Reactions of a Ru(II) Phenyl Complex with Substrates that Possess C–N or C–O Multiple Bonds: C–C Bond Formation, N–H Bond Cleavage, and Decarbonylation Reactions

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Introduction

Insertions of substrates that possess multiple bonds into transition metal alkyl, aryl, or hydride bonds provide a fundamental class of reaction that is central to many catalytic cycles. Although insertions of olefin C=C bonds into metal−alkyl, −acyl, −hydride, or −aryl bonds have substantial precedent,1-5 examples of direct observation of insertion reactions involving C–O or C–N multiple bonds of imines, ketones, aldehydes, or related substrates (with the exception of CO and CO 2) are scarce relative to analogous insertions of olefins (Scheme 1).3-6 This is especially true for late transition metal systems, while examples of insertion reactions of C–O or C–N multiple bonds (especially involving the formation of metallacycles) are more prevalent for early transition metal systems.7-11 A potential explanation for the scarcity of insertion reactions involving metal−carbon bonds and substrates with C–O or C–N multiple bonds is the difference in bond dissociation energies (BDEs) for the unsaturated compounds. However, since insertion reactions of C≡X bonds into M−R bonds result in the transformation of C≡X double bonds into C–X single bonds, consideration of the relative BDEs of C≡X (X = C, O, or N) double bonds and C≡X single bonds perhaps provides a more complete picture, and rationalizing reactivity on the basis of typical BDEs for C–C, C–O, and C–N multiple bonds may be too simplistic. Another factor that potentially exacerbates

Scheme 1. Insertion of Olefin, Imine, or Carbonyl Group into M−R′ Bond to Produce C–C and M−X Bonds

R 2C=XR′ + M−R → M−XR + R 2C=R′

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the predisposition against C=O and C=N insertion (relative to C=C insertion) is the resulting M−X (X = N or O) BDEs. For late transition metal systems, it has been demonstrated that M−C(sp²) BDEs can be greater than M−NR₂ BDEs and of similar magnitude to M−OR BDEs.²²⁻²³ Thus, if it is assumed that the C−C BDEs of the inserted products are of similar magnitude, the enthalpic factors that dictate the relative propensity for C−X insertion into M−C bonds are the difference in C=X/C−X BDEs and the relative M−X BDEs making general predictions for classes of substrates complex. Another potential difference between insertion reactions involving C=X bonds and those involving C=C bonds is the access to both monohapto and dihapto coordination modes for the former while the latter is restricted to dihapto coordination.

An increased understanding of the factors that dictate the course of potential insertion reactions involving C=N or C=O multiple bonds could lead to the development of new pathways for carbon−carbon bond formation. For example, several advances in catalytic transformations of aromatic carbon−hydrogen bonds have been recently reported.²⁴⁻⁻⁴¹ Due in part to the atom economical nature of these transformations, the addition of carbon−hydrogen bonds across multiple bonds has emerged as a promising area within organic synthesis.²⁹⁻⁻³³

![Scheme 2. Possible Reaction Pathway for the Formation of Amidinate Complexes 2 and 3](image)

Our group has been exploring the utilization of Ru(II) complexes for the catalytic hydrosylation of olefins.⁵⁴⁻⁻⁵⁶ For example, TpRu(CO)(NCMe)(Ph) (1) (Tp = hydridotris(pyrrozolyl)borate) catalyzes the hydrosylation of ethylene and α-olefins, and heteroaryl systems of the type TpRu(CO)(NCMe)(Ar) (Ar = 2-thiényl or 2-furyl) catalyze the regioselective addition of furan or thiophene 2-position C−H bonds across the C=C bond of ethylene. To date, our studies have focused on the hydrosylation of olefins; however, extension of the C−C bond-forming step to unsaturated substrates other than olefins would ultimately expand the synthetic utility of these reactions. Herein, we report on experimental and computational studies that probe reactions of substrates that possess C−O or C−N multiple bonds with the Ru(II) phenyl complex TpRu(CO)(NCMe)(Ph) (1).

## Results and Discussion

### Experimental Studies

The reaction of TpRu(CO)(NCMe)- (Ph) (1) with either N,N-dimethylcarbodiimide or N,N-di-n-hexylcarbodiimide results in the formation of the corresponding Ru(II) amide complexes TpRu(CO)\{N,N-(Ph)NC(Ph)N(Ph)\} (2) and TpRu(CO)\{N,N-(n-hexyl)NC(Ph)N(n-hexyl)\} (3), respectively (Scheme 2). The amide complexes 2 and 3 are characterized by νCO = 1937 and 1929 cm⁻¹, respectively, in their IR spectra, and ¹H and ¹³C NMR spectra are consistent with C₆ molecular symmetry. Complexes 2 and 3 are the only observable species by NMR spectroscopy (in crude reaction mixtures) and are isolated pure in 39% and 58% yield, respectively, after workup. The formation of amide complex 3 is consistent with the net insertion of C≡N bonds of the carbodiimides into the Ru−Ph bond of the \{TpRu(CO)(Ph)\} fragment followed by chelation to form the aminate moiety (Scheme 2). Insertions of carbodiimides into lanthanide, main group, and electron-deficient early transition metal M−R bonds have been reported.⁵⁷⁻⁻⁶²

![Scheme 2. Possible Reaction Pathway for the Formation of Amidinate Complexes 2 and 3](image)
Scheme 3. Formation of TpRu(CO)(CN'Bu)(Ph) (5), Observation of Insertion of Isonitrile into the Ru–Phenyl Ligand, and Preparation of TpRu(CO)(Ph)(PMe3) (7)

Heating a solution of complex 1 and N-methylacetamide results in the production of free benzene and the amide complex TpRu(CO){N,O-O-C(Me)N(Me)} (4) as the only observable TpRu species in the 1H NMR spectra of crude reaction mixtures (eq 1). The production of benzene has been confirmed by NMR spectroscopy of reactions run in deuterated solvents and NMR tubes. Complex 4 could not be separated from the excess N-methylacetamide (see Experimental Section). Rather than insertion of C=O, complex 1 reacts with N-methylacetamide to initiate N–H bond cleavage and produce benzene and complex 4. Reports of reactions with transition metal systems that involve activation of carboxamide N–H bonds are relatively rare.63 Heating a solution of 1 and N,N-dimethylacetamide (which lacks an N–H bond) results in decomposition to NMR-silent ruthenium complexes; similar observations (i.e., decomposition of 1) are made when complex 1 is heated in neat CD6.55 The reaction of TpRu(CO)(NCMe)(Ph) (1) with CN'Bu forms the ligand-substitution product TpRu(CO)(CN'Bu)(Ph) (5) in quantitative yield by 1H NMR spectroscopy and 33% isolated yield after workup (Scheme 3). Neither extended thermolysis nor photolysis of complex 5 in C6D6 or CD3CN affords isonitrile insertion into the Ru–Ph bond to form TpRu(CO)-{C(Ph)=N'Bu}L (L = CD3CN or C6D6). Assuming that L = benzene or acetonitrile might result in thermodynamically disfavored insertion processes; complex 5 was heated to 100 °C in benzene in the presence of PMe3. Under these conditions, the formation of TpRu(CO){C(Ph)=N'Bu}(PMe3) (6) in equilibrium with complex 5 and free PMe3 is observed (Scheme 3). Salient characterization features of 6 include a resonance at 11.0 ppm in the 31P NMR spectrum, a singlet at 1.21 ppm, and a doublet (JPh = 10 Hz) at 1.27 ppm in the 1H NMR spectrum assigned as the resonances due to the ‘Bu group and the coordinated PMe3, respectively. In addition, following the transformation by IR spectroscopy reveals a new CO absorption at 1927 cm⁻¹ (νCO = 1952 cm⁻¹ for 5) and a decrease in the intensity of the absorption due to the isonitrile C≡N bond. The changes observed by IR spectroscopy are consistent with isonitrile insertion into the Ru–phenyl bond and are inconsistent with insertion of the CO ligand. The independent preparation of TpRu(CO)(Ph)(PMe3) (7) verified that the reaction of TpRu(CO)(CN'Bu)(Ph) (5) and PMe3 does not produce complex 7 (Scheme 3). Insertion of isonitriles into metal–alkyl or –aryle bonds have been previously observed or proposed to occur in catalytic cycles.66–72 Removal of the volatiles from the mixture of 5, 6, and PMe3 in C6D6 (including all free PMe3) and dissolution of the nonvolatiles in C6D6 result in the conversion of 6 back to free PMe3 and complex 5 as determined by NMR spectroscopy. Determination of Keq at temperatures ranging from 70 to 110 °C allowed a linear van’t Hoff plot for the equilibrium between complex 5/PMe3 and complex 6 (Figure 1). The van’t Hoff analysis yields an estimated ΔH = +9(1) kcal/mol and ΔS = +20(3) eu. Thus, the insertion is disfavored by change in enthalpy, supporting the notion that a relatively strong M–L BDE is required to trap the insertion product and allow observation of this species. Cardaci et al. have elucidated the thermodynamic parameters for insertion of CN‘Bu into Fe(II) methyl bonds of cationic octahedral complexes to yield η1-coordinated iminoacyl ligands.73 For these systems, ΔH ranged from −1.6 to −1.9 kcal/mol with ΔS of −5 to −7 eu.

The reaction of complex 1 and benzaldehyde at 90 °C results in net decarbonylation to produce TpRu(CO)(Ph) (8) and benzene (eq 2). Consistent with the formation of a cis-dicarboxyl

![Figure 1](image)

Figure 1. Plot of ln(Keq) versus 1/T (van’t Hoff plot) for the equilibrium between complex 5/PMe3 and complex 6 (R² = 0.96).

complex, the IR spectrum of 8 reveals $\nu_{CO} = 2041$ and 1973 cm$^{-1}$. In addition, $^{1}$H and $^{13}$C NMR spectra reveal resonances consistent with $C_{5}$ molecular symmetry, and the reaction of 8 with trimethylamine-N-oxide in acetonitrile (90 °C) producesTpRu(CO)(NCMe)(Ph) (1). Both stoichiometric and catalytic metal-mediated decarbonylation reactions involving aldehydes have been reported.74–80

For the conversion of TpRu(CO)(NCMe)(Ph) (1) and benzaldehyde to 8 and benzene, the production of benzene could potentially arise from the phenyl ligand of 1 or the phenyl group of the aldehyde. The reaction of 1 with p-tolualdehyde produces benzene and TpRu(CO)$_2$(p-tolyl) (9) (eq 2). Consistent with a dicarbonyl complex, the IR spectrum of 9 exhibits $\nu_{CO} = 2039$ and 1971 cm$^{-1}$, and NMR spectra reveal resonances for the Tp ligand that are indicative of the presence of a mirror plane of symmetry. Slow evaporation of a pentane solution of 9 provided a single-crystal suitable for a solid-state X-ray diffraction study. The ORTEP of 9 is shown in Figure 2, and Table 1 presents selected crystallographic data. Regardless of the specific mechanism for C–H bond cleavage, the production of benzene clearly indicates that the pathway for decarbonylation involves the activation of an aldehyde C–H bond and subsequent (or simultaneous) C–H bond formation with the phenyl ligand of 1 to produce benzene. The aryl groups coordinated to Ru in the final dicarbonyl products TpRu(CO)$_2$-(Ar) are derived from the aldehyde.

Figure 2. ORTEP (30% probability) of TpRu(CO)$_2$(p-tolyl) (9) (hydrogen atoms have been omitted for clarity); selected bond lengths (Å) and bond angles (deg): Ru1–C10 1.857(2); Ru1–C11 1.866(2); Ru1–C12 2.087(2); Ru1–N1 2.120(1); Ru1–N3 2.177(2); Ru1–N5 2.122(1); Ru1–C12–C13 124.7(2); C12–Ru1–C10 89.19(8); C12–Ru1–C11 89.71(8); N1–Ru1–N3 83.69(5); N1–Ru1–N5 85.08(5); N3–Ru1–N5 85.15(5); C12–Ru1–N3 172.50(6); Ru1–C10–O1 179.1(2); Ru1–C11–O2 178.2(2); C10–Ru1–C11 90.07(8).

Table 1. Selected Crystallographic Data and Collection Parameters for Complex 9

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<th>complex</th>
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<tr>
<td>b, Å</td>
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<tr>
<td>c, Å</td>
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<td>78.105(1)</td>
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<tr>
<td>γ, deg</td>
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<tr>
<td>V(A$^3$)</td>
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<tr>
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</tr>
<tr>
<td>GOF</td>
<td>1.029</td>
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</table>

* The crystallographic asymmetric unit also contains a disordered molecule of pentane and a disordered half-molecule of toluene.

Scheme 4. Stabilization of Insertion Products by Either a C–H Agostic Interaction or π-Interaction with the Phenyl Ring

of Ru amido or alkoxide complexes, and the decomposition is analogous to that observed upon heating 1 in neat C$_{6}$D$_{6}$.

Computational Studies of Insertion Reactions. Computational studies were performed to help delineate the details of possible insertion reactions of C=H bonds into the Ru–Ph bond of complex 1. Insertion reactions of five substrates have been studied and are compared herein: (1) ethylene, (2) HN=C=H (methyleneimine), (3) H$_2$C=O (formaldehyde), (4) the parent carbodiimide HN=CC=NH, and (5) the parent isonitrile C≡NH. In addition, the energetics for decarbonylation of H$_2$C=O have been studied computationally. The “Tab” ligand (tris(azo)borate) and HCN were used to model Tp and MeCN, respectively. In previous research, Tab was shown to reproduce the structure and energetics of the full Tp models for C–H activation potential energy surfaces to within ±2% and ~2 kcal/mol, respectively.81 For all substrates other than ethylene, free energy changes for insertion reactions are reported relative to the most stable, i.e., monohapto-coordination mode (rather than relative to the higher-energy π-coordination modes). In addition, products that result from insertion of ethylene, HN=CH$_2$, or H$_2$C=O can potentially interact with the metal center’s open coordination site through a C–H agostic interaction or a π-interaction via the phenyl ring (Scheme 4). For the insertion of formaldehyde and ethylene, the π-coordination mode of the (Tab)Ru(CO)$_2$(OCH$_2$Ph) and (Tab)Ru(CO)(CH$_2$CH$_2$Ph) products, respectively, are calculated to be marginally more stable than their corresponding C–H agostic conformers (Scheme 4), while the order of conformer stability is reversed for the product of imine insertion (Tab)Ru(CO)(N(H)CH$_2$Ph). All reported

(76) Beck, C. M.; Rathmill, S. E.; Park, Y. J.; Chen, J.; Crabtree, R. H.; Liable-Sands, L. M.; Rheingold, A. L. Organometallics 1999, 18, 5311–5317.
energetic data involving these products are relative to the lowest-energy coordination mode.

**Computational Results for Ethylene, Methyleneimine, and Formaldehyde.** To observe insertion of a substrate into the Ru−Ph bond of complex 1, coordination to the Ru metal center is necessary. Given previous studies on TpRu(CO)(NCMe)(R) systems,54–56,82 ligand exchange with NCMe seems the most plausible pathway. Thus, the binding energy of the substrates to \{(Tab)Ru(CO)(Ph)\} could play a role in possible insertion reactions. Scheme 5 shows the calculated free energy changes upon coordination of substrate to the five-coordinate, 16-electron model \{(Tab)Ru(CO)(Ph)\}. According to the calculations, the relative binding free energies for the most stable \(\sigma\)-coordination modes are (free energy change relative to HN\(\text{CH}_2\) given in parentheses): methyleneimine > ethylene (7.2 kcal/mol) > formaldehyde (13.5 kcal/mol). The relative calculated ground-state free energy changes, as well as the relative free energies of activation for the insertion of ethylene, HN\(\text{CH}_2\), and H\(\text{C}=\text{O}\) follow identical trends (Scheme 6). That is, the insertion of formaldehyde is calculated to be more favorable and more kinetically facile than ethylene or HN\(\text{CH}_2\).

Interestingly, while the insertion of ethylene and formaldehyde are calculated to be thermodynamically favorable by −5.5 and −10.1 kcal/mol, respectively, the insertion of HN\(\text{CH}_2\) is calculated to be thermally disfavored by 8.3 kcal/mol. The calculated barriers for the insertion step reveal that the relative rates should follow the trend (calculated free energies of activation given in parentheses): formaldehyde (10.4 kcal/mol) > H\(\text{C}=\text{H}\) (18.6 kcal/mol) > methyleneimine (27.0 kcal/mol). Scheme 6 depicts the structures of the transition states for insertion of methyleneimine and formaldehyde. The transition states possess planar, four-centered active sites similar to that previously found for the insertion of ethylene into the Ru−Ph bond of (Tab)Ru(CO)(Ph).55 The insertion transition states are best characterized as “early” on their respective reaction coordinates given the long C−C\(\text{ipso}\) (≥1.95 Å) and short C−X (10% or less compared to their ground-state values). The isomerization of (Tab)Ru(CO)(Ph)L (L = methyleneimine or formaldehyde) from the more stable \(\sigma\)-coordination mode to the \(\pi\)-coordination mode is calculated to be significantly less favorable for methyleneimine (\(\Delta G^\dagger = +14.0 \text{ kcal/mol}\)) than for formaldehyde (\(\Delta G^\dagger = +2.3 \text{ kcal/mol}\)), a result that is potentially exacerbated experimentally by substitution of the hydrogen

**Scheme 5. Calculated Binding Free Energies (kcal/mol) of Methyleneimine, Ethylene, and Formaldehyde to \{(Tab)Ru(CO)(Ph)\}**

<table>
<thead>
<tr>
<th></th>
<th>(\Delta G_{\text{addition}}) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN(\text{CH}_2)</td>
<td>−18.0 ((\sigma)-coordination)</td>
</tr>
<tr>
<td>HN(\text{CH}_2)</td>
<td>−4.0 ((\pi)-coordination)</td>
</tr>
<tr>
<td>H(\text{C}=\text{CH}_2)</td>
<td>−10.8 ((\pi)-coordination)</td>
</tr>
<tr>
<td>O=(\text{CH}_2)</td>
<td>−4.5 ((\pi)-coordination)</td>
</tr>
<tr>
<td>O=(\text{CH}_2)</td>
<td>−2.2 ((\sigma)-coordination)</td>
</tr>
</tbody>
</table>

*Data for methyleneimine and formaldehyde correspond to the starting material with the substrate in the \(\sigma\)-coordination mode; ethylene is \(\pi\)-coordinated. The \(\beta\)-agostic isomers for Ru−O\(\text{CH}_2\)Ph and Ru−CH\(\text{CH}_2\)Ph are calculated to be 2.0 and 1.3 kcal/mol, respectively, higher in free energy than the corresponding \(\sigma\)-conformers. The \(\beta\)-agostic conformer for Ru−N\(\text{H}\)\(\text{CH}_2\)Ph is calculated to be 0.8 kcal/mol lower in free energy than the corresponding \(\pi\)-conformer.*
atoms on the imine with more sterically bulky groups (Scheme 7). Thus, the calculations suggest that observation of imine insertion may be kinetically inhibited by, among other possibilities, unfavorable isomerization to the π-coordination mode from the σ-coordination mode, which is attributable in part to the strong imine–Ru σ-bonding in the π'-coordination mode. Experimentally, the insertion of ethylene into the Ru–Ph bond of complex 1 to produce TpRu(CO)(NCMe)(CH$_2$CH$_2$Ph) has been directly observed, which is consistent with the calculated favorable coordination of ethylene and relatively low free energy of activation for ethylene insertion into the Ru–Ph bond. Given that formaldehyde insertion is calculated to be thermally favorable (ΔG = −10.1 kcal/mol) and calculated to proceed with a relatively low free energy of activation (ΔG° = 10.4 kcal/mol), the failure to observe insertion reactions of aldehydes or ketones when reacted with TpRu(CO)(NCMe)(Ph) is likely attributable in part to the weak coordination of the carbonyl group to the metal center and thus an inability to displace the acetonitrile ligand and/or thermodynamically favorable C–H activation and decarbonylation of the aldehyde (see below).

The differences in the free energies of activation for insertion of formaldehyde, ethylene, and methyleneimine are similar to the differences in ground state energies between these systems (Scheme 8). The relative energies for ground states and transition states are inversely related, with the energy differences in the transition states less pronounced than those in the ground states. The free energy changes upon coordination of ethylene and formaldehyde to (Tab)Ru(CO)(Ph), relative to the ΔG for coordination of methyleneimine, are 7.2 (ethylene) and 13.5 kcal/mol (formaldehyde). The free energies of activation of insertion into the Ru–Ph bond, relative to the ΔG° for insertion of methyleneimine, are 8.2 (ethylene) and 16.6 kcal/mol (formaldehyde). Thus, according to the calculations, the differences in activation barrier for insertion of formaldehyde, methyleneimine, and ethylene into the Ru–Ph bond of (Tab)-Ru(CO)(Ph) are likely due to differences in ground state energies of (Tab)Ru(CO)(Ph)L (L = formaldehyde, methyleneimine, or ethylene).

**Computational Results for Carbodiimide.** Scheme 9 depicts calculated free energy changes for the insertion of HN=CD=NH into the Ru–Ph bond of (Tab)Ru(CO)(Ph) using the σ-coordination mode of the carbodiimide. The insertion of carbodiimide into the Ru–Ph bond of 1 provides an interesting contrast to the insertion of imine for three reasons: (1) net carbodiimide insertion into the Ru–Ph bond of 1 has been experimentally observed, (2) the first step involves formal insertion of a C=N bond in both processes, and (3) kinetic access to insertion of a carbodiimide provides the opportunity to trap the initial insertion product via formation of a chelating amidinate ligand. In contrast to methyleneimine, the insertion of a C=N bond of HN=CD=NH into the Ru–Ph bond of 1 is

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(82) Arrowood, B. N.; Lail, M.; Gunnoe, T. B.; Boyle, P. D. *Organometallics* 2003, 22, 4692–4698.
Scheme 10. Calculated Free Energies (kcal/mol) for Insertion of Isonitrile into the Ru–Ph Bond of (TpRu(CO)(Ph)) and Subsequent Coordination of PH3

Calculated to be exergonic by 10.0 kcal/mol with an activation barrier of 25.1 kcal/mol (Scheme 9). Thus, although this reaction step is calculated to have a similar free energy of activation compared to insertion of the imine HN=CH2, it is calculated to be substantially more favorable thermodynamically with $\Delta G = 18.3$ kcal/mol. The formation of a chelating amidinate ligand is calculated to be quite favorable with an overall change in free energy of $-22.4$ kcal/mol versus the $\eta^1$ product of initial carbodiimide insertion. Thus, conversion of (Tab)Ru(CO)(Ph)-($\eta^1$-HN=CN=NH) to the amide complex (Tab)Ru(CO)(κ²-N,N-HNC(Ph)NH) is calculated to be favorable by a substantial $-32.4$ kcal/mol.

The computational results for methyleneimine and the parent carbodiimide suggest that the experimentally observed differences between carbodiimides (net insertions observed) and imines (net insertions not observed) may be derived from thermodynamic differences. The calculated activation barriers for the insertion of methyleneimine and the parent carbodiimide into the Ru–Ph bond of (Tab)Ru(CO)(Ph) are quite similar with $\Delta G^\ddagger = 1.9$ kcal/mol (Schemes 6 and 9). In both cases, the stable $\sigma$-coordinated mode (relative to the $\pi$-coordinated mode) likely contributes to the calculated substantial Gibbs free energy of activation. Furthermore, conversion of the product from carbodiimide insertion to a chelating amidinate ligand provides a significant driving force and an additional 22.4 kcal/mol of stabilization.

**Computational Results for Isonitrile.** Free energy changes for insertion of isonitrile into the Ru–Ph bond of (Tab)Ru(CO)(Ph)(C≡NH) and subsequent coordination of PH3 were calculated (Scheme 10). The initial insertion is calculated to occur with $\Delta G^\ddagger = 17.9$ kcal/mol and an unfavorable change in free energy of $\Delta G = +5.0$ kcal/mol. Coordination of PH3 is calculated to stabilize the insertion product by $-7.5$ kcal/mol, providing an overall $\Delta G = -2.5$ kcal/mol for the conversion of (Tab)Ru(CO)(Ph)(C≡NH) and PH3 to (Tab)Ru(CO)(C(Ph)-NH)(PH3). The calculations are qualitatively consistent with experimental results discussed above. For example, heating a benzene solution of TpRu(CO)(CNBu)(Ph) (S) in the absence of phosphine results in no observed changes; however, heating 5 in the presence of PMe3 allows observation of an equilibrium between 5/PMe3 and the insertion product TpRu(CO)(C(Ph)=N/Bu)(PMe3) (6).

**Computational Results for Decarbonylation.** Calculations reveal that aldehyde insertion into the Ru–Ph bond of (Tab)Ru(CO)(Ph) should be facile and favorable (see above). However, reaction of TpRu(CO)(NCMe)(Ph) with benzaldehyde or p-tolualdehyde results in decarbonylation reactions to produce benzene and TpRu(CO)3(Ar) (Ar = Ph or p-tolyl). The net decarbonylation reactions likely proceed by cleavage of an aldehyde C–H bond, C–H bond formation with the phenyl ligand (to produce benzene), and deinsertion of CO from an acyl ligand. We have previously reported that fragments of the type (TpRu(CO)(R)) can react with aromatic C–H bonds to produce R–H and (TpRu(CO)(Ar)) systems with calculated transition states that involve concerted C–H bond breaking and R–H bond formation.55,56 Calculations reveal a similar transition state for C–H activation of formaldehyde by (Tab)Ru(CO)-(Ph) (Scheme 11). The C–H activation transition state for formaldehyde is structurally similar to related $\sigma$-bond metathesis-type transition states in which the metal is within bonding distance with the transannular hydrogen atom (previously referred to as oxidative hydrogen migration);46 planar, four-centered active site with obtuse angle at the hydrogen being transferred (Ht) and a near covalent Ru–H distance (1.69 Å). The calculated $\Delta G^\ddagger$ for aldehyde C–H activation is relatively small (18.6 kcal/mol) compared with analogous calculated value for benzene C–H activation (21.2 kcal/mol) by (Tab)Ru(CO)-(Me) but is larger than the corresponding value for furan C–H activation (17.4 kcal/mol).55,56 These results suggest that if decarbonylation can be avoided, catalysts for the addition of aldehyde C–H bonds across olefin C=C bonds might be possible with closely related Ru(II) systems. The calculations indicate that aldehyde C–H activation has a more substantial activation barrier than insertion of the C≡O bond into the Ru–Ph bond; however, the initial products of aldehyde C–H activation (benzene and an $\eta$-formyl complex) are more stable than the product of C≡O insertion by 3.2 kcal/mol (Scheme 11). Furthermore, the decarbonylation step to produce (Tab)-Ru(CO)2(H) is highly favorable and is calculated to produce products that are 46.9 kcal/mol more stable than starting materials (5) and CH2O. Thus, the calculations suggest that carbonyl insertion is kinetically feasible but is likely difficult to observe due to facile and thermally favorable decarbonylation.

**Calculated Bond Dissociation Energies.** We have calculated the energetics for insertion of ethylene, formaldehyde, methylene imine, HN=CN=NH, and isonitrile into a Ru(II) phenyl bond. To probe the possible correlation of C=X/C=X BDE on insertion parameters, the BDEs of these substrates and their hydrogenated counterparts have been calculated (Table 2). Comparing either the calculated $\Delta H$ for insertion or the $\Delta H^\ddagger$ for insertion with the $\Delta$BDE for the entire series does not reveal any correlation. For example, the change in calculated N–C BDE upon conversion of H2C=CN=NH (155.2 kcal/mol) to H2C=CH-NH2 (81.9 kcal/mol) results in the least unfavorable $\Delta$BDE (73.3 kcal/mol) among the series methyleneimine, ethylene ($\Delta$BDE = 84.3 kcal/mol), and formaldehyde ($\Delta$BDE = 87.0 kcal/mol), yet insertion of methyleneimine is calculated to be least favorable ($\Delta H_{\text{insertion}} = +7.1$ kcal/mol) and to possess the largest $\Delta H^\ddagger$ for insertion (25.1 kcal/mol). However, the $\Delta$BDE for HN=CN=NH is calculated to be substantially more favorable when compared to the $\Delta$BDE of methyleneimine ($\Delta$BDE = 18.3 kcal/mol) with the calculated $\Delta\Delta H_{\text{insertion}} = 18.4$ kcal/mol.
Thus, the calculated N–C BDE of H₂N–C(H)dNH (96.0 kcal/mol) being larger than that of H₃C–NH₂ (81.9 kcal/mol, see Table 2) provides a possible rationalization for the calculated $\Delta H^\text{insertion}$ for HN–C(H)dNH being exothermic while that of HN–CH₂ is endothermic. While BDEs obviously impact the likelihood of insertion reactions occurring, establishing general trends based on simple comparison of BDEs is not likely to be possible.

**Summary and Conclusions.** The combination of experimental and computational studies on insertion of C–X multiple bonds into the Ru(II) phenyl bond of the fragment {TpRu(CO)–(Ph)} leads us to the following conclusions.

1. The scarcity of direct observation of insertion of C=N or C=O multiple bonds into M–H, M–R, or M-Ar bonds is not attributable in general to an inherently large activation barrier due to the large BDEs of C=N/C=O multiple bonds.

2. For TpRu(CO)(NCMe)(Ph), the failure to observe imine insertions is proposed to arise from a substantial activation barrier (attributable, at least in part, to strong $\eta^1$-binding of the imine) in combination with an unfavorable change in free energy for formation of the insertion product.

3. The failure to observe insertion of aldehyde C=O bonds is likely due to the highly favorable and kinetically accessible aldehyde C–H activation/decarbonylation.

4. Insertion of isonitrile into the Ru–Ph bond of TpRu(CO)-(CN'Bu)(Ph) (5) is thermally disfavored, and the addition/coordination of PMe₃ provides a driving force to observe the *kinetically accessible* insertion by trapping the insertion product.

5. Similar to imines, the insertion of carbodiimides is likely to proceed with a relatively high activation barrier; however, the insertion is overall thermodynamically favorable and the formation of chelating amidinate ligand provides a large enthalpic gain that allows trapping through formation of a very stable product.

6. Given the calculated weak binding of formaldehyde to the model (Tab)Ru(CO)(Ph) fragment, the failure to experimentally observe insertion of ketones into the Ru–Ph bond of complex 1 could be attributable to the difficulty in coordinating the ketone substrates in a dihapto-coordination mode.

7. For systems of the type {TpRu(L)(R)} that have been demonstrated to activate C–H bonds, catalytic reactions that involve the hydroarylation of C–X multiple bonds are potentially viable for some systems (e.g., carbodiimides and isonitriles) if conditions can be found for release of the product of insertion (via C–H activation of an external substrate). Extension of such transformations to other substrates (e.g., aldehydes, ketones, imines) will require tuning to overcome the limitations identified herein.

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**Table 2. Calculated BDEs for Ethylene, HN=C=NH, Formaldehyde, Methyleneimine, Isonitrile, and the Products of Hydrogenation**

<table>
<thead>
<tr>
<th>substrate</th>
<th>BDE</th>
<th>substrate</th>
<th>BDE</th>
<th>$\Delta BDE$</th>
<th>$\Delta H^\text{insertion}$</th>
<th>$\Delta H^\text{insertion}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C=O</td>
<td>176.9</td>
<td>H₂C–OH</td>
<td>89.9</td>
<td>87.0</td>
<td>−12.7</td>
<td>7.5</td>
</tr>
<tr>
<td>H₂C=CH₂</td>
<td>171.8</td>
<td>H₂C–CH₁</td>
<td>87.5</td>
<td>84.3</td>
<td>−5.8</td>
<td>17.7</td>
</tr>
<tr>
<td>HN=C=NH</td>
<td>151.0</td>
<td>H₂N–C(H)dNH</td>
<td>96.0</td>
<td>55.0</td>
<td>−11.3</td>
<td>22.3</td>
</tr>
<tr>
<td>H₂C=NH</td>
<td>155.2</td>
<td>H₂C–NH₂</td>
<td>81.9</td>
<td>73.3</td>
<td>7.1</td>
<td>25.1</td>
</tr>
<tr>
<td>C≡NH</td>
<td>208.1</td>
<td>H₂C≡NH</td>
<td>155.2</td>
<td>52.8</td>
<td>3.7</td>
<td>16.6</td>
</tr>
</tbody>
</table>

*Bond dissociation enthalpies (kcal/mol) calculated using a modified G3 method employing correlation consistent basis sets that has been shown to yield an average accuracy in calculated thermodynamics of ±1 kcal/mol (DeYonker, N. J.; Cundari, T. R.; Wilson, A. K. J. Chem. Phys., in press).*

*Average bond dissociation enthalpy for C≡N; calculated from HN=C=NH → C≡P+2 NH (II).*
Experimental Section

General Methods. 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 (O₂(g) < 15 ppm for all reactions). Photolysis experiments were performed using a 450 W power supply, 450 W lamp, and a quartz cooling jacket filled with flowing water. Acetonitrile was purified by passage through two columns of activated alumina followed by distillation from CaH₂. Dichloromethane and hexanes were purified by passage through two columns of activated alumina. Benzene, diethyl ether, pentane, tetrahydrofuran, and toluene were purified by distillation from sodium/benzophenone. Acetone- d₆, CD₃CN, C₆D₆, CDCl₃, and C₆D₅CD₃ were degassed via three freeze–pump–thaw cycles and stored over activated 4 Å sieves. 1H and 13C NMR spectra were obtained on a Mattson Genesis II spectrometer as thin films on a KBr plate or in solution using a 1997 frequency-locked 1H NMR spectrometer and referenced against external 1H NMR (1) and TpRu(CO)(NCMe)(OTf) have been previously reported. The carbodiimides, N,N′-di-n-hexylcarbodiimide and N,N′-diphenylcarbodiimide, were prepared by a procedure reported for N,N′-di-n-hexylcarbodiimide. Benzaldehyde and p-toluic acid were passed through a plug of activated neutral alumina prior to use. Acetone was stirred over activated 4 Å sieves prior to use, and acetonitrile was purified by fractional distillation under reduced pressure from P₂O₅. All other reagents were used as purchased from commercial sources.

TpRu(CO)(N,N′-Ph)(N(Ph)NC(Ph)(N(Ph)) (2). A thick-walled pressure tube was charged with 1 (0.246 g, 0.535 mmol) and THF (18 mL). To the colorless solution was added N,N′-diphenylcarbodiimide (0.372 g, 1.94 mmol) in THF (2 mL), and the mixture was heated in an oil bath at 90 °C for 48 h during which time the solution changed from colorless to yellow. The volatiles were removed under reduced pressure to produce a yellow oil. A precipitate formed upon stirring the oil in pentane for 24 h. The solid was collected by vacuum filtration, washed with additional pentane, and dried in vacuo (0.129 g, 39% yield). IR (KBr): νCO = 1937 cm⁻¹. 1H NMR (CDCl₃, δ): 8.09, 7.81, 7.64, 7.48 (6H, 1:1:2:2 ratio, each a d, Tp CH 3/5 position), 7.22–7.17 (5H overlapping m’s, phenyl CH), 6.98–6.93 (5H, overlapping m’s, phenyl CH), 6.83–6.81 (2H, m, phenyl CH), 6.54–6.52 (3H, overlapping m’s, phenyl CH), 6.37, 6.10 (3H, 1:2:1 ratio, each a t, Tp CH 4 position). ¹³C(¹H) NMR (CDCl₃, δ): 202.8 (Ru- CO), 170.1 (NCCN), 147.3, 145.6, 139.0, 135.4, 135.2, 129.3, 129.2, 128.5, 128.1, 124.6, 122.0 (phenyl and Tp 3/5 positions, one resonance is absent likely due to coincidental overlap), 105.8, 105.5 (Tp 4 positions). Anal. Calcd for C₃₉H₂₅BN₉OrU: C, 56.78; H, 4.11; N, 18.27. Found: C, 56.71; H, 3.94; N, 18.26.

TpRu(CO)(N,N′-hx)(NC(Ph)(N(hx)) (3). A thick-walled pressure tube was charged with 1 (0.187 g, 0.405 mmol) and THF (18 mL). To the colorless solution was added N,N′-di-n-hexylcarbodiimide (0.398 g, 1.89 mmol) in THF (2 mL), and the mixture was heated in an oil bath at 90 °C for 72 h during which time the solution changed from colorless to yellow. The volatiles were removed under reduced pressure to produce a yellow oil. The mixture was purified using column chromatography on silica gel, eluting with neat toluene. The product eluted as a light green band. The toluene was removed under reduced pressure to produce a yellow-green oil. The product is highly soluble in all common organic solvents, and all attempts at isolation of a solid failed. The oil was isolated and dried in vacuo (0.149 g, 58% yield). IR (KBr): vCO = 1929 cm⁻¹. ¹H NMR (CDCl₃, δ): 7.86, 7.77, 7.64, 7.63 (6H, 1:1:2:2 ratio, each a d, Tp CH 3/5 position), 7.44–7.41 (2H, m, phenyl CH), 7.32–7.25 (3H, overlapping m’s, phenyl CH), 6.32, 6.13 (3H, 1:2:1 ratio, each a t, Tp CH 4 position), 2.91–2.65 (4H, m, −NCH₂), 1.36–1.01 (16H, overlapping br m’s, −CH₂−). ¹³C(¹H) NMR (CDCl₃, δ): 203.5 (Ru-CO), 175.0 (NCCN), 145.0, 138.8, 135.1, 134.7, 132.2, 128.8, 128.4, 128.3 (phenyl and Tp 3/5 positions), 105.7, 104.9 (Tp 4 positions), 48.4, 32.5, 32.0, 26.9, 22.9 (CH₃), 14.4 (CH₄). Anal. Calcd for C₃₉H₂₅BN₉OrU: C, 54.46; H, 6.69; N, 18.14. Found: C, 54.46; H, 6.65; N, 18.13.

TpRu(CO)(N,O-(Me)NC(Me)(O) (4). A thick-walled pressure tube was charged with 1 (0.203 g, 0.441 mmol) and THF (15 mL). To the colorless solution was added N-methylacetamide (0.175 mL, 2.29 mmol) in THF, and the mixture was heated in an oil bath to 90 °C for 24 h during which time the solution changed from colorless to yellow. The volatiles were removed under reduced pressure to produce a yellow oil that was dried in vacuo. Attempts to separate the excess N-methylacetamide from 4 were not successful. For example, complex 4 decomposes on solid-supports constructed from silica gel, activated alumina, or deactivated alumina. Attempts at recrystallization from multiple solvents (including mixtures) failed to produce pure material. Efforts to sublime the N-methylacetamide under reduced pressure (~30 °C and ~20 mTorr) resulted in the decomposition of 4. Heating a 1:1 mixture of 1 and N-methylacetamide resulted in the decomposition of 1. Last, a mixture of the previously reported TpRu(CO)(NCMe)-(OTf) and lithium N-methylacetamidate were reacted in attempts to independently synthesize 4; however, no reaction was observed at ambient conditions and decomposition was observed at elevated temperatures. Since 4 could not be separated from N-methylacetamide, characterization data include only IR and ¹H NMR spectroscopy. IR (KBr): vCO = 1944 cm⁻¹. ¹H NMR (CDCl₃, δ): 7.77, 7.42, 7.57, 7.48 (4H total, 1:1:1:1 ratio, each a d, Tp CH 3/5 position), 7.63 (2H total, overlapping d’s, Tp CH 3/5 position), 6.34, 6.15, 6.13 (3H total, 1:1:1 ratio, each a t, Tp CH 4 position), 2.83 (3H total, s, −CH₃), 1.92 (3H total, s, −CH₃).
Sample Procedure for Reaction of TpRu(CO)(CNBu)(Ph) (5) with PMe3 to Produce TpRu(CO)(PMe3)(CPh)=N(Bu)) (6). A J-Young NMR tube was charged with 1 (0.029 g, 0.057 mmol) and C6D6 (1.0 mL). To the colorless solution was added PMe3 (0.025 mL, 0.28 mmol). The mixture was heated to 100 °C and monitored periodically by 1H NMR spectroscopy over the course of 24 h at which time it was determined that the system had reached equilibrium between 5 and complex 6. IR (thin film on KBr) analysis revealed complex 5 (νCO = 1912 cm⁻¹ and νCN = 2143 cm⁻¹) and a new complex assigned as TpRu(CO)(PMe3)(CPh)=N(Bu) (6) with νCO = 1927 cm⁻¹. 1H NMR (C6D6, δ): 8.75, 7.56, 6.23 (3H, 1:1:1 ratio, each a d, Tp CH 3/5 position), 6.81 (1H, tt, JHH = 7 Hz and JH灾 = 1 Hz, phenyl para-CH3), 6.60 (1H, dt, JHH = 7 Hz and JH灾 = 1 Hz, phenyl meta-CH3), 5.95 (1H, br dd, JH灾 = 7 Hz and JH灾 = 1 Hz, phenyl ortho-CH3), other Tp CH 3/5 and phenyl CH resonances overlap with resonances due to complex 5, 6.11, 5.81, 5.59 (3H, 1:1:1 ratio, each a d, Tp CH position), 1.27 (9H, d, Jp-C = 10 Hz, P(CH3)3), 1.21 (9H, s, CH3). 31P[1H] NMR (C6D6, δ): 11.0 (PM3). The volatiles were removed in vacuo (including all PM3), and the resulting oil was taken up in C6D6 (1.0 mL). Heating this solution to 100 °C for 72 h resulted in conversion predominantly to complex 5 and free trimethylphosphine, as determined by 1H NMR, 31P[1H] NMR, and IR spectroscopy.

TpRu(CO)(PMe3)(Ph) (7). A colorless solution of 1 (0.208 g, 0.451 mmol) and trimethylphosphine (0.20 mL, 2.3 mmol) in THF (20 mL) was heated in an oil bath at 90 °C for 24 h. After the heating, the volatiles were removed in vacuo to produce a colorless oil. The oil was dissolved in dichloromethane (2 mL), and pentane (15 mL) was added. The resulting white solid was stored for ~12 h at ~20 °C, collected by vacuum filtration, washed with cold pentane, and dried in vacuo (0.095 g, 43% yield). IR and 1H NMR spectroscopy of crude reaction products revealed only complex 9. IR (KBr): νCO = 2039, 1971 cm⁻¹. 1H NMR (CDCl3, δ): 7.74, 7.37 (3H, 1:2 ratio, each a d, Tp CH 3/5 position), 7.70 (3H, overlapping d’s, Tp CH 3/5 position), 6.82 (4H, br s, phenyl CH2), 6.27, 6.19 (3H, 1:2 ratio, each a t, Tp CH position), 2.27 (3H, s, -CH3). Variable-temperature NMR studies showed that the broad singlet due to the aryl hydrogens begins to decoalesce at ~20 °C to produce two resonances that are not fully resolved at ~60 °C. 13C[1H] NMR (CDCl3, δ): 199.8 (Ru-CO), 149.2 (Ru-phenyl ipso), 144.1, 143.9, 141.5, 135.2, 135.1, 131.9, 127.9 (phenyl and Tp 3/5 positions), 106.0 (Tp 4 position, overlap of resonances), 21.1 (p-tolyl-CH3). Anal. Calcd for C13H18BN6O2Ru: C, 46.08; H, 4.88; N, 16.97. Found: C, 45.58; H, 4.24; N, 17.46.

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showed decomposition of the starting Ru complex 1 to NMR-silent materials without evidence of new diamagnetic Ru systems.

Acetophenone. To a screw-cap NMR tube was added a solution of 1 (0.015 g, 0.033 mmol) and acetophenone (0.005 mL, 0.043 mmol) in C₆D₆ (1.0 mL). The mixture was heated to 90 °C and monitored periodically by ¹H NMR spectroscopy over the course of 24 h. Analysis by NMR spectroscopy showed decomposition of the starting Ru complex 1 to NMR-silent materials without evidence of new diamagnetic Ru systems.

N-Benzylideneaniline. To a screw-cap NMR tube was added a solution of 1 (0.011 g, 0.024 mmol) and N-benzylideneaniline (0.004 g, 0.022 mmol) in C₆D₆ (1.0 mL). The mixture was heated to 90 °C and monitored periodically by ¹H NMR spectroscopy over the course of 24 h. Analysis by NMR spectroscopy showed decomposition of the starting Ru complex 1 to NMR-silent materials without evidence of new diamagnetic Ru systems.

N-Benzylidinemethylamine. To a screw-cap NMR tube was added a solution of 1 (0.016 g, 0.035 mmol) and N-benzylidinemethylamine (0.005 mL, 0.040 mmol) in C₆D₆ (1.0 mL). The mixture was heated to 90 °C and monitored periodically by ¹H NMR spectroscopy over the course of 24 h. Analysis by NMR spectroscopy showed decomposition of the starting Ru complex 1 to NMR-silent materials without evidence of new diamagnetic Ru systems.

Computational Methods. Calculations employ the Gaussian98 and Gaussian03 packages. B3LYP calculations were performed on the experimental models described in the text. Ruthenium and the main group elements were described with the Stevens (CEP31G) relativistic effective core potentials and valence basis sets. The valence basis sets of main group elements (boron, carbon, nitrogen, oxygen) were augmented with a d polarization function (ξ₄ = 0.80). For Ru complexes, the geometry was optimized for the singlet spin state, and all the geometries were fully optimized without any symmetry constraints.

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Supporting Information Available: Full details of computational studies and details of X-ray data collection and structure solution for complex 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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