR and IR spectroscopy as well as elemental analysis. Salient spectroscopic features of complexes **7** and **8** include ^1H and ^{13}C spectra that are consistent with asymmetric complexes as well as singlets in the ^{31}P NMR spectra at 17.2 ppm and 17.0 ppm, respectively, and $\nu_{CN} = 2082$ cm^{-1} and 2066 cm^{-1}, respectively.

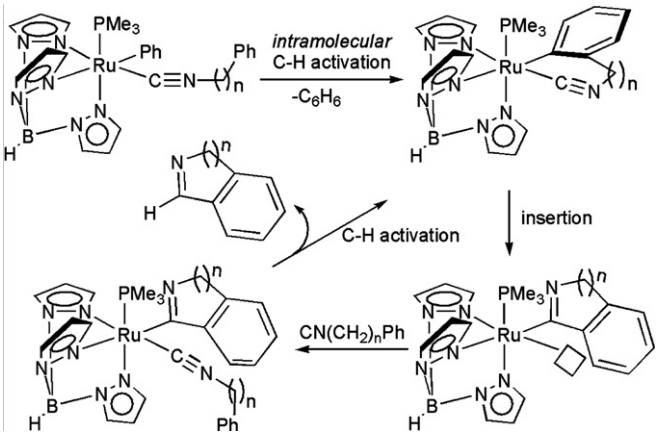


(1)

Several attempts were made to induce stoichiometric C–H activation of the tethered phenyl ring as well as catalytic production of cyclic imine using complexes **7** and **8**. Both thermal (100 °C) and photolytic reactions of complex **7** or **8** in C_6D_6 in the presence of excess isonitrile resulted in either no reaction, formation of an uncharacterized TpRu product, which is likely the bis-isonitrile complex $TpRu\{CN(CH_2)_n\}_2Ph$ ($n = 1$ or 2) (see Section 4) and free trimethylphosphine or decomposition to ^1H NMR silent paramagnetic species. In each reaction, no evidence of intramolecular C–H activation to produce free benzene from the



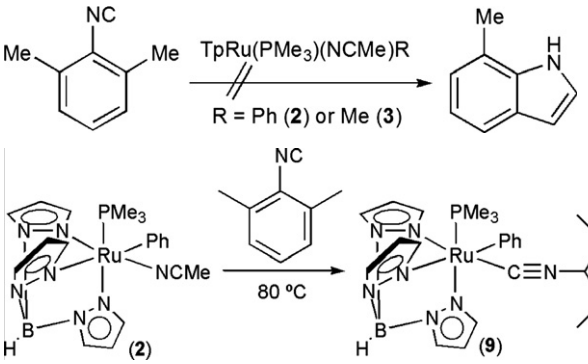
Scheme 5. Calculated {B3LYP/CEP-31G(d) level of theory} Gibbs free energies (given in kcal/mol, 298 K) for isonitrile insertion into Ru–Ph bonds of (Tab)Ru(L)(Ph)(C≡NH) as a function of ancillary ligand identity (L = CO or PH_3).



Scheme 6. Proposed pathway for the intramolecular hydroarylation of isonitriles.

phenyl ligand of **7** or **8** was obtained, and monitoring the reactions by GC-FID did not reveal evidence of new organic product(s). Heating solutions of **7** or **8** in cyclohexane-d_{12} (100 °C) in the absence of excess free isonitrile for 3 days did not result in observable reaction, which demonstrates the stability of **7** and **8**. In addition, photolysis of benzene solutions of **7** and **8**, in the absence of excess isonitrile, results in decomposition to multiple intractable products.

To further study the potential for intramolecular isonitrile activation, the reactivity of **2** with 2,6-xylyl-isonitrile to potentially produce 7-methylindole from benzylic C–H activation and net 1,1-insertion of the isonitrile was studied (Eq. (2)). Jones and co-workers have reported a ruthenium catalyst for this reaction in which the catalytic transformation likely proceeds by activation of a benzylic C–H bond of coordinated 2,6-xylyl-isonitrile [55]. Heating (80 °C) a solution of **2** with excess free 2,6-xylyl-isonitrile in C_6D_6 results in the formation of $TpRu(PMe_3)$(CN-xylyl)Ph (**9**) and acetonitrile (^1H and ^{31}P NMR spectroscopy) (Eq. (3)). Prolonged heating of **9** at 100 °C results in the formation of a new TpRu product, which is likely TpRu(CN-xylyl)$_2$Ph (see Section 4), and free trimethylphosphine with no evidence of formation of free benzene or 7-methylindole. The same results were observed when a C_6D_6 solution of complex **9** (produced in situ) was reacted under photolytic conditions.



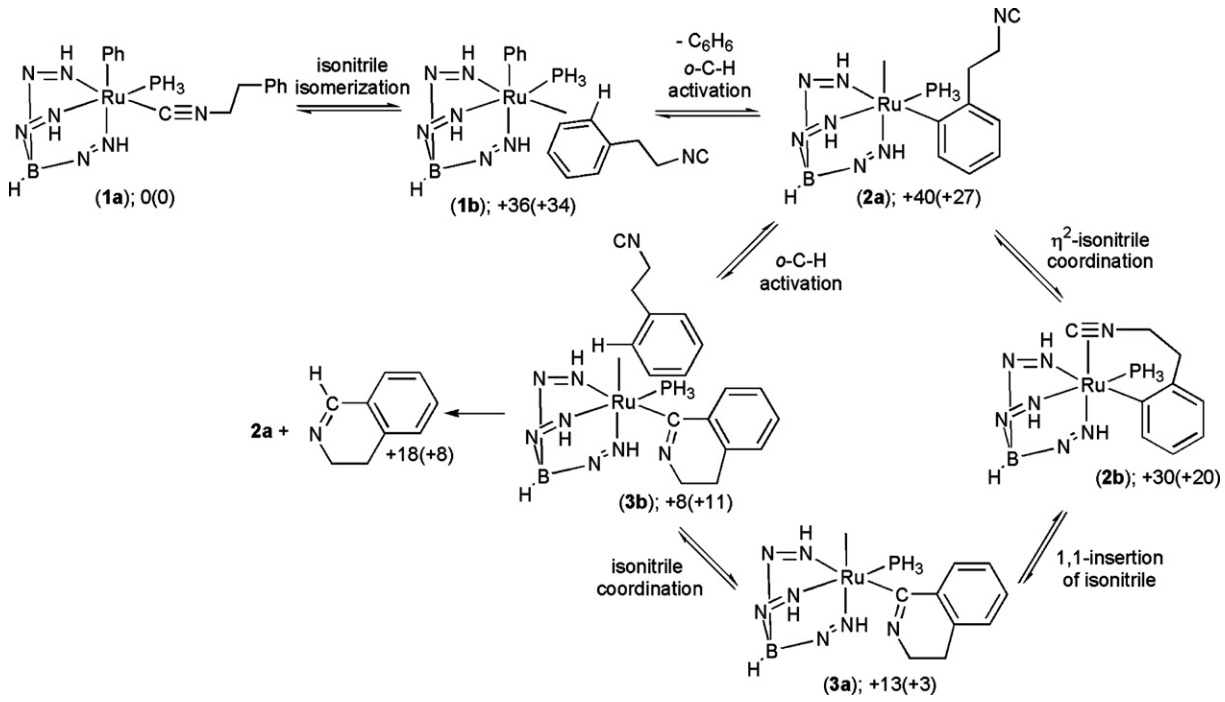
(2)

(3)

2.2. Computational studies

Theoretical calculations were performed to delineate the details of intramolecular isonitrile hydroarylation (not experimentally observed) mediated by complex **4**. The computational results are summarized in Scheme 7. The "Tab" ligand {(tris(azo)borate)} and PH_3 were used to model Tp and PMe_3, respectively. In previous research, Tab has shown to reproduce the structure and energetics of the full Tp ligand in potential energy surfaces for C–H activation to within $\leqslant$2% and ~2 kcal/mol, respectively [63]. Computational studies were limited to the reactivity of β-phenethylisonitrile since the product of hydroarylation, 3,4-dihydroisoquinoline, is known and isolable [64], compared to the product from intramolecular hydroarylation of benzylisonitrile, isoindole, which is reported to be unstable [65].

In order to enter the proposed catalytic cycle, complex **1a** must undergo intramolecular C–H activation to release



Scheme 7. Calculated {B3LYP/CEP-31G(d) level of theory} enthalpies and free energies (given in parentheses, 298 K) for the hydroarylation of phenethylisonitrile mediated by (Tab)Ru(PH_3)(C≡NCH_2CH_2Ph)Ph. $\Delta H(\Delta G)$ values are given in kcal/mol relative to starting complex (Tab)Ru(PH_3)(C≡NCH_2CH_2Ph)Ph (**1a**).

benzene and form the metallacycle **2b** (Scheme 7). The first step of the proposed mechanism involves isomerization of the η^1-*C*-coordinated β-phenethylisonitrile to place the *ortho* C–H bond to be activated in closer proximity with the metal. While an agostic isomer was sought, the geometry obtained upon DFT optimization of **1b** corresponds more closely to a weak η^2-C=C adduct of benzene rather than a true η^2-C–H agostic system (Fig. 1). The **1a** → **1b** transformation is calculated to be endothermic by 36 kcal/mol. Calculating the binding enthalpy of methylisonitrile to (Tab)Ru(PH_3)Ph reveals a value of 39 kcal/mol. Thus, the η^2-C=C interaction is very weak and estimated to be in the range of ~3 kcal/mol. The calculated enthalpy difference for the **1a** → **1b** transformation corresponds almost entirely to the energetics of dissociating the isonitrile ligand from the complex, compensated minimally by a weak π-arene interaction.

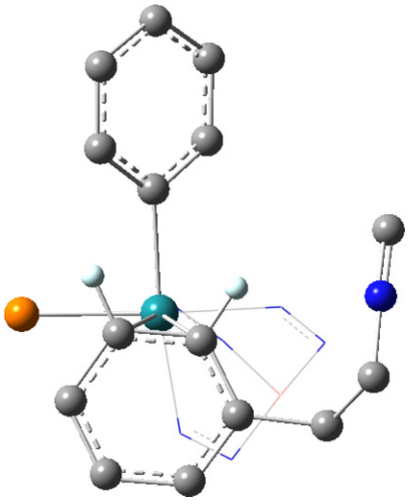


Fig. 1. Calculated geometry of (Tab)Ru(PH_3)(η^2-*C*,*C*- $C_6H_5CH_2CH_2NC$) (**1b**). The Tab ligand is depicted in wireframe, and hydrogen atoms are omitted for clarity except those closest to the ruthenium.

Aromatic C–H activation from **1b** to produce benzene and the unsaturated 16-electron complex (Tab)Ru(PH_3)(*o*-$C_6H_4CH_2CH_2NC$) (**2a**) is calculated to be close to thermoneutral ($\Delta H_{rxn} = +4$ kcal/mol, see Scheme 7), which implies that the Ru–C bond strengths for the Ru–Ph and Ru–C≡NCH_2CH_2Ph ligands are approximately the same. The BDE(C–H) for benzene and BDE(C_{ortho}–H) for $C_6H_5CH_2CH_2NC$ were calculated to both be ~109 kcal/mol, further supporting the similar Ru–$C_{aryl/isonitrile}$ BDEs. This reaction step proceeds through a transition state (**TS1**) where the imaginary frequency is computed at 1298i cm^{-1} (Fig. 2). The calculated reaction coordinate involves purely H_{ortho}-exchange from the isonitrile group to the phenyl ring. Furthermore, the calculated $\Delta H^{\ddagger}$ of 28 kcal/mol (**1b** → **TS1**) is due primarily to the arene C–H bond activation since that the C(phenyl)–Ru distance is smaller than C(isonitrile)–Ru bond by ~0.1 Å. **TS1** leads to a weak agostic complex (**I-2a**), which then dissociates benzene to form **2a**. This process, **I-2a** → **2a**, is calculated to be endothermic by 2.5 kcal/mol.

Coordination (η^2) of the pendant N≡C arm of **2a** produces the 18-electron complex **2b** (Fig. 3). The conversion

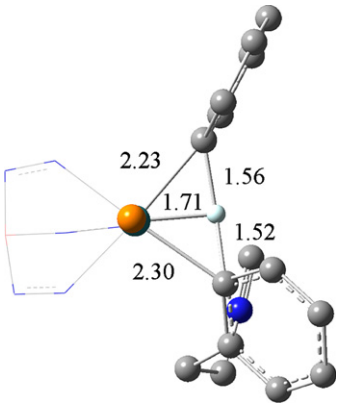


Fig. 2. Calculated geometry of **TS1**. The Tab ligand is depicted in wireframe, and hydrogen atoms are omitted for clarity except the activated hydrogen (salient bond distances are given).

of **2a** to **2b** is calculated to be exothermic ($\Delta H = -10$ kcal/mol, Scheme 7) with a favorable change in Gibbs free energy of −7 kcal/mol. Examples of nitriles coordinated in an η^2 mode are relatively rare [66–71], and a search of the Cambridge Structural Database reveals no examples of η^2-coordinated isonitrile ligands. The minimal binding energy gained by side-on ligation of the isonitrile moiety to the 16-electron complex **2a** to yield **2b** is likely partially offset by greater steric hindrance (~1 kcal/mol) in the latter that is engendered by rotating the CH_2CH_2NC arm of the isonitrile into a conformation suitable for binding to Ru. Furthermore, bending of the C≡N–C group from 178° (**2a**) to 151° (**2b**) is calculated to cost an additional 4 kcal/mol for the $C_6H_4CH_2CH_2NC$ fragment.

The 1,1-isonitrile insertion reaction, **2b** to **3a**, Fig. 4, is calculated to be exothermic by a substantial 17 kcal/mol, Scheme 7, and largely reflects the greater stability of the 3,4-dihydroisoquinolinyl ligand (Q) in **3a** versus the κ^2-$C_6H_4CH_2CH_2NC$ ligand (Z) of complex **2b** (calculated ΔH_{Q-Z} for the organic radical fragments is −31 kcal/mol; Scheme 8). The enthalpy gain from the 1,1-insertion of the isonitrile is offset to a degree by a stronger Ru–C bond for **2b** (ligand Z) as compared to **3a** (ligand Q) {calculated $\Delta BDE(C–H)_{Q-Z} = +10$ kcal/mol}, and to a lesser extent the loss of the weak η^2-N≡C interaction in **2b**. Moreover, isonitrile rearrangement prior to the 1,1-insertion step requires bending of the isocyanide group for ring closure. This intermediate (**I-3**, Fig. 4) was found, and its formation from **3a** is calculated to be exothermic by 15 kcal/mol from **3a**, reflecting the strong σ-donor character of the isonitrile. There is a low energy TS (imaginary frequency = 185i cm^{-1}) for the **2b** → **I-3** transformation with a small calculated enthalpic barrier of 4.8 kcal/mol.

We have calculated the **I-3** → **3a** transformation to form the second ring of the desired product to be exothermic by 1.5 kcal/mol. No search for an **I-3** → **3a** transition state was initiated since it is anticipated that this putative insertion step proceeds without a significant activation barrier.

The coordination of a second equivalent of phenethylisonitrile to **3a** via a C=C bond is mildly exothermic ($\Delta H_{rxn} = -5$ kcal/mol), but endergonic by +8 kcal/mol. This reflects weak η^2-C=C binding, which is estimated at ~3 kcal/mol in the **1a** → **1b** step of the process (see above). The release of product, 3,4-dihydroisoquinoline (Z–H), from the Ru species by C–H activation of phenethylisonitrile is calculated to be endothermic by 10 kcal/mol. This likely reflects the intrinsically lower bond strength of Q–H versus Z–H {calculated $\Delta BDE(C–H)_{Q-Z} = +10$ kcal/mol}.

Complex **1a** is calculated to be the most thermodynamically stable species in the catalytic cycle, and even without calculated transition states the highest points on the potential energy surface are +40 kcal/mol (**2a** + benzene) on the enthalpy surface and +34 kcal/mol (**1b**) on the free energy surface (Scheme 7). The isonitrile ligand in the starting material complex **1a** is strongly bound (35–40 kcal/mol) and loss of this binding, coupled with almost no thermodynamic gain from π-arene interaction of the phenethylisonitrile substrate renders virtually any transformation from starting material **1a** significantly uphill, including the catalytic cycle for isonitrile hydroarylation (Scheme 7). Assuming a system could be designed that permits access to an active species like **2a**, subsequent steps in the catalytic cycle

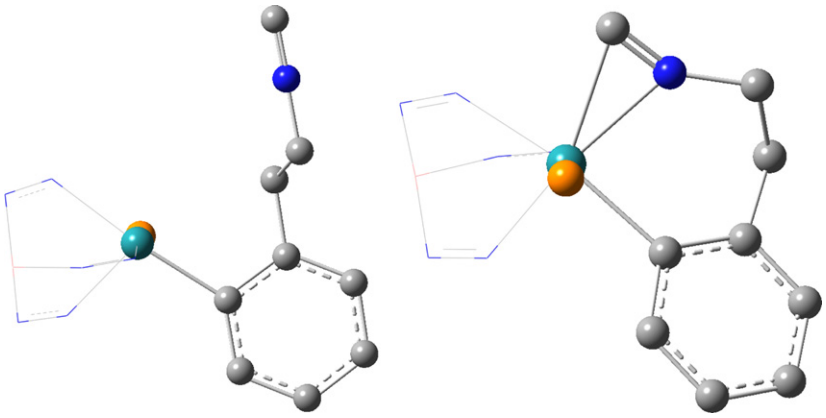


Fig. 3. Calculated geometries of **2a** (left) and **2b** (right). The Tab ligand is depicted in wireframe, and hydrogen atoms are omitted for clarity.

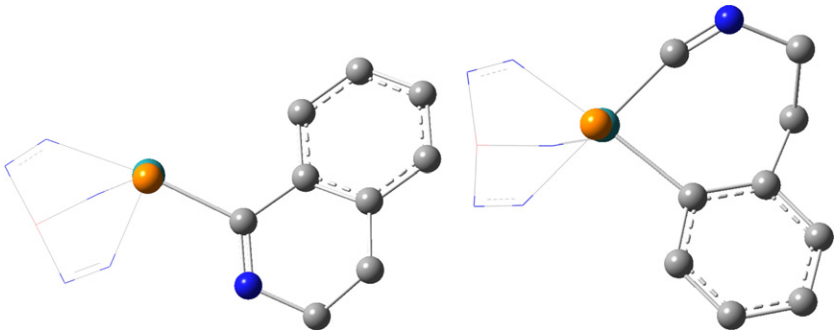
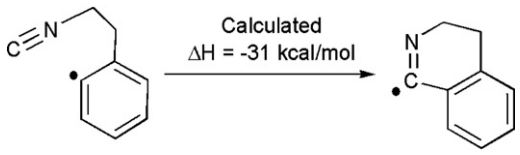


Fig. 4. Calculated geometry of **3a** (left) and **I-3** (right). The Tab ligand is depicted in wireframe, and hydrogen atoms are omitted for clarity.



Scheme 8. Calculated {B3LYP/CEP-31G(d) level of theory} enthalpy change conversion of organic radical "Z" from **2b** to the 3,4-dihydroisoquinolinyl radical "Q" from **3a**.

are thermodynamically reasonable due to greater intrinsic stability of the fused ring hydroarylation product ($\Delta H_{Q-Z} = -31$ kcal/mol; $\Delta H_{QH-QZ} = -22$ kcal/mol).

3. Conclusions

The combined experimental and computational studies focused on intra- and intermolecular hydroarylation of isonitriles using the Ru(II) complexes $TpRu(PMe_3)(NCMe)R$ lead to the following conclusions:

(1) The lack of reactivity of $TpRu(PMe_3)(CN^tBu)Ph$ (**6**) toward intermolecular hydroarylation of *t*-butylisonitrile, even in the presence of Lewis bases that could "trap" a coordinatively unsaturated insertion product, is likely due to a thermodynamic bias against the 1,1-insertion of the isonitrile into the Ru–Ph bond. The isonitrile is the only π-acid ligand in the coordination sphere of the relatively electron-rich Ru(II) complex, and, thus, significant metal-to-ligand π-back-bonding likely provides a thermodynamic predilection against the net 1,1-insertion.

(2) The lack of catalytic intramolecular hydroarylation of isonitriles, or any well-defined stoichiometric conversion along the proposed catalytic cycle, mediated by $TpRu(PMe_3)(CNR)Ph$ {$R = CH_2Ph$ (**7**), $R = CH_2CH_2Ph$ (**8**)} is likely due to a highly endothermic reaction to generate reactive intermediates that can undergo intramolecular C–H activation of the isonitrile (e.g., **1a** to **1b** in Scheme 7). Subsequent steps are likely thermodynamically reasonable due to the intrinsic stability of the fused ring imine product compared to the isonitrile starting material. A possible entrée to a more favorable catalytic cycle could be via pathways in which the strong Ru–isonitrile interaction is maintained insofar as possible until the second ring of the desired product is formed, perhaps through a mechanism that entails loss of the trimethylphosphine ligand or another weakly coordinated coligand.

4. Experimental

4.1. Materials

All solvents were degassed by N_2 (g) purging prior to use. Acetonitrile was purified by passage through two columns of activated alumina followed by distillation from CaH_2. Dichloromethane and hexanes were purified by passage through two columns of activated alumina. Benzene, pentane, tetrahydrofuran and toluene were purified by distillation from sodium/benzophenone. CD_3CN, C_6D_6 and $CDCl_3$ were degassed via three freeze–pump–thaw cycles and stored over activated 4 Å molecular sieves, and C_6D_{12} was used as received in glass ampules sealed under N_2. Synthetic and characterization details of TpRu(CO)(NCMe)Ph (**1**) [56], $TpRu(PMe_3)(NCMe)Ph$ (**2**) [61], $TpRu(PMe_3)(NCMe)Me$ (**3**) [60], $TpRu(CO)(CN^tBu)Ph$ (**4**) [59], $TpRu(CO)\{C(Ph)=N(^tBu)\}(PMe_3)$ (**5**) [59] and $TpRu(PMe_3)(CN^tBu)Ph$ (**6**) [60] have been previously reported. Benzylisonitrile, β-phenethylisonitrile and 2,6-dimethyl-phenylisonitrile were purchased from Sigma–Aldrich and used as received. All other reagents were used as purchased from commercial sources.

4.2. Measurements

All reactions and procedures were performed under anaerobic conditions in a nitrogen filled glovebox or using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and monitored by an oxygen analyzer {O_2(g) < 15 ppm for all reactions}. Photolysis experiments were performed using a 450 W power supply, 450 W lamp, and a quartz cooling jacket with flowing water. ^1H and ^{13}C NMR spectra were obtained on either a Varian Mercury 300 MHz or Varian Mercury 400 MHz spectrometer (operating frequencies for ^{13}C NMR are 75 and 100 MHz, respectively) and referenced against tetramethylsilane using residual proton signals (^1H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). Resonances due to the Tp ligand are listed by

chemical shift and multiplicity only (all coupling constants for the Tp ligand are ~2 Hz). ^{31}P NMR spectra were obtained on a Varian Mercury 400 MHz (operating frequency 161 MHz) spectrometer and referenced against external 85% H_3PO_4. Unless otherwise noted, NMR spectra were acquired at room temperature. IR spectra were obtained on a Mattson Genesis II spectrometer as thin films on a KBr plate. Elemental analyses were performed by Atlantic Microlabs, Inc.

4.3. Syntheses/reactions

4.3.1. Reactivity of TpRu(PMe$_3$)(NCMe)Ph (2) and t-butylisonitrile

Method A. *t*-Butylisonitrile (0.020 mL, 0.018 mmol) was added to a colorless solution of **2** (0.018 g, 0.0035 mmol) in C_6D_6 (0.7 mL), and the solution was transferred to a screw-cap NMR tube. This solution was heated to 80 °C (5 h) to form previously reported TpRu(PMe$_3$)(CN^{t}Bu)Ph (**6**) (^{1}H NMR spectroscopy). The solution was then heated to 90 °C and monitored periodically by ^{1}H NMR spectroscopy. After 24 h, the reaction showed no change by ^{1}H NMR spectroscopy.

Method B. *t*-Butylisonitrile (0.025 mL, 0.025 mmol) was added to a colorless solution of **2** (0.022 g, 0.0048 mmol) in C_6D_6 (0.7 mL) and transferred to a screw-cap NMR tube. This solution was heated to 80 °C (5 h) to form TpRu(PMe$_3$)(CN^{t}Bu)Ph (**6**) (^{1}H NMR spectroscopy). The reaction was then placed under photolytic conditions and monitored periodically by ^{1}H NMR spectroscopy. After 12 h the reaction showed no change by ^{1}H NMR spectroscopy.

4.3.2. Thermolysis of TpRu(PMe$_3$)(CN^{t}Bu)Ph (6) and trimethylphosphine

t-Butylisonitrile (0.007 mL, 0.0062 mmol) was added to a colorless solution of **2** (0.017 g, 0.0033 mmol) in C_6D_6 (0.7 mL) and transferred to a screw-cap NMR tube. This solution was heated to 60 °C (15 h) to form TpRu(PMe$_3$)(CN^{t}Bu)Ph (**6**) (^{1}H NMR spectroscopy). Trimethylphosphine (0.007 mL, 0.008 mmol) was added to the colorless solution. The resulting solution was heated to 100 °C and monitored periodically by ^{1}H NMR spectroscopy. After 24 h the reaction showed no change by ^{1}H NMR spectroscopy.

4.3.3. Preparation of TpRu(PMe$_3$)(CNCH$_2$Ph)Ph (7)

A colorless solution of **2** (0.209 g, 0.411 mmol) and benzylisonitrile (0.15 mL, 1.2 mmol) in THF (20 mL) was heated in an oil bath to 80 °C for 6 h. After the heating period, the volatiles were removed in vacuo to produce a colorless oil. The oil was dissolved in dichloromethane and purified by column chromatography on silica gel eluting with dichloromethane. The product came off as a light yellow band. The dichloromethane was reduced to approximately 1 mL, under vacuum, and hexanes were added to precipitate a white solid. The white solid was collected by vacuum filtration, washed with pentane, and dried in vacuo (0.114 g, 48% yield). IR (KBr): $\nu_{CN} = 2066\ cm^{-1}$. ^{1}H NMR (C_6D_{12}, δ): 7.56, 7.52, 7.42, 7.40 (4H total, 1:1:1:1 ratio, each a d, Tp C*H* 3/5 position), 7.30, 6.92 (2H total, 1:1 ratio, each a d, Tp C*H* 3/5 position), 7.23-7.12 (5H total, m, overlapping phenyl C*H*), 6.91–6.89 {2H total, d (overlapping with Tp-3,5), phenyl C*H*}, 6.64–6.62 (3H total, m, overlapping phenyl C*H*), 6.02, 6.01, 5.79 (3H total, 1:1:1 ratio, each a t, Tp C*H* 4 position), 4.65, 4.75 (2H total, AB pattern, CH_2), 1.14 {9H total, d, $^2J_{HP} = 8$ Hz, P(CH_3)$_3$}. ^{13}C NMR ($CDCl_3$, δ): 179.1 (d, $^2J_{CP} = 19$ Hz, Ru-*C*N or Ru-phenyl *ipso*), 172.1 (d, $^2J_{CP} = 13$ Hz, Ru-phenyl *ipso* or Ru-*C*N), 143.5, 143.4, 143.3, 143.1, 143.0, 142.8, 136.1, 134.7, 134.5, 133.8, 128.7, 127.8, 127.1, 124.7, 119.1 (phenyl and Tp 3/5 positions, note: one resonance missing due to coincidental overlap), 104.9, 104.7 (Tp 4 positions, 2:1 ratio due to coincidental overlap), 48.6 (CN*C*H$_2$Ph), 18.0 {d, $^1J_{CP} = 28$ Hz, Ru-P(*C*H$_3$)$_3$}. ^{31}P NMR ($CDCl_3$, δ): 17.2 (s). Anal. Calc. For $C_{27}H_{33}BN_7PRu$: C, 53.44; H, 5.31; N, 16.78. Found: C, 53.71; H, 5.41; N, 16.57%.

4.3.4. Preparation of TpRu(PMe$_3$)(CNCH$_2$CH$_2$Ph)Ph (8)

A colorless solution of **2** (0.192 g, 0.377 mmol) and β-phenethylisonitrile (0.15 mL, 1.1 mmol) in THF (20 mL) was heated in an oil bath to 80 °C for 6 h. After the heating period, the volatiles were removed in vacuo to produce a colorless oil. The oil was dissolved in dichloromethane and purified by column chromatography on silica gel eluting with dichloromethane. The product came off as a light yellow band. The eluent was reduced to approximately 1 mL, under vacuum, and hexanes were added to precipitate a white solid. The white solid was collected by vacuum filtration, washed with pentane, and dried in vacuo (0.072 g, 32% yield). IR (KBr): $\nu_{CN} = 2082\ cm^{-1}$. ^{1}H NMR (C_6D_{12}, δ): 7.54, 7.51, 7.39, 7.37, 7.28, 6.61 (6H total, 1:1:1:1:1:1 ratio, each a d, Tp C*H* 3/5 position), 7.06-6.98 (5H, m, overlapping phenyl C*H*), 6.91–6.88 (2H, d, $^3J_{HH} = 8$ Hz, phenyl C*H*), 6.65–6.62 (3H, m, overlapping phenyl C*H*), 6.20, 5.99, 5.78 (3H total, 1:1:1 ratio, each a t, Tp C*H* 4 position), 3.79–3.66 (2H total, m, α-CH_2), 2.84 (2H total, overlapping d's, $^3J_{HH} = 7$ Hz, β-CH_2), 1.12 {9H total, d, $^2J_{HP} = 8$ Hz, P(CH_3)$_3$}. ^{13}C NMR ($CDCl_3$, δ): 176.4 (d, $^2J_{CP} = 18$ Hz, Ru-*C*N or Ru-phenyl *ipso*), 172.5 (d, $^2J_{CP} = 13$ Hz, Ru-phenyl *ipso* or Ru-*C*N), 143.4, 143.3, 143.0, 143.2, 143.0, 142.7, 137.9, 134.6, 135.5, 133.8, 133.7, 128.9, 128.7, 126.9, 124.7, 119.0 (phenyl and Tp 3/5 positions), 104.9, 104.7 (Tp 4 positions, 2:1 ratio due to coincidental overlap), 45.7 (CN*C*H$_2$CH$_2$Ph) 37.8 (CNCH$_2$*C*H$_2$Ph), 18.0 {d, $^1J_{CP} = 28$ Hz, Ru-P(*C*H$_3$)$_3$}. ^{31}P NMR ($CDCl_3$, δ): 17.0 (s). Anal. Calc. For $C_{27}H_{33}BN_7PRu$: C, 54.19; H, 5.52; N, 16.39. Found: C, 53.58; H, 5.54; N, 16.10%.

4.3.5. Thermolysis of TpRu(PMe$_3$)(NCMe)Ph (2) and benzylisonitrile

Benzylisonitrile (0.030 mL, 0.025 mmol) was added to a colorless solution of **2** (0.020 g, 0.0039 mmol) in C_6D_6

(0.7 mL) and transferred to a screw-cap NMR tube. The solution was heated to 80 °C and monitored periodically by ^{1}H NMR spectroscopy. After 9 h the complex TpRu(P-Me_3)($CNCH_2Ph$)Ph (**7**) had formed. After prolonged heating (30 h), a second Ru complex was present (Tp resonances and free trimethylphosphine). The data from the ^{1}H NMR spectrum of the new complex are consistent with the partial formation of TpRu($CNCH_2Ph$)$_2$Ph: (C_6D_6, δ) 7.98, 7.75, 7.69 (5H total, 1:2:2 ratio, each a d, Tp C*H* 3/5 position), one Tp C*H* 3/5 position missing due to coincidental overlap, phenyl resonances missing due to coincidental overlap with excess benzylisonitrile, 6.29 (2H total, t, Tp C*H* 4 position), one Tp C*H* 4 position missing due to coincidental overlap, 4.02 (2H total, d, $^2J_{HH} = 7.2$ Hz CH_2), 0.82 {9H total, d, $^2J_{HP} = 2.7$ Hz, free P(CH_3)$_3$}. After 90 h, the complex decomposed. The formation of new organic molecule(s) was not observed by GC-FID.

4.3.6. Thermolysis of TpRu(PMe$_3$)(NCMe)Ph (2) and β-phenethylisonitrile

β-Phenethylisonitrile (0.030 mL, 0.022 mmol) was added to a colorless solution of **2** (0.022 g, 0.0042 mmol) in C_6D_6 (0.7 mL) and transferred to a screw-cap NMR tube. The solution was heated to 80 °C and monitored periodically by ^{1}H NMR spectroscopy. After 9 h, the complex TpRu(P-Me_3)($CNCH_2CH_2Ph$)Ph (**8**) had formed. After prolonged heating (30 h), a second Ru complex was present (Tp resonances and free trimethylphosphine). The data from the ^{1}H NMR spectrum of the new complex are consistent with the partial formation of TpRu($CNCH_2CH_2Ph$)$_2$Ph: (C_6D_6, δ) 7.84, 7.67(2H total, 1:1 ratio, each a d, Tp C*H* 3/5 position), four Tp C*H* 3/5 positions missing due to coincidental overlap, phenyl resonances missing due to coincidental overlap with excess β-phenethylisonitrile, 6.31 (2H total, t, Tp C*H* 4 position), one Tp C*H* 4 position missing due to coincidental overlap, 3.50-3.48 (2H total, m, α-CH_2), 3.01–2.98 (2H total, m, β-CH_2), 0.82 {9H total, d, $^2J_{HP} = 2.7$ Hz, free P(CH_3)$_3$}. After 90 h, the complex had decomposed. Also, the formation of new organic molecule(s) was not observed by GC-FID.

4.3.7. Thermolysis of TpRu(PMe$_3$)($CNCH_2Ph$)Ph (7)

A colorless solution of **7** (0.012 g, 0.0021 mmol) in cyclohexane-d_{12} (0.7 mL) was added to a screw-cap NMR tube. The reaction was heated to 100 °C and monitored periodically by ^{1}H NMR spectroscopy. After prolonged heating (70 h), ^{1}H NMR spectroscopy revealed no reaction.

4.3.8. Thermolysis of TpRu(PMe$_3$)($CNCH_2CH_2Ph$)Ph (8)

A colorless solution of **8** (0.010 g, 0.0017 mmol) in cyclohexane-d_{12} (0.7 mL) was added to a screw-cap NMR tube. The solution was heated to 100 °C and monitored periodically by ^{1}H NMR spectroscopy. After prolonged heating (70 h), ^{1}H NMR spectroscopy revealed no reaction. Note: a small amount of benzene (~4%) was produced but no other changes in the NMR spectrum were observed.

4.3.9. Photolysis of TpRu(PMe$_3$)(NCMe)Ph (2) and benzylisonitrile

Benzylisonitrile (0.020 mL, 0.016 mmol) was added to a colorless solution of **2** (0.016 g, 0.0031 mmol) in C_6D_6 (0.7 mL) and transferred to a screw-cap NMR tube. The solution was photolyzed and monitored periodically by ^{1}H NMR spectroscopy. After 18 h, the complex had undergone partial ligand exchange to form TpRu(P-Me_3)($CNCH_2Ph$)Ph (**7**). After prolonged reaction time (190 h), no additional changes were noted.

4.3.10. Photolysis of TpRu(PMe$_3$)(NCMe)Ph (2) and β-phenethylisonitrile

β-Phenethylisonitrile (0.020 mL, 0.015 mmol) was added to a colorless solution of **2** (0.015 g, 0.0030 mmol) in C_6D_6 (0.7 mL) and transferred to a screw-cap NMR tube. The solution was photolyzed and monitored periodically by ^{1}H NMR spectroscopy. After 18 h, the complex had undergone ligand exchange to form TpRu(PMe_3)-($CNCH_2CH_2Ph$)Ph (**8**). After prolonged reaction time (90 h), a second Ru complex was present (Tp resonances and free trimethylphosphine), but the reaction did not fully convert from the ligand exchange product. After 190 h the complex showed only minimal change by ^{1}H NMR spectroscopy.

4.3.11. Photolysis of TpRu(PMe$_3$)($CNCH_2Ph$)Ph (7) and benzylisonitrile

Benzylisonitrile (0.020 mL, 0.016 mmol) was added to a colorless solution of **7** (0.023 g, 0.0040 mmol) in C_6D_6 (0.7 mL) and transferred to a screw-cap NMR tube. The solution was photolyzed and monitored periodically by ^{1}H NMR spectroscopy. After 20 h, ^{1}H NMR showed a mixture of complex **7** and a new complex. This new complex possessed inequivalent Tp resonances, a new CH_2 resonance, and a new PMe_3 resonance. However, after 90 h, it could not be fully converted, and since the phenyl resonances of the starting material overlap with free isonitrile it cannot be conclusive whether or not this is the intramolecular C–H activation product.

4.3.12. Photolysis of TpRu(PMe$_3$)($CNCH_2CH_2Ph$)Ph (8) and β-phenethylisonitrile

β-Phenethylisonitrile (0.012 mL, 0.0087 mmol) was added to a colorless solution of **8** (0.016 g, 0.0027 mmol) in C_6D_6 (0.7 mL) and transferred to a screw-cap NMR tube. The solution was photolyzed and monitored periodically by ^{1}H NMR spectroscopy. After prolonged reaction time (30 h), a second Ru complex was present {Tp resonances, CH_2 resonances (phenethylisonitrile) and free trimethylphosphine}. However, after 90 h, it could not be fully converted, and since the phenyl resonances of the starting

material overlap with free isonitrile it cannot be conclusive whether or not this is the intramolecular C–H activation product.

4.3.13. Photolysis of $TpRu(PMe_3)(CNCH_2Ph)Ph$ (7)

A colorless solution of **7** (0.015 g, 0.026 mmol) in C_6D_6 (0.7 mL) was added to an NMR tube fitted with a rubber septum. The solution was photolyzed for 20 h and monitored by ^1H NMR spectroscopy. The TpRu complex decomposed to a paramagnetic species for which the resonances had broadened into the baseline of the ^1H NMR spectrum.

4.3.14. Photolysis of $TpRu(PMe_3)(CNCH_2CH_2Ph)Ph$ (8)

A colorless solution of **8** (0.015 g, 0.025 mmol) in C_6D_6 (0.7 mL) was added to an NMR tube fitted with a rubber septum. The solution was photolyzed for 20 h and monitored by ^1H NMR spectroscopy. The TpRu complex decomposed to a paramagnetic species where the resonances had broadened into the baseline of the ^1H NMR spectrum.

4.3.15. Thermolysis of $TpRu(PMe_3)(NCMe)Ph$ (2) and 4-phenyl-2-butanone

4-Phenyl-2-butanone (0.025 mL, 0.17 mmol) was added to a colorless solution of **2** (0.023 g, 0.045 mmol) in C_6D_6 (0.7 mL) and transferred to screw-cap NMR tube. The solution was heated to 80 °C and monitored periodically by ^1H NMR spectroscopy. After 8 h, the ^1H NMR spectrum showed H/D exchange at the Tp-4 positions, and after 18 h the Ru complex had decomposed to a paramagnetic ^1H NMR silent species.

4.3.16. Thermolysis of $TpRu(PMe_3)(NCMe)Ph$ (2) and 2,6-xylylisonitrile

2,6-Xylyl-isonitrile (0.016 g, 0.012 mmol) was added to a colorless solution of **2** (0.016 g, 0.0031 mmol) in C_6D_6 (0.7 mL) and transferred to a screw-cap NMR tube. The reaction was heated to 80 °C and monitored periodically by ^1H NMR spectroscopy. After 3 h the complex $TpRu(PMe_3)$(CN-xylyl)Ph (**9**) had formed. IR (KBr): $\nu_{CN} = 2025\ cm^{-1}$. ^1H NMR (C_6D_6, δ): 7.58 (2H total, overlapping d's, Tp C*H* 3/5 position), 7.32 (1H total, d, Tp C*H* 3/5 position), 7.52–7.46 (5H total, m, overlapping phenyl C*H*), 6.77 (3H total, br s, phenyl C*H*), Tp C*H* 3/5 position missing due to overlap with solvent and phenyl (3H total), 6.01, 5.99, 5.80 (3H total, 1:1:1 ratio, each a t, Tp C*H* 4 position), 2.20 {6H total, s, $(CH_3)_2$}, 1.08 {9H total, d, $^2J_{HP} = 8$ Hz, $P(CH_3)_3$}. ^{31}P NMR (C_6D_6, δ): 14.4 (s). After prolonged heating (100 °C, 130 h), a second uncharacterized Ru complex was observed, consistent with the partial formation of $TpRu(CN\text{-}xylyl)_2Ph$: ($C_6D_6$, δ) 7.94, 7.70 (3H total, 2:1 ratio, each a d, Tp C*H* 3/5 position), three Tp C*H* 3/5 positions missing due to coincidental overlap, 6.99–6.77 (6H total, m, overlapping phenyl C*H*), 6.72–6.67 (5H total, m, phenyl C*H*), 5.97 (2H total, t, Tp C*H* 4 position), one Tp C*H* 4 position missing due to coincidental overlap, 2.29 {12H total, s, $(CH_3)_4$}, 0.82 {9H total, d, $^2J_{HP} = 2.7$ Hz, free $P(CH_3)_3$}. However, after 180 h of heating the ^1H NMR spectrum revealed decomposition to multiple intractable materials.

4.4. Computational methods

The MOE program [72] and the MMFF94 [73] 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 [74]. The B3LYP functional (Becke's three-parameter hybrid exchange functional [75] using the LYP correlation functional containing both local and non-local terms of Lee, Yang, and Parr) [76] and VWN (Slater local exchange functional [77] plus the local correlation functional of Vosko, Wilk, and Nusair) [78] were employed in conjunction with the Stevens valence basis sets and effective core potentials [79,80]. Closed-shell (diamagnetic) and open-shell (paramagnetic) species were modeled within the restricted and unrestricted Kohn–Sham formalisms, respectively. All systems were fully optimized in the gas-phase without symmetry constraint and analytic calculations of the energy Hessian were performed to obtain harmonic vibrational frequencies for each complex. These frequencies were also used to confirm species as minima (all frequencies positive) or transition states (only one negative frequency) and to obtain free energies (using unscaled vibrational frequencies) in the gas phase at 1 atm and 298.15 K. Transition states were analyzed via calculation of the intrinsic reaction coordinate to assess the nature of the reactants and products they connected. Basis set superposition effects were not included in the reported energetics.

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