Functionalization of Benzylic Carbon–Hydrogen Bonds. Mechanism and Scope of the Catalytic Synthesis of Indoles with [Ru(dmpe)$_2$]

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A unique route for the synthesis of indoles from *o*-tolyl isocyanides using Ru(dmpe)$_2$(H)(naphthyl) and Ru(dmpe)$_2$H$_2$ as catalysts has been examined. The scope of this method for indole preparation has been examined with a variety of *o*-tolyl isocyanides, including 3-, 4-, and 5-R-*o*-tolyl isocyanides (where R = methyl, methoxy, or fluoro), 2,6-xylyl isocyanide, 2,6-diethylphenyl isocyanide, 2-ethylphenyl isocyanide, *o*-tolyl isocyanide, and 6-ethyl-*o*-tolyl isocyanide. The mechanism of indole formation has been investigated using kinetic and isotope effect experiments to differentiate key product-determining steps of the cycle. Results are consistent with a mechanism involving irreversible CNR coordination prior to intramolecular oxidative addition of the *o*-methyl C–H bond. Competitive isotope effect studies using d_0- and $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha',3,5$-$d_8$-labeled 4-*tert*-butyl-2,6-xylyl isocyanides indicate virtually no isotope effect (k_H/k_D = 1.08) when the selection of which bond to active is intermolecular. Use of 4-*tert*-butyl-2,6-xylyl-α,α,α-d_3 isocyanide shows that C–H activation is faster than C–D activation (k_H/k_D = 2.6) in an intramolecular competition, where the choice of C–H and C–D bonds to activate is within one xylyl isocyanide. The reaction with 2,6-diethylphenyl isocyanide to give 3-methyl-7-ethylindole is first order in [Ru(dmpe)$_2$(H)(naphthyl)] and zero order in [CNR]. While hindered 2,6-disubstituted phenyl isocyanides eliminate free indoles catalytically, less hindered isocyanides give stable indole N–H oxidative addition adducts with [Ru(dmpe)$_2$]. The resulting cis and trans N–H activated complexes are thermodynamically the most stable species in solution. N–H addition products were also formed with substituted indoles, pyrrole, pyrazole, indazole, and pyrrolidine. Blocking the N–H position of indole with a methyl group results in C–H oxidative addition of ruthenium at the 2-position of the ring. *trans*-RuH(3-methylindole-*N*)(dmpe)$_2$ crystallizes in orthorhombic space group *Pnnm* (No. 58) with, a = 17.263(10) Å, b = 10.668(10) Å, c = 13.524(10) Å, V = 2491(6) Å^3, and Z = 4. *trans*-RuH(5-methoxyindole-*N*)(dmpe)$_2$ crystallizes in monoclinic space group $P2_1/c$ (No. 15) with, a = 9.065(2) Å, b = 16.379(3) Å, c = 19.196(5) Å, β = 92.06(4)°, V = 2848(2) Å^3, and Z = 4. *trans*-RuH(5-fluoroindole-*N*)(dmpe)$_2$ crystallizes in monoclinic space group $P2_1/c$ (No. 15) with, a = 8.854(4) Å, b = 16.45(1) Å, c = 18.873(8) Å, β = 93.95(4)°, V = 2743(5) Å^3, and Z = 4. *cis*-RuH(*N*-methylindole-*C*^{2})(dmpe)$_2$ crystallizes in monoclinic space group $P2_1/c$ (No. 15) with, a = 15.08(1) Å, b = 10.173(8) Å, c = 18.09(2) Å, β = 114.49(7)°, V = 2526(8) Å^3, and Z = 4.

Introduction

The search for novel indole syntheses has inspired organic chemists for over 100 years and is significant due to the biological prevalence of the indole ring.[1] The indole nucleus is found in the essential amino acid tryphtophan,[2] and indole derivatives have consequently been found to have physiological applications as clinical drugs, ranging from antibiotics to sedatives. Therein lies the importance for new improved routes for the synthesis and functionalization of the indole ring system.

Until recently, indole synthesis relied primarily on well-established methods such as the Fischer indole synthesis, the Madelung cyclization of *N*-acyl-*o*-toluidines, the reductive cyclization of *o*-nitrobenzyl ketones, the Batcho–Lenngruber synthesis of indoles from *o*-nitrotoluenes and dimethylformamide acetal, and the Gassman synthesis of indoles from *N*-haloanilines.[3] All of these approaches involve classic organic synthetic methodology and display typical organic reactivity patterns. The use of transition metal complexes as reagents for the synthesis of complex organic compounds has been under development for at least several decades, and many extraordinary organic transformations of profound potential have been realized.[4-6] With the advent and continuing refinement of transition-metal-assisted organic synthetic methodology, a number of new and potentially quite versatile methods for both the synthesis and functionalization of indoles have been developed,[7-9] as shown in Scheme 1. Although most of the fundamental organometallic reaction chemistry used in the synthesis of indoles has been known for at least a decade, only recently were these processes applied to

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(1) Houlihan, W. J. *Heterocyclic Compounds: Indoles—Part 1*; John Wiley & Sons, Inc.: New York, 1970.

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(3) Hegedus, L. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1113–1226.

(4) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks Cole Publishing Co.: Monterey, CA, 1985.

(5) Davis, S. D. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: Oxford, U.K., 1982.

(6) Powell. *Principles of Organometallic Chemistry*; Chapman & Hall: London, 1988.

(7) Hegedus, L. S.; Allen, G. F.; Waterman, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 2674–2676.

(8) Kametani, T.; Takahashi, K.; Ihara, M.; Fukumoto, K. *Heterocycles* **1975**, *3*, 691–695.

(9) Crotti, C.; Cenini, S.; Rindone, B.; Tollari, S.; Demartin, F. *J. Chem. Soc., Chem. Commun.* **1986**, 784–786.

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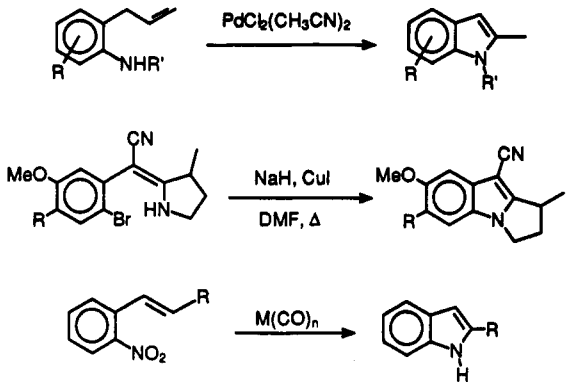
Scheme 1. Transition-Metal-Mediated Synthesis of Indoles

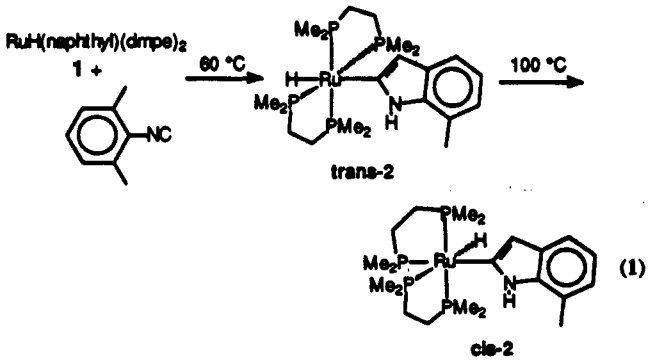


complex multifunctional organic substrates with the intent of accomplishing the total synthesis of a natural product.

A recent report from our laboratories expanded the list of metal complexes that generate indoles to include a ruthenium complex that is capable of catalytically transforming 2,6-xylyl isocyanide into 7-methylindole.[10] In this paper, we present a detailed study of the mechanism of this rearrangement and establish the generality of the method. N–H activation reactions are also presented, and their relevance to the indole-forming reactions is discussed.

Results and Discussion

Formation of Indole from 2,6-Xylyl Isocyanide. The thermal reaction of Ru(dmpe)$_2$(H)(naphthyl) (1) at 60 °C for 24 h in the presence of 1 equiv of 2,6-xylyl isocyanide leads to the reductive elimination of naphthalene and the formation of a new organometallic complex, *trans*-RuH(7-methylindole-C^2)(dmpe)$_2$ (*trans*-2). The ^{1}H NMR spectrum of the product shows a hydride quintet resonance at δ −12.742 (J = 23.2 Hz), consistent with a *trans*-RuHX(dmpe)$_2$ complex. Further heating of the solution at 100 °C results in conversion of this trans complex to the cis isomer of *trans*-2 (eq 1).[10] The hydride resonance of this new product appears as a doublet of quartets at δ −8.955 (J = 83.6, 24.4 Hz), characteristic of a *cis*-RuHX(dmpe)$_2$ complex.



(1)

The cis-indole complex eliminates free 7-methylindole at higher temperatures in the presence of hydrogen. Heating a solution of *cis*-2 to 140 °C under 0.65 atm of H_2 leads to the clean formation of 7-methylindole and RuH_2(dmpe)$_2$ (3). The reaction becomes catalytic if the complex RuH_2(dmpe)$_2$ is used rather than the naphthyl hydride complex 1 as the catalyst precursor. Heating a solution of 1 equiv of 2,6-xylyl isocyanide and RuH_2(dmpe)$_2$ at 140 °C in C_6D_6 in a sealed tube for 24 h results in the formation of a 98% yield (NMR) of the free indole with no change in the amount of 3. With lower catalyst:isocyanide ratios, a competing dead-end side reaction is observed in which the isocyanide inserts into the N–H bond of the 7-methylindole product in a 1,1 fashion (eq 2). The formation of

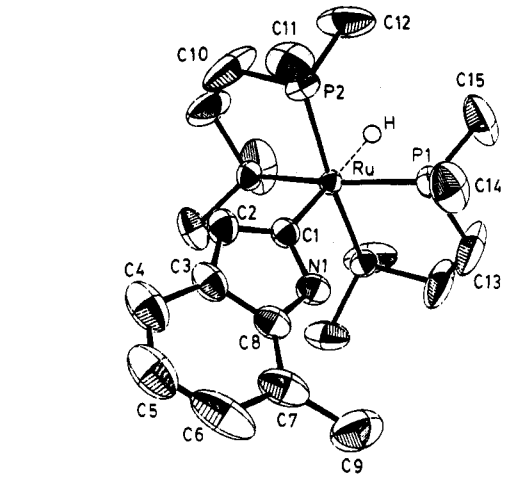
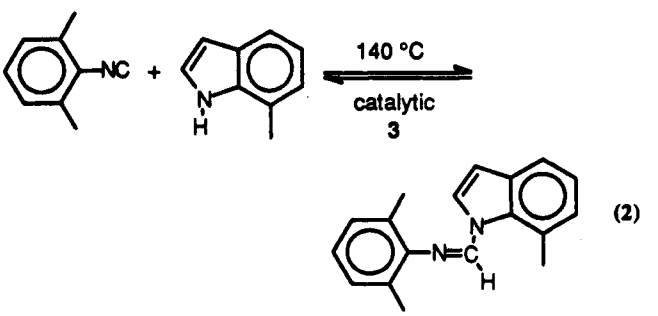


Figure 1. ORTEP drawing of *trans*-Ru(H)(7-methylindole-C^2)(dmpe)$_2$. Ellipsoids are shown at the 50% probability level.



(2)

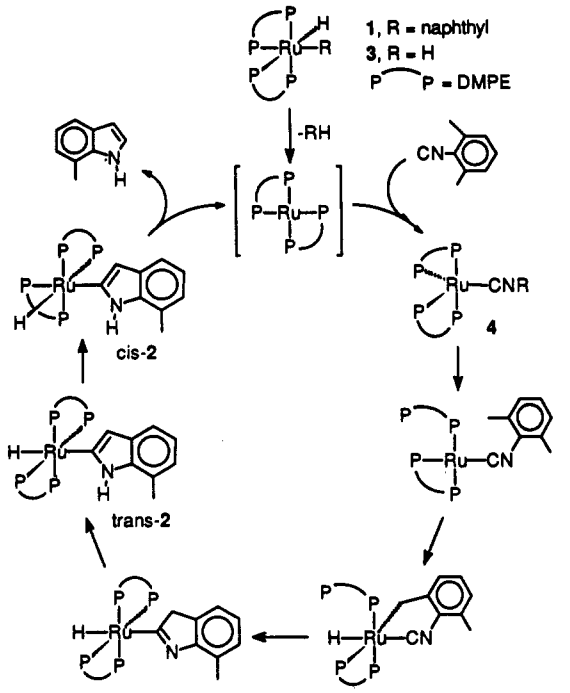
this species is apparently reversible, as continued thermolysis at 140 °C ultimately results in the net conversion of the 2,6-xylyl isocyanide to 7-methylindole in >90% yield. Reaction of 50 mg of 2,6-xylyl isocyanide with 30 mg of 3 (5:1 mole ratio) in 0.6 mL of C_6D_6 (94 h, sealed tube) results in the formation of 7-methylindole in 70% isolated yield after sublimation. No reaction occurs under similar conditions in the absence of 3.

Complex *trans*-2 was isolated as yellow-orange crystals from the reaction of 1 with 2,6-xylyl isocyanide at 60 °C. A single-crystal X-ray structural determination shows the indole ring bound at the 2-position (Figure 1). The compound crystallizes in orthorhombic space group $Cmc2_1$ with Z = 4, which requires that the complex be located in a special position. The ruthenium and indole ring lie on a mirror plane that bisects the C–C bond of each of the dmpe ligands.

Irradiation of dihydride 3 (λ > 300 nm) in the presence of 2,6-xylyl isocyanide gives a new complex in ~25% yield. The ^{1}H NMR spectrum of the sample shows resonances for a complex with a single 2,6-xylyl isocyanide ligand (δ: 6.993, d, J = 7.4 Hz, 2 H; 6.856, t, J = 7.5 Hz, 1 H; 2.672, s, 6 H) and two dmpe ligands (δ 1.30, br s, 24 H). This complex forms *trans*-2 quantitatively upon standing at 25 °C for several days and is assigned as the simple isocyanide adduct Ru(2,6-xylyl isocyanide)(dmpe)$_2$ (4). 3 is known

(10) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640–5641.

Scheme 2. Proposed Mechanism for Catalytic Indole Production



to lose hydrogen readily upon photolysis, generating the unsaturated intermediate [Ru(dmpe)$_2$] that can be trapped by 2 e$^-$ donor ligands.[11]

2,6-Diethylphenyl isocyanide also reacts with dihydride **3** to give free 3-methyl-7-ethylindole catalytically. Reaction of a 1:5 mixture of **3** and the isocyanide in a sealed tube at 140 °C showed complete conversion to the indole after only 7 h, with no change in the amount of **3**. None of the species corresponding to the product in eq 2 was observed under these conditions. By comparison, the analogous reaction of **3** with 2,6-xylyl isocyanide was substantially slower, requiring on the order of 20 h to proceed to completion.

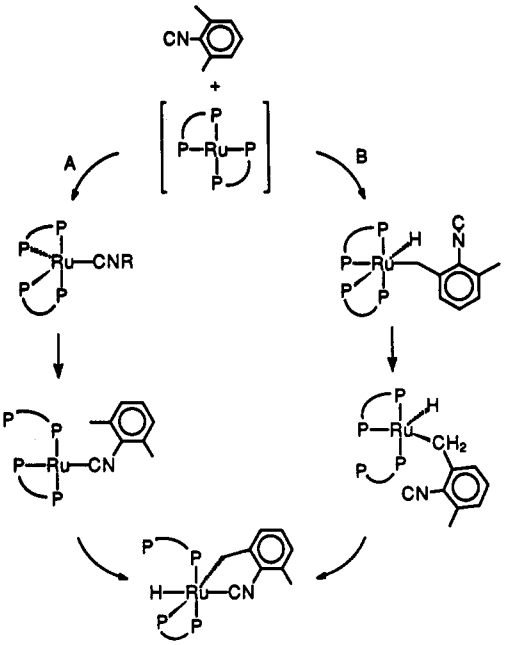
Mechanism of Indole Formation. The formation of free indole from 2,6-xylyl isocyanide has been proposed to occur by way of the cycle shown in Scheme 2.[10] Further studies have been conducted to examine the possibility that perhaps alternate reaction sequences are responsible for the production of *trans*-**2**.

The first step involves the generation of the unsaturated species [Ru(dmpe)$_2$], followed by reaction with isocyanide. Kinetic studies were undertaken to determine which of these steps was rate determining. The kinetics of the reaction of 2,6-diethylphenyl isocyanide with naphthyl hydride complex **1** at 60 °C to give the trans-indole hydride complex RuH(3-methyl-7-ethylindole-C^2)(dmpe)$_2$ were monitored at varying concentrations of the isocyanide (in excess). The disappearance of **1** followed first-order kinetics, although at the higher isocyanide concentrations side reactions with the free isocyanide complicated the reaction. While not investigated in great detail, these side reactions are metal promoted, as heating a C_6D_6 solution of 2,6-diethyl isocyanide at 100 °C for several weeks results in no decomposition. Table 1 lists the initial rates of disappearance of **1** obtained from the slopes of plots of [**1**] vs time. The rates are independent of [CNR], indicating that loss of naphthalene from **1** is the rate-determining step.

Table 1. Rate Data for Reaction of 1 with 2,6-Diethylphenyl Isocyanide at 60 °C in C_6D_6

[1], M	[CNR], M	10^5k, s^{-1}	[1], M	[CNR], M	10^5k, s^{-1}
0.019	0.019	3.2	0.019	0.113	2.6
0.019	0.057	3.3	0.019	0.189	3.7

Scheme 3. Alternative Pathways for Formation of Indole Framework



With the formation of the coordinatively unsaturated species [Ru(dmpe)$_2$] as the rate-determining step in the reaction of **1** with isocyanide, the next step could involve either coordination of isocyanide or oxidative addition of the *o*-tolyl C–H bond. Scheme 3 shows these two possible pathways, either of which would lead to *trans*-**2**. Earlier studies with phenyl isocyanide provided supportive evidence for path A, as the formation of both Ru(CNPh)(dmpe)$_2$ and Ru(CNPh)$_2$(η^2-dmpe)(η^1-dmpe) was observed.[12]

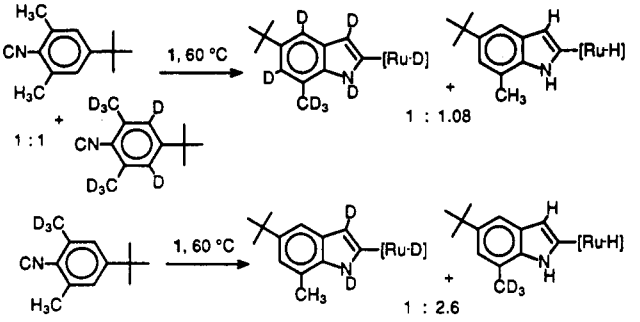
In order to decipher the sequence of these steps, kinetic isotope effect studies were conducted to see at what stage C–H or C–D bond breaking processes were important. Two experiments were designed to sort out the step affected by deuterium substitution. An intermolecular competition was probed by heating **1** in the presence of an excess of a 1:1 mixture of 4-*tert*-butyl-2,6-xylyl-$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha',3,5$-$d_8$ isocyanide and 4-*tert*-butyl-2,6-xylyl-d_0 isocyanide (Scheme 4). The ratio of the two products formed was determined by integration of the 7-methyl resonance relative to the coincident *tert*-butyl groups of the trans-indole hydride products. A value for the intermolecular kinetic selectivity of $k_H/k_D = 1.08$ (±0.2) was determined.

A second kinetic isotope selectivity experiment was designed in which the metal was forced to compete intramolecularly for C–H and C–D bonds. Specifically, 4-*tert*-butyl-2,6-xylyl-α,α,α-d_3 isocyanide was reacted with **1** at 60 °C (Scheme 4). Indole formation in this circumstance can occur by activation of either the C–H or C–D bond. Integration of the hydride resonance relative to

(11) Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Pertuz, R. N.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1992**, *114*, 7425–7435.

(12) Jones, W. D.; Kosar, W. P. *Organometallics* **1986**, *5*, 1823–1829.

Scheme 4. Competitive Isotope Effect Experiments for Indole Formation ([Ru] = Ru(dmpe)$_2$)

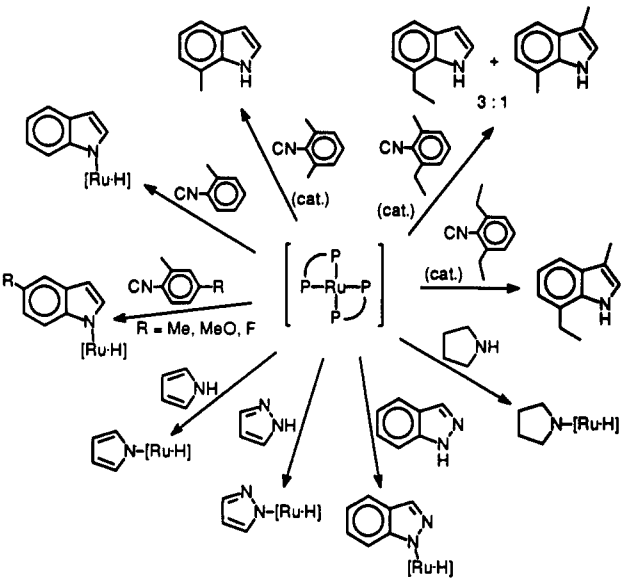


the 7-methyl resonance in the ^{1}H NMR spectrum provided a value of k_H/k_D = 2.6 (±0.2) for the intramolecular kinetic isotope effect.

Examination of pathways A and B in Scheme 3 indicates that if C–H (or C–D) oxidative addition were to precede isocyanide binding (path B), both the intermolecular and intramolecular competition reactions would be expected to show the same isotope effect, anticipated to be in the range of k_H/k_D = 2–3 on the basis of other studies of the oxidative addition of sp^3-hybridized C–H bonds to electron-rich metal centers.[13] However, observation of no isotope effect in the intermolecular competition is more consistent with a mechanism involving *irreversible* isocyanide coordination prior to C–H oxidative addition (path A). Since the deuterated and undeuterated substrates would bind to [Ru(dmpe)$_2$] with equal rates (i.e., the transition state for isocyanide coordination would be the same regardless of deuteration), the product ratio would be expected to be 1:1, or k_H/k_D = 1. If the isocyanide were to bind reversibly prior to C–H (or C–D) cleavage, then a significant isotope effect would have been observed, since the rate-determining transition state would now be different for the two substrates. In the intramolecular competition, however, rate-determining isocyanide binding would be followed by a choice of either C–H or C–D oxidative addition, and an isotope effect would be anticipated for this step. The observed value of k_H/k_D = 2.6 is in line with what would be expected for this type of oxidative addition. Note that while the rate-determining step involves loss of naphthalene from **1**, the product-determining step involves C–H or C–D cleavage and consequently displayed an isotope effect.

Once the oxidative addition has occurred, formation of the indole nucleus would occur by migration of the methylene group to the isocyanide (i.e., alkyl migration as opposed to isocyanide insertion). This insertion would be driven by closure of the η^1-dmpe chelate ring and would account for the formation of the trans-indole hydride complex as the kinetic product of the reaction. A tautomerization of the methylene hydrogen is required to complete the aromatization of the indole ring, but this step occurs spontaneously under the reaction conditions. All of these steps occur rapidly at 60 °C once naphthalene is lost from **1**. Observation of a small amount of the 2,6-xylyl isocyanide complex at room temperature in the photolysis experiment described earlier indicates that the highest barrier for this sequence (probably the step involving C–H oxidative addition to the η^1-dmpe intermediate) is about 25 kcal/mol ($\tau_{1/2} \cong$ 1 d at 25 °C).

Scheme 5. Summary of Reactions of Ru(dmpe)$_2$(H)(naphthyl) ([Ru] = Ru(dmpe)$_2$)



In completing the catalytic cycle, a trans to cis isomerization takes place more gradually ($\Delta G^{\ddagger} \cong$ 31 kcal/mol), requiring temperatures of ~100 °C for reasonable rates. Since the isomerization is observed to go to completion, the cis isomer must be thermodynamically preferred over the trans isomer. The final reductive elimination of indole is the most difficult step in the sequence, requiring heating to 140 °C in the presence of a trap for the [Ru(dmpe)$_2$] fragment. Dihydrogen serves in this latter function, resulting in the stable dihydride complex **3** and free indole. Furthermore, dihydride **3** is apparently labile at 140 °C and therefore acts as a storage site for the ruthenium(0) fragment.

Scope of Indole Formation. A wide variety of other isocyanides also react with naphthyl hydride complex **1** and/or dihydride **3** to produce indole-containing complexes as summarized in Scheme 5. Reaction of 6-ethyl-*o*-tolyl isocyanide allows the determination of the selectivity for primary vs secondary C–H activation. Heating a solution of **1** with this isocyanide at 60 °C gives both *trans*-RuH(7-methylindole-C^2)(dmpe)$_2$ and *trans*-RuH(3,7-dimethylindole-C^2)(dmpe)$_2$ products. Prolonged thermolysis at this temperature results in the formation of the cis isomers, as was seen in the case of 2,6-xylyl isocyanide. The catalytic production of both free indoles from the isocyanide is accomplished with **3** as catalyst at 140 °C. A 3:1 ratio of these two products indicates a modest preference for primary activation over secondary activation. The ratio does not change over the course of the reaction, and since indole formation is irreversible, it must reflect the kinetic selectivity for the C–H activation/isonitrile insertion sequence.

Attempts to extend the catalytic formation of indoles from less hindered isocyanides have taken a slightly different course. Reaction of *o*-tolyl isocyanide with dihydride **3** under catalytic conditions (140 °C) results only in isocyanide decomposition. Unhindered phenyl isocyanides are known to undergo oligomerization at room temperature,[14] so heating to 140 °C leads to the rapid destruction of these materials before interaction with a

(13) See: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819 and references therein.

(14) *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, pp 1060–1063.

ruthenium complex can take place. This undesirable side reaction can be avoided if *o*-tolyl isocyanide is heated to 60 °C with 1, conditions that serve as a more mild source of [Ru(dmpe)$_2$]. In this case, two products are observed in addition to the expected RuH(indole-C^2)(dmpe)$_2$. One is the simple ruthenium(0) complex Ru(CN-*o*-tolyl)-(dmpe)$_2$, and the other is the indolenine complex in which the aromaticity of the indole is not complete. The quantity of these species varies over time, as each is transformed into successive intermediates until the thermodynamically preferred *trans*-indole-C^2 hydride is ultimately formed. The trans isomer slowly converts to the cis isomer, which undergoes hydrogenolysis with H_2 (1 atm, 140 °C, 7 h) to give a quantitative yield (NMR) of free indole and **3**.

Attempts to prepare the indole hydride complexes independently by thermolysis of naphthyl hydride complex **1** with indole at 60 °C gave an entirely new product. A single new isomeric product forms in which the N–H bond has undergone addition to the ruthenium(0) metal center. The ^{1}H NMR spectrum shows a hydride quintet and two dmpe singlets indicates a trans structure. Reaction of a solution of **3** with free indole (1.6 equiv) at 140 °C also gives this trans N–H activation product. Continued heating (24 h) results in the appearance of the cis N–H addition product (53%) in addition to the trans isomer (11%) and **3** (36%).

The reaction of 2-ethylphenyl isocyanide with **1** at 60 °C proceeds to give initially (24 h) *trans*- and finally (76 h) *cis*-RuH(3-methylindole-C^2)(dmpe)$_2$ as major products. Raising the temperature to 100 °C for 8 h results in the formation of *cis*- and *trans*-RuH(3-methyl-indole-*N*)-(dmpe)$_2$ in a 4:1 ratio. No change in this product ratio is seen upon heating to 140 °C. Independent formation of these latter two N–H insertion products occurs in the reaction between 2-ethylphenyl isocyanide with **3** at 140 °C. The trans N–H insertion product is formed exclusively from **1** and free 3-methylindole at 60 °C. This procedure allowed the isolation and full characterization of the pure product *trans*-RuH(3-methylindole-*N*)(dmpe)$_2$.

A single-crystal X-ray structural determination confirms the trans geometry of an N-bound indole ring (Figure 2). The complex crystallizes in orthorhombic space group *Pnnm* with $Z = 4$, which requires that the molecule sit in a special position. As with *trans*-**2**, the indole and ruthenium atom (and hydride ligand) lie in a mirror plane, but now the plane generates a second dmpe ligand from the first. In this octahedral geometry, the four phosphorus atoms are bent away from the indole ring at angles of 94–98°. The plane of the indole ring lies between the two symmetry-related dmpe ligands.

Reactions of 4-R-*o*-tolyl isocyanides were also examined, where R = methoxy, methyl, or fluoro. As observed with 2-ethylphenyl isocyanide, these reactions did not yield free indole but produced complexes with a σ-bound indole instead. In all cases, reaction of naphthyl hydride complex **1** with the isocyanide at 60 °C resulted initially in the *trans*-RuH(5-R-indole-C^2)(dmpe)$_2$ complexes, followed by isomerization to the cis-indole-C^2 hydride complex at 100 °C. Sustained heating gives the complex *cis*-RuH(5-R-indole-*N*)(dmpe)$_2$ followed by the more stable trans-indole-*N* hydride isomer. This sequence is outlined in Scheme 6. Trans N–H insertion products were also cleanly produced by thermolysis of **1** in the presence of the corresponding indole. In the case of R = methoxy, hydrogenolysis of *cis*-RuH(5-R-indole-C^2)(dmpe)$_2$ at 140 °C was examined, giving free 5-methoxyindole and **3** in quantitative NMR yield.

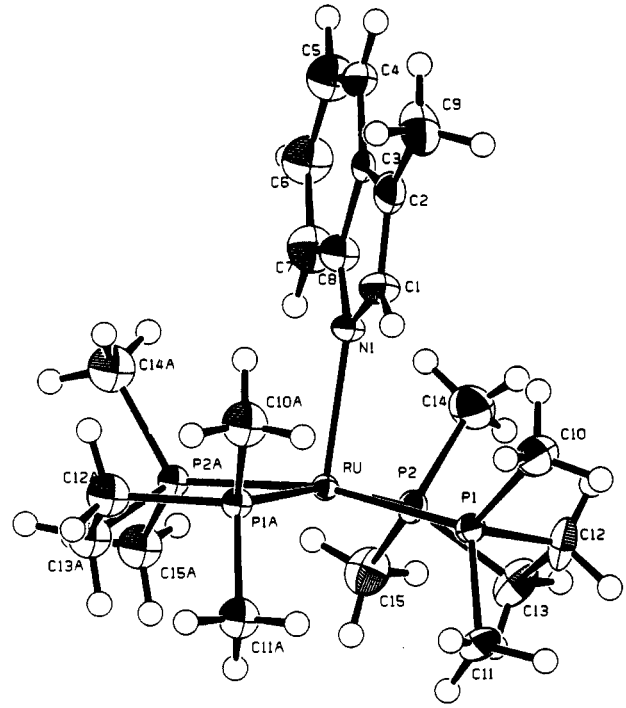
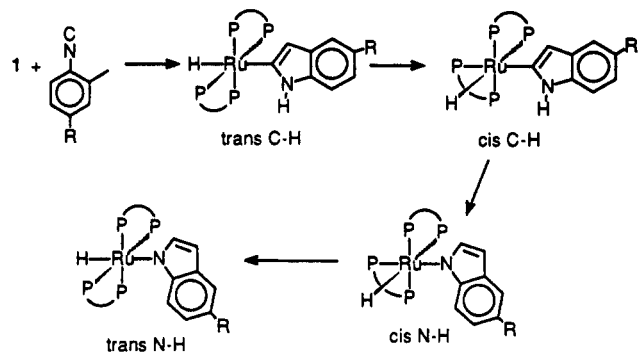


Figure 2. ORTEP drawing of *trans*-RuH(3-methylindole-*N*)(dmpe)$_2$. Ellipsoids are shown at the 50% probability level.

Scheme 6. Overall Sequence of Formation of Metal-Bound Indole Isomers



Single-crystal X-ray structural determinations of the thermodynamically preferred trans N-bound indole products with R = methoxy and fluoro were made (Figures 3 and 4). The complex crystallizes in both cases in monoclinic space group $P2_1/c$ with the molecule in a general position. In fact, the complexes crystallize in similar sites within the unit cell, with the only difference being the nature of the R group. Besides the attachment of the indole ring through nitrogen, the four phosphorus atoms are seen to be bent away from the indole ring by 93–98°. The chelating dmpe ligands coordinate to ruthenium with a bite angle of ~84°, with the angle between adjacent dmpe phosphorus atoms at ~95°. The plane of the indole ring is skewed to the RuP_4 axes, bisecting each dmpe chelate so as to avoid steric interaction with the methyl groups attached to phosphorus. Note that the opposite orientation was observed with *trans*-RuH(3-methylindole-C^2)(dmpe)$_2$.

The effect of blocking the N–H addition site with a methyl group was also examined in order to determine if C–H activation would occur, and if so, would it occur at the 2- or 3-position of the indole ring. For this purpose,

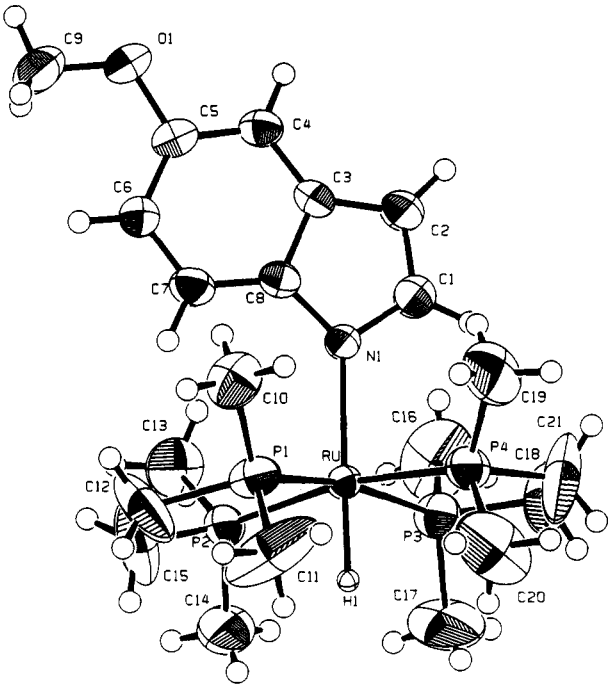


Figure 3. ORTEP drawing of *trans*-RuH(5-methoxyindole-*N*)(dmpe)$_2$. Ellipsoids are shown at the 50% probability level.

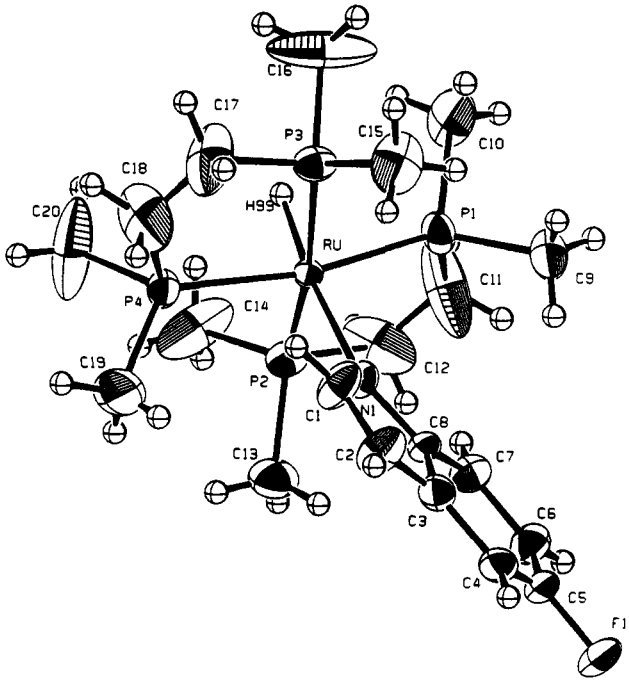


Figure 4. ORTEP drawing of *trans*-Ru(dmpe)$_2$(H)(5-fluoroindole-C^2). Ellipsoids are shown at the 50% probability level.

N-methylindole was reacted with 1 at 60 °C. The reaction gave a single product that displayed a hydride ligand resonance consistent with a *cis*-RuHX(dmpe)$_2$ complex and a singlet at δ 6.391 for the vinylic hydrogen of the five-membered indole ring. A single-crystal X-ray structure determination was undertaken to unequivocally assign the site of activation. As shown in Figure 5, the indole adds at the 2-position of the ring, resulting in the same isomer as observed with other isocyanide insertion reactions. However, the cis isomer is readily formed here, perhaps due to steric interactions of the *N*-methyl group that destabilize the trans isomer. By comparison, the

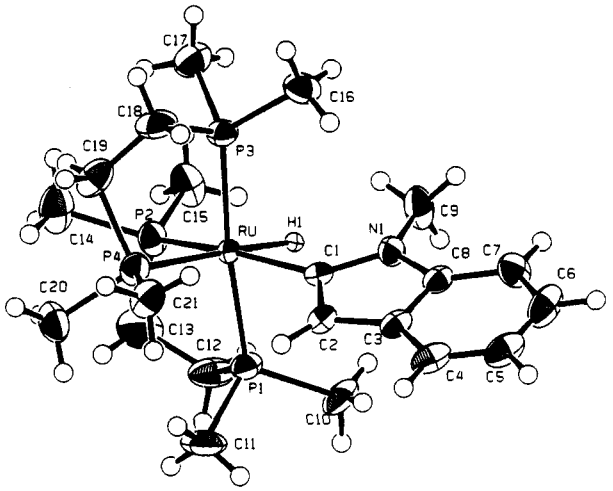


Figure 5. ORTEP drawing of *trans*-Ru(dmpe)$_2$(H)(*N*-methylindole-C^2). Ellipsoids are shown at the 50% probability level.

analogous non-N-methylated complexes all display vinylic resonances for the 3-hydrogen that are shifted ~0.5 ppm downfield compared with the N-methylated complex.

The complex *cis*-RuH(*N*-methylindole-C^2)(dmpe)$_2$ crystallizes in monoclinic space group $P2_1/c$ with $Z = 4$ in a general position. The internal dmpe chelate angles of ~84° are similar to those seen in the trans isomers. A bending of the adjacent groups toward the hydride ligand is seen here, as already noted in previous compounds.

Attempts were also made to synthesize indoles using 5-R-*o*-tolyl isocyanides (R = Me, F). In every example, heating solutions of 1 and the isocyanide to 60 °C led only to decomposition of the isocyanide. Similar reactions of 3-R-*o*-tolyl isocyanides (R = Me, F) and 1 at 60 °C gave some of the trans-indole hydride product, along with extensive decomposition. Further studies with isocyanide derivatives substituted in the 3- and 5-positions were abandoned.

As mentioned earlier, several metal-mediated approaches to indole synthesis have appeared in the literature.[7-9] The present system offers a method for generating 7-substituted indoles catalytically, as these products are readily freed from the metal center. The present series of steps for generating an indole is most similar to the lithiation procedure reported by Saegusa and Ito in 1984.[15] In this reaction, benzylic deprotonation of an *o*-tolyl isocyanide by *n*-butyllithium at low temperatures is followed by intramolecular cyclization by attack on the isocyanide carbon. Acidification leads to formation of an indole derivative. Saegusa and Ito demonstrated the general applicability of this reaction with a variety of substituted *o*-tolyl phenyl isocyanides. In the ruthenium system, the C–H activation step plays the role of the stoichiometric lithiation reaction, except that the reaction is reversible and does not require an acidic workup.

The 1912 Madelung synthesis provides another example in which formation of indole derivatives is characterized by intramolecular cyclization of *N*-(2-alkylphenyl)alkanamide by a strong base at high temperature.[2] Again, the postulated mechanism involves proton abstraction from a weakly acidic *o*-alkyl group, followed by intramolecular addition to the amide carbonyl. Synthetic utility of this

(15) Ito, Y.; Kobayaashi, K.; Seko, N.; Saegusa, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 73–84.

method is limited to alkanamides able to sustain strongly basic and high-temperature conditions. Consequently, this procedure has only been successful with less hindered ortho-substituted phenyl isocyanides.

A third example, while not analogous to our system, exemplifies some of the synthetic limitations of traditional methods. The cyclization of arylhydrazones in dilute hydrochloric acid leading to indoles, widely known as the Fischer indole synthesis, remains the most versatile and widely applied organic reaction for the formation of the indole ring.[2] Nevertheless, many indoles cannot be easily synthesized by this method.

The present transition-metal system offers the advantage that the metal center can act as both a Lewis acid and a Lewis base. Furthermore, neutral conditions and lower reaction temperatures are used and the relatively facile synthesis of indole derivatives not easily obtained by traditional organic means is achieved. The only limitation appears to be in derivatives in which N–H activation is competitive.

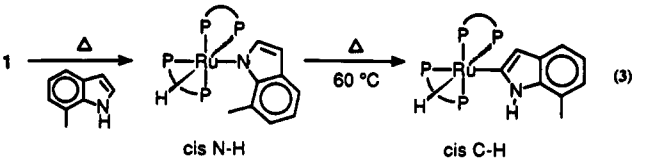
N–H Insertion Reactions

The oxidative addition of N–H groups to the [Ru(dmpe)$_2$] fragment was found to be a general reaction. At 60 °C in benzene solution, pyrrole reacts with naphthyl hydride complex **1** to give a product with a hydride quintet in the ^{1}H NMR spectrum indicative of a trans H–X addition product. The aromatic region of the spectrum shows two broad singlets for the α- and β-hydrogens of the pyrrole ring. This N–H addition product was isolated in analytically pure form by removal of the volatiles and sublimation of the naphthalene at 40 °C.

The reaction of **1** and pyrazole resulted in an instantaneous reaction at room temperature. An ^{1}H NMR spectrum recorded at this time indicated loss of naphthalene from **1** and the formation of the cis N–H activated product in ~25% yield, as denoted by the appearance of a doublet of quartets (δ –7.915). The corresponding N–H activated trans isomer subsequently appeared upon standing for 7 days (12%), concomitant with more cis isomer formation (now 72%). Heating to 60 °C immediately led to the complete loss of **1** and the formation of a 3:1 ratio of the cis and trans isomers. The cis isomer under these conditions slowly converted over the next 8 days to the trans isomer, which was then isolated in analytically pure form.

A similar reaction takes place between **1** and indazole, with about 50% reaction occuring rapidly at 25 °C. A 1.7:1 trans:cis ratio of the N–H insertion products was observed after 36 h at 60 °C. The saturated amine pyrrolidine also reacts with **1** at 60 °C to give the trans and cis N–H insertion products in ~1:1 ratio after 12 h. This ratio changes to 3:1 upon heating for 37 h, indicating again a thermodynamic preference for the trans product.

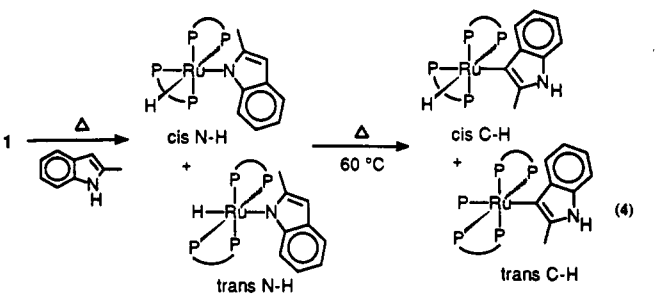
Thermolysis of **1** with 7-methylindole proved most informative, since it explained why 2,6-disubstituted phenyl isocyanides were the only recognized substrates in reactions where free indoles were formed in a catalytic fashion. At 60 °C, the initial products are the cis N–H insertion product (68%) and the cis C–H insertion product (22%) at the 2-position, with a small amount of the trans N–H insertion product also seen (7%). The cis N–H insertion product disappears completely upon heating to 100 °C for 18 h as more of the cis C–H product appears (87%) along with a trace of the trans C–H insertion product (2%) (eq 3). The amount of trans N–H insertion product



(3)

remains relatively constant (8%). This experiment demonstrates that when the indole possesses a methyl group in the 7-position, the N–H insertion products are destabilized relative to the cis C–H activation products. The C–H activation products are labile and hence allow the catalytic cycle to continue.

The effects of steric interference are also noted in the reaction of **1** with 2-methylindole. Here, the hydride region of the ^{1}H NMR spectrum shows resonances in regions other than those where the cis and trans indole-*C*^{2} and indole-*N* complexes occur. C–H activation is proposed to occur at the 3-position of the ring in this case, thereby accounting for the presence of all four isomers observed (cis and trans N–H activation products plus cis and trans 2-methylindole-*C*^{3} isomers) (eq 4).



(4)

In the present study, N–H metalated complexes ranging from substituted indoles, pyrrole, pyrazole, and indazole to cyclic amines have been studied and characterized. Current literature accounts of N–H activation by early-transition-metal complexes include those by Bergman et al., involving generation of zirconocene methyl amide followed by N–H activation of *tert*-butylamine,[16] and by Rothwell et al.,[17] detailing the synthesis of (2,6-Ph$_2$C$_6$H$_3$O)$_2$Ti(NHC$_6$H$_5$)$_2$ compounds. In addition, Bercaw and Hillhouse also described the N–H activation of ammonia by Cp*MH$_2$, where M = Zr or Hf.[18] Roundhill and co-workers have performed a series intramolecular phosphorus "chelate-assisted" N–H oxidative additions to Ir(I) and Rh(I) complexes.[19] Their approach uses a tertiary phosphine moiety as an anchor from which N–H addition is induced to a low-valent transition-metal center.

Of special significance to the present studies, Merola and Ladipo reported earlier last year that heating [Ir(COD)(PMe$_3$)$_3$]Cl with heterocyclic amines, like pyrrole, indole, 3-methylindole, and 7-azaindole, leads to the facile production of amidoiridium hydride compounds through

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(17) Rothwell, I. P.; Hill, J. E.; Profilet, R. D.; Fanwick, P. E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664–665.
(18) Bercaw, J. E.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 5472–5478.
(19) Roundhill, D. M.; Hedden, D.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 6738–6744. Roundhill, D. M.; Hedden, D. *Inorg. Chem.* **1986**, *25*, 9–15. Roundhill, D. M.; Hedden, D.; Park, S. *Organometallics* **1986**, *5*, 2151–2152. Roundhill, D. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1974**, *96*, 3098–3105. Roundhill, D. M. *Inorg. Chem.* **1970**, *9*, 254–258.

oxidative addition of the N–H bond.[20] Jones and Dong also showed N–H activation through the synthesis of $(C_5Me_5)Rh(PMe_3)(H)$(pyrrole-*N*) from the thermal reaction at 60 °C of $(C_5Me_5)Rh(H)(PMe_3)(Ph)$ with pyrrole.[21] Facile activation of amide N–H bonds by iron and ruthenium phosphine complexes were recently characterized by Landis and Schaad.[22] Landis suggests design of late-transition-metal-catalyzed hydroaminations may be achieved by using amides as synthetic equivalents of ammonia, since analogous reaction chemistry does not happen with alcohols, water, and simple amines.

Bryndza and Tam reported the synthesis of Pt(II) alkyl amide complexes, which undergo the first known examples of CO insertion into late transition metal–nitrogen bonds.[23] Such platinum–nitrogen bond reactivity implies that catalytic chemistry involving metal amides might be possible. In addition, Casalnuovo and co-workers described the first successful catalytic hydroamination of an olefin by a transition-metal-catalyzed N–H activation mechanism. Independent intermediate characterization and labeling studies indicated an overall cis addition of the N–H group across the exo face of norbornylene.[24] As a final example, Marks and Gagne demonstrated that organolanthanide centers can also facilitate unusual types of olefin insertion processes that can be incorporated into novel catalytic cycles.[25]

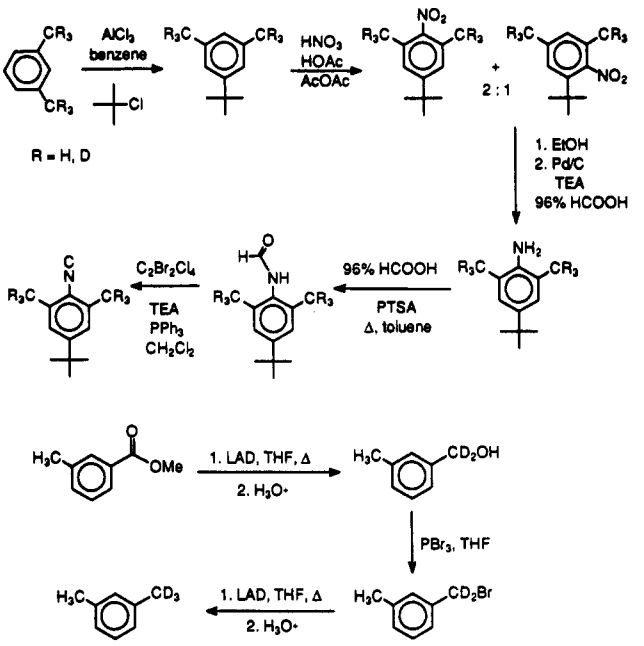
Conclusions

In summary a new route for the synthesis of indoles using the [Ru(dmpe)$_2$] fragment has been found. The method is catalytic for formation of 7-substituted indoles from 2,6-disubstituted isocyanides and stoichiometric for the formation of N–H activated indoles. In the latter cases, hydrogenolysis leads to the formation of free indole and $Ru(dmpe)_2H_2$. A mechanism involving intramolecular C–H activation of a bound isocyanide is found to be operating in the indole-forming reaction. The addition of N–H bonds to the unsaturated ruthenium fragment is also found to be a general reaction.

Experimental Section

The metal complexes synthesized in these experiments are air sensitive, and all manipulations of these compounds were carried out under inert atmospheric conditions of dry nitrogen via a high-vacuum line or in a Vacuum Atmospheres Corp. Dri-Lab glovebox. All materials used in the synthesis of organic and inorganic compounds were obtained commercially from Aldrich or MSD Isotopes. *cis*-Ru(dmpe)$_2$(H)(naphthyl) was prepared according to a literature procedure.[26] High-field ^{1}H NMR, ^{31}P NMR, and ^{13}C NMR spectra were recorded on a Bruker WH 400 or 400 AMX NMR spectrometer. All NMR spectra were recorded in C_6D_6 unless otherwise noted. Perdeuterated benzene (99.99% D) was obtained from MSD Isotopes and vacuum-distilled from potassium benzophenone ketyl. Elemental analyses were performed by Desert Analytics. Single-crystal X-ray diffraction studies were done on an Enraf-Nonius CAD4 diffractometer. The deuterated isocyanides were synthesized according to the procedure outlined in Scheme 7. Synthetic details and characterization data for the deuterated and other isocyanides are given in the supplementary material.

Scheme 7. Synthetic Scheme for Labeled Isocyanides



Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 4-*tert*-Butyl-2,6-xylyl-α,α,α-d_3 Isocyanide. A 5.0-mg sample of 4-*tert*-butyl-2,6-xylyl-α,α,α-d_3 isocyanide (0.0263 mmol) and 13.9 mg of Ru(dmpe)$_2$(H)(naphthyl) (0.0263 mmol) were placed in an NMR tube attached to a ground-glass joint equipped with a vacuum adapter in the glovebox. Into this sample was condensed 1 mL of C_6D_6 on the vacuum line. The NMR tube was then frozen in liquid nitrogen, freeze–pump–thaw-degassed three times, and sealed under vacuum. The reaction mixture was heated to 60 °C, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy at 12, 24, and 36 h. The sample was evaporated under vacuum, and the excess free isocyanide was extracted from the crude product by washing with hexane, followed by removal of free naphthalene by sublimation at 40 °C. The yellow powder was redissolved in C_6D_6, and the resultant ^{1}H NMR spectrum was used for the analysis of the intramolecular isotope effect. The isotopic ratio k_H/k_D was determined to be 2.6 (average of four runs), as described under Results and Discussion.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 4-*tert*-Butyl-2,6-xylyl Isocyanide. A 5.5-mg (0.0267-mmol) sample of 4-*tert*-butyl-2,6-xylyl isocyanide was placed in a resealable NMR tube, which was then placed under vacuum and taken into the glovebox. A 14-mg (0.0267-mmol) quantity of Ru(dmpe)$_2$(H)(naphthyl) was added. The NMR tube was taken out of the box, 1 mL of C_6D_6 condensed in, and the sample freeze–pump–thaw-degassed three times. The tube was then sealed under vacuum. After 24 h of heating at 60 °C, the quantitative formation of *trans*-Ru(dmpe)$_2$(H)(5-*tert*-butyl-7-methylindole-C^2) was seen in the ^{1}H NMR spectrum. ^{1}H NMR, δ: 7.196, s, 1 H; 7.082, s, 1 H; 6.105, s, 1 H; 2.544, s, 3 H; 1.582, s, 9 H; 1.211, d, 24 H; 1.266, br m, 4 H; 1.539, br m, 4 H; −12.735, qnt, 1 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 4-*tert*-Butyl-2,6-xylyl-$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha',3,5$-$d_8$ Isocyanide. A 5.5-mg (0.0259-mmol) sample of 4-*tert*-butyl-2,6-xylyl-$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha',3,5$-$d_8$ isocyanide was placed into a resealable NMR tube. A 13.0-mg (0.0259-mmol) quantity of Ru(dmpe)$_2$(H)(naphthyl) was added, and 1 mL of C_6D_6 was condensed in on a vacuum line. An ^{1}H NMR spectrum recorded after 24 h of thermolysis at 60 °C showed quantitative product formation. ^{1}H NMR, δ: 1.582, s, 9 H; 1.213, d, 24 H; 1.265, br m, 4 H; 1.537, b m, 4 H.

Competitive Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 4-*tert*-Butyl-2,6-xylyl-d_0/-d_3 Isocyanide. 4-*tert*-Butyl-2,6-

(20) Merola, J. S.; Ladipo, F. T. *Inorg. Chem.* **1990**, *29*, 4172–4173.
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(23) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939–940.
(24) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738–6744. Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971–973.
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(26) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843–855.

xylyl-d_0 isocyanide and 4-*tert*-butyl-2,6-xylyl-$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha',3,5$-$d_8$ isocyanide (20 mg (0.107 mmol) each) were added along with 50 mg of Ru(dmpe)$_2$(H)(naphthyl) (0.0946 mmol) to a resealable NMR tube to which 1 mL of C_6D_6 was added. The sample was heated at 60 °C for 36 h in an oil bath, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. Excess free isocyanide was extracted from the crude product by a hexane wash, followed by removal of free naphthalene by sublimation at 40 °C. An ^{1}H NMR spectrum of the residue in C_6D_6 was analyzed for the intermolecular isotope effect. As observed above, independent reaction of Ru(dmpe)$_2$(H)(naphthyl) with either the d_0 or d_8 isocyanide indicated the presence of a coincident resonance at δ 1.582 for the *tert*-butyl group located at the 5-position of the ruthenium-bound indoles. The isotopic ratio k_H/k_D = 1.08 was determined by integration of the *tert*-butyl group resonance of the resulting metal-bound indole compounds (representing the total amount of both indole products formed) and the resonance of the methyl group on the indole of the C–H activated isocyanide (average of two runs).

Effect of Isocyanide Concentration on the Rate of the Catalytic Cycle. Four samples containing 10 mg of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) in 1 mL of C_6D_6 with 3 μL (0.0189 mmol), 9 μL (0.0567 mmol), 19 μL (0.114 mmol), and 30 μL (0.189 mmol), respectively, of 2,6-diethylphenyl isocyanide were sealed under vacuum in NMR tubes. ^{1}H NMR spectra were recorded at 3-h intervals after thermolysis at 60 °C. Substantial polymerization was seen in the ^{1}H NMR spectra recorded at 18, 21, and 24 h. The method of initial rates allowed for a more accurate representation of the data. In the analysis of the four concurrent experiments, the resonances of the starting material Ru(dmpe)$_2$(H)(naphthyl) and the product *trans*-Ru(dmpe)$_2$(H)(3-methyl-7-ethylindole-C^2) were integrated relative to one another in order to calculate the extent of reaction.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 6-Ethyl-*o*-tolyl Isocyanide. A 15-mg (0.028-mmol) sample of Ru(dmpe)$_2$(H)(naphthyl) and 4 μL (0.027 mmol) of 6-ethyl-*o*-tolyl isocyanide were dissolved in 0.5 mL of C_6D_6 in an NMR tube, and the tube was sealed under vacuum. The sample was heated to 60 °C, and NMR spectra were recorded over the next 76 h. The temperature was increased to 100 °C, and spectra were recorded over the next 8 h. The interpretation of the spectra is presented under Results and Discussion. ^{1}H NMR for *trans*-RuH(7-ethylindole-C^2)(dmpe)$_2$, δ: 7.62, m, 1 H; 7.396, s, 1 H; 7.2, m, 1 H; 6.903, s, 1 H; 6.065, s, 1 H; 2.947, q, 2 H; 1.444, t, 3 H; 1.230, s, 12 H; 1.189, s, 12 H; −12.737, qnt, J = 22 Hz, 1 H. ^{1}H NMR for *trans*-RuH(3,7-dimethylindole-C^2)(dmpe)$_2$, δ: 7.3, d, 1 H; 7.0, t, 1 H; 2.800, s, 3 H; −12.826, qnt, J = 23 Hz, 1 H; other resonances not assigned. ^{1}H NMR for *cis*-RuH(7-ethylindole-C^2)(dmpe)$_2$, δ: 8.108, s, 1 H; 7.672, d, 1 H; 7.194, t, 1 H; 6.918, d, 1 H; 6.307, s, 1 H; 2.884, q, 2 H; −8.976, dq, J = 84, 24 Hz, 1 H; other resonances not assigned.

Reaction of 6-Ethyl-*o*-tolyl Isocyanide with Ru(dmpe)$_2$H$_2$ (3). A 12-mg (0.03-mmol) sample of **3** and 5.5 μL of 6-ethyl-*o*-tolyl isocyanide were dissolved in 0.5 mL of C_6D_6 in an NMR tube, and the tube was sealed under vacuum. The sample was heated to 140 °C for 12 h, at which time an ^{1}H NMR spectrum showed only resonances for **3**, 7-ethylindole, and 3,7-dimethylindole. ^{1}H NMR for 7-ethylindole, δ: 7.916, s, 1 H; 7.635, d, 1 H; 7.192, t, 1 H; 7.049, d, 1 H; 6.887, d, 1 H; 6.583, d, 1 H; 2.680, q, 2 H; 1.200, t, 3 H. ^{1}H NMR for 3,7-dimethylindole, δ: 7.83, s, 1 H; 7.551, d, 1 H; 7.190, t, 1 H; 7.040, d, 1 H; 6.635, s, 1 H; 2.315, s, 3 H; 2.241, s, 3 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with *o*-Tolyl Isocyanide. A benzene solution of Ru(dmpe)$_2$(H)(naphthyl) (53 mg, 0.1 mmol) and *o*-tolyl isocyanide was heated to 60 °C for 24 h. The solution was filtered to remove the flocculent isocyanide polymer precipitate, the volatiles were removed under vacuum, and *trans*-Ru(dmpe)$_2$(H)(indole-C^2) was isolated. Yield: 25 mg (45%). In a separate experiment conducted in an NMR tube in C_6D_6 solvent, further heating produced other isomers as described under Results and Discussion. ^{1}H NMR for Ru(dmpe)$_2$(CN-*o*-tolyl), δ: 7.22, d, J = 7.8 Hz, 1 H; 7.15, m, 2 H; 6.993, t, J = 7.2 Hz, 1 H; 2.528, s, 3 H; 1.278, s, 32 H. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(indolenine-C^2), δ: 7.815, d, J = 8 Hz, 1 H; 7.698, d, J = 7.8 Hz, 1 H; 7.535, t, J = 7.5 Hz, 1 H; 7.29, m, 1 H; 3.326, s, 2 H; −12.243, qnt, J = 22 Hz, 1 H. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(indole-C^2), δ: 7.735, d, J = 7.6 Hz, 1 H; 7.369, d, J = 7.7 Hz, 1 H; 7.302, s, 1 H; 7.244, t, J = 7.3 Hz, 1 H; 7.107, t, J = 7.1 Hz, 1 H; 6.043, s, 1 H; 1.213, s, 12 H; 1.144, s, 12 H; −12.805, qnt, J = 22.7 Hz, 1 H. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(indole-C^2), δ: 7.98, s, 1 H; 7.780, d, J = 7.6 Hz, 1 H; 7.315, d, J = 7.4 Hz, 1 H; 7.244, t, J = 7.4 Hz, 1 H; 7.127, t, J = 7.4 Hz, 1 H; 6.285, s, 1 H; 0.8–1.5, m, 32 H; −9.085, dq, J = 84, 25.2 Hz, 1 H. Anal. Calcd (found) for $RuP_4NC_{20}H_{39}$: C, 46.32 (46.33); H, 7.60 (7.60); N, 2.70 (3.00).

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with Indole. A 100-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mol) and 22 mg of indole (0.0189 mol) were dissolved in 1 mL of C_6D_6 in an NMR tube, which was freeze–pump–thaw-degassed three times before flame-sealing. After 22 h of heating at 60 °C, the solvent was evaporated, with subsequent sublimation at 40 °C to remove free naphthalene. The remaining product was extracted with hexane and solvent removed under vacuum, leaving a white powder. Yield: 90 mg (89%). Anal. Calcd (found) for $RuP_4C_{20}H_{39}N$: C, 46.33 (46.35); H, 7.58 (7.56); N, 2.70 (2.69). ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(indole-N), δ: 8.124, d, 1 H; 7.2–7.4, m, 2 H; 7.199, d, 1 H; 7.085, s, 1 H; 6.951, s, 1 H; 1.639, m, 4 H; 1.266, m, 4 H; 1.103, d, 24 H; −19.982, qnt, J = 22 Hz, 1 H. ^{31}P NMR (C_6D_6), δ: 44.361, d, J_{P-H} = 22 Hz. Further heating of the benzene solution of the trans N–H insertion product led to the formation of the cis N–H insertion product. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(indole-N), δ: 8.365, d, J = 8.3 Hz, 1 H; 8.089, d, J = 7.6 Hz, 1 H; 7.55–7.7, br s, 1 H; 7.460, t, J = 7.2 Hz, 1 H; 7.304, t, J = 7.2 Hz, 1 H; 7.003, s, 1 H; −7.450, dq, J = 96, 27 Hz, 1 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 2-Ethylphenyl Isocyanide. A 10-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 2.5 mg of 2-ethylphenyl isocyanide (0.0189 mmol) were dissolved in 1 mL of C_6D_6 in an NMR tube, which was then freeze–pump–thaw-degassed before flame-sealing. The sample was subsequently heated to temperatures between 60 and 140 °C and the progress of the reaction monitored by ^{1}H NMR spectroscopy. Yields of the respective products observed during the course of the reaction were calculated on the basis of ^{1}H NMR integrations of the hydride region. Details of this experiment are described under Results and Discussion. ^{1}H NMR for *trans*-RuH(3-methylindole-C^2)(dmpe)$_2$, δ: 7.985, d, 1 H; 7.428, d, 1 H; 7.298, t, 1 H; 2.875, s, 3 H; −12.838, qnt, J = 24 Hz, 1 H. ^{1}H NMR for *cis*-RuH(3-methylindole-C^2)(dmpe)$_2$, δ: 7.796, d, 1 H; 7.535, br s, 1 H; 7.328, t, 1 H; 7.19, m, 1 H; 7.102, d, 1 H; 2.858, s, 3 H; 0.8–1.5, m, 32 H; −9.241, dq, J = 88, 24 Hz, 1 H. ^{1}H NMR for *cis*-RuH(3-methylindole-N)(dmpe)$_2$, δ: 8.291, d, 1 H; 7.968, d, 1 H; 7.468, t, 1 H; 7.324, t, 1 H; 7.024, s, 1 H; 2.848, s, 3 H; −7.439, dq, J = 96, 28 Hz, 1 H. ^{1}H NMR for *trans*-RuH(3-methylindole-N)(dmpe)$_2$, δ: 8.292, d, 1 H; 7.974, t, 1 H; 7.339, t, 1 H; 7.119, d, 1 H; 6.855, s, 1 H; 2.798, s, 3 H; 1.662, m, 4 H; 1.322, m, 4 H; 1.118, d, 24 H; −19.903, qnt, J = 22 Hz, 1 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 3-Methylindole. A 100-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.189 mmol) and 25 mg of 3-methylindole (0.189 mmol) were dissolved in 20 mL of C_6H_6 in an ampule, and the mixture was heated to 60 °C for 36 h. The solvent was removed under vacuum and naphthalene removed by sublimation at 40 °C. The material was extracted with hexane to remove any remaining impurities, giving pure *trans*-RuH(3-methylindole-N)(dmpe)$_2$. Yield: 90 mg (89%). Anal. Calcd (found) for $RuP_4C_{21}H_{41}N$: C, 47.38 (47.35); H, 7.76 (7.77); N, 2.63 (2.61).

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 4-Methyl-*o*-tolyl Isocyanide. A 10-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 2.5 mg of 4-methyl-*o*-tolyl isocyanide (0.0189 mmol) were placed into an NMR tube, and 1 mL of C_6D_6 was added. The sample was degassed, and the tube was flame-sealed under vacuum. The progress of the reaction upon heating between 70 and 100 °C was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(5-methylindole-C^2), δ: 8.001,

d, 2 H; 7.052, s, 1 H; 6.962, s, 1 H; 5.982, s, 1 H; 2.529, s, 3 H; 1.4–1.6, m, 8 H; 1.183, d, 24 H; –12.780, qnt, J = 23 Hz, 1 H. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(5-methylindole-C^2), δ: 7.940, s, 1 H; 7.546, s, 1 H; 7.238, m, 1 H; 6.949, d, 1 H; 6.222, s, 1 H; 2.629, s, 3 H; 0.9–1.5, m, 8 H; 0.899, d, 32 H; –9.092, dq, J = 84, 24 Hz, 1 H. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(5-methylindole-N), δ: 8.273, d, 1 H; 7.299, m, 2 H; 7.106, d, 2 H; 6.968, d, 1 H; 2.719, s, 3 H; 0.5–1.4, m, 8 H; 0.513, d, 32 H; –7.541, dq, J = 85, 25 Hz, 1 H. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(5-methylindole-N), δ: 7.499, s, 1 H; 7.065, d, 1 H; 7.035, m, 2 H; 6.795, d, 1 H; 2.612, s, 3 H; 1.604, m, 4 H; 1.232, m, 4 H; 1.056, d, 24 H; –19.917, qnt, 1 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 4-Methoxy-*o*-tolyl Isocyanide. A 10-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 2.5 mg of 4-methoxy-*o*-tolyl isocyanide (0.0189 mmol) were dissolved in 1 mL of C_6D_6 in an NMR tube in the glovebox. This sample was degassed, and the tube was flame-sealed under vacuum. The sample was subsequently heated to temperatures between 70 and 150 °C and the progress of reaction monitored by ^{1}H NMR spectroscopy. Yields of the respective products observed during the course of the reaction were calculated on the basis of ^{1}H NMR integrations of the hydride region. ^{1}H NMR (THF-d_8) for *trans*-Ru(dmpe)$_2$(H)(5-methoxyindole-C^2), δ: 8.051, br s, 1 H; 6.765, d, 1 H; 6.737, d, 1 H; 6.56, s, 1 H; 5.578, s, 1 H; 3.663, s, 3 H; 1.5–1.8, m, 8 H; 1.376, d, 24 H; –12.904, qnt, J = 23 Hz, 1 H. ^{1}H NMR (THF-d_8) for *cis*-Ru(dmpe)$_2$(H)(5-methoxyindole-C^2), δ: 8.051, br s, 1 H; 6.566, s, 1 H; 6.165, d, 1 H; 6.111, d, 1 H; 5.807, s, 1 H; 3.650, s, 3 H; 1.2–1.8, m, 8 H; 1.20, d, 32 H; –9.181, dq, J = 84, 24 Hz, 1 H. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(5-methoxyindole-N), δ: 8.222, d, 1 H; 7.473, d, 1 H; 7.253, dd, 1 H; 6.935, d, 1 H; 3.755, s, 3 H; 0.6–1.5, m, 8 H; 0.524, d, 32 H; –7.493, dq, J = 97, 27 Hz, 1 H. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(5-methoxyindole-N), δ: 7.490, d, 1 H; 7.115, d, 1 H; 7.034, m, 2 H; 6.873, s, 1 H; 3.757, s, 3 H; 1.626, m, 4 H; 1.206, m, 4 H; 1.114, s, 12 H; 1.094, s, 12 H; –19.963, qnt, J = 23 Hz, 1 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 5-Methoxyindole. A 48-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0908 mmol) and 13.3 mg of 5-methoxyindole (0.0908 mmol) were dissolved in 20 mL of C_6H_6 in an ampule, and the mixture was heated to 60 °C for 24 h. The solvent was evaporated under vacuum and free naphthalene removed by sublimation at 40 °C. The material was then washed with hexane to remove any remaining impurities, leaving pure *trans*-Ru(dmpe)$_2$(H)(5-methoxyindole-N). Yield: 47 mg (98%). Anal. Calcd (found) for $RuP_4C_{21}H_{41}N$: C, 45.98 (45.86); H, 7.53 (7.51); N, 2.55 (2.53).

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 4-Fluoro-*o*-tolyl Isocyanide. A 12-mg (0.023-mmol) sample of Ru(dmpe)$_2$(H)(naphthyl) and 3 mg (0.022 mmol) of 4-fluoro-*o*-tolyl isocyanide were dissolved in 0.5 mL of C_6D_6 in an NMR tube. The tube was sealed under vacuum, and the mixture was heated to 60 °C. An ^{1}H NMR spectrum recorded after 20 h showed a single product, assigned as *trans*-Ru(dmpe)$_2$(H)(5-fluoroindole-C^2). Prolonged heating resulted in isomerization to the corresponding cis isomer. Further heating at 110 °C for several days caused the smooth transition to *cis*-Ru(dmpe)$_2$(H)(5-fluoroindole-N). ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(5-fluoroindole-C^2), δ: 7.396, dd, 1 H; 7.042, m, 1 H; 6.846, td, 1 H; 5.934, s, 1 H; 1.363, m, 4 H; 1.252, m, 4 H; 1.194, s, 12 H; 1.102, s, 12 H; –12.848, qnt, J = 23 Hz, 1 H. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(5-fluoroindole-C^2), δ: 7.950, s, 1 H; 7.433, dd, 1 H; 6.987, m, 1 H; 6.846, dt, 1 H; 6.170, s, 1 H; –9.151, dq, J = 84, 24 Hz, 1 H; dmpe resonances not assigned. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(5-fluoroindole-N), δ: 8.230, m, 1 H; 7.739, dd, 1 H; 7.219, s, 1 H; –7.560, dq, J = 96, 24 Hz, 1 H; other resonances obscured by solvent.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 5-Fluoroindole. A 48-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0908 mmol) and 13.3 mg (0.0908 mmol) of 5-fluoroindole were dissolved in 15 mL of C_6H_6, and the solution was placed in an ampule in the glovebox. The reaction mixture was heated to 75 °C for 2 days. The solvent was evaporated under vacuum and free naphthalene removed by sublimation at 40 °C. The material was then washed with hexane to remove any remaining impurities, giving pure *trans*-Ru(dmpe)$_2$(H)(5-fluoroindole-N). Yield: 40 mg (83%). ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(5-fluoroindole-N), δ: 7.741, d, 1 H; 7.049, m, 2 H; 6.994, m, 1 H; 6.795, d, 1 H; 1.548, m, 4 H; 1.163, m, 4 H; 1.079, s, 12 H; 1.061, s, 12 H; –20.086, qnt, J = 22 Hz, 1 H. Anal. Calcd (found) for $RuP_4C_{20}H_{38}FN$: C, 44.77 (44.67); H, 7.14 (7.10); N, 2.61 (2.12).

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with *N*-Methylindole. A 100-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.189 mmol) and 24.8 mg of *N*-methylindole (0.189 mmol) dissolved in ~15 mL of C_6H_6 were placed in an ampule, and the mixture was heated to 75 °C in an oil bath for 26 h. The contents of the ampule were transferred to a round-bottom flask, where the solvent was removed under vacuum and naphthalene sublimed from the crude material at 40 °C. The product was recrystallized from a mixture of hexane–tetrahydrofuran in the glovebox. Yield: 89 mg (89%). ^{1}H NMR, δ: 7.759, d, 1 H; 7.435, d, 1 H; 7.303, t, 1 H; 7.271, t, 1 H; 6.391, br s, 1 H; 4.158, s, 3 H; 0.7–1.5, br d, 32 H; –9.222, dq, 1 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 3-Methyl-*o*-tolyl Isocyanide. A mixture of 10 mg of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 2.5 mg of 3-methyl-*o*-tolyl isocyanide (0.0189 mmol) was placed in an NMR tube, and 1 mL of C_6D_6 was added. The sample was then degassed, and the tube was flame-sealed under vacuum. After thermolysis for 24 h at 60 °C, two products were observed, identified as *trans*-Ru(dmpe)$_2$(H)(4-methylindolenine-C^2) and *trans*-Ru(dmpe)$_2$(H)(4-methylindole-C^2), in a 2:3 ratio based upon ^{1}H NMR integrations of the hydride region. The reaction was halted at this point since increasing decomposition made monitoring the reaction difficult. ^{1}H NMR for *trans*-RuH(4-methylindolenine-C^2)(dmpe)$_2$, δ: 7.775, dd, 2 H; 7.4, d, 2 H; 5.327, s, 2 H; 2.673, s, 3 H; 1.36–1.60, m, 8 H; 1.083, d, 24 H; –10.842, dq, J = 85, 25 Hz, 1 H. ^{1}H NMR for *trans*-RuH(4-methylindole-C^2)(dmpe)$_2$, δ: 7.775, dd, 2 H; 7.4, m, 2 H; 6.054, s, 1 H; 2.790, s, 3 H; 1.3–1.6, m, 8 H; 1.219, d, 24 H; –12.854, qnt, 1 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 3-Fluoro-*o*-tolyl Isocyanide. A 10-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 2.6 mg of 3-fluoro-*o*-tolyl isocyanide (0.0189 mmol) were dissolved in 1 mL of C_6D_6 in an NMR tube. The sample was degassed, and the tube was flame-sealed under vacuum. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Even at early stages in this thermal reaction carried out at 60 °C, severe decomposition was highly evident.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 5-Methyl-*o*-tolyl Isocyanide. A 10-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 5 mg of 5-methyl-*o*-tolyl isocyanide (0.0382 mmol) were dissolved in 1 mL of C_6D_6 in an NMR tube. The sample was degassed, and the tube was flame-sealed under vacuum. The reaction mixture was heated to 60 °C, and reaction progress was monitored by ^{1}H NMR spectroscopy. After 24 h, only the *trans*-Ru(dmpe)$_2$(H)(6-methylindolenine-C^2) complex observed. Characteristic chemical shifts were seen: δ –10.82 ppm, a trans hydride denoted by a quintet pattern; δ 6.02 ppm, a vinylic proton; and a doublet centered at δ 1.22 ppm, indicative of a trans dmpe orientation. The reaction was stopped after 24 h due to severe decomposition, which made further study difficult.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 5-Fluoro-*o*-tolyl Isocyanide. A 10-mg sample of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 2.3 mg of 5-fluoro-*o*-tolyl isocyanide (0.0189 mmol) were dissolved in 1 mL of C_6D_6 in an NMR tube. The sample was degassed, and the tube was flame-sealed under vacuum. The reaction mixture was heated at 60 °C for 36 h. Severe decomposition had occurred such that no characteristic resonances were observed by ^{1}H NMR spectroscopy.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with Pyrrole. A mixture of 100 mg of Ru(dmpe)$_2$(H)(naphthyl) (0.189 mmol) and 12.6 mg of pyrrole (18.9 mmol) dissolved in 15 mL of C_6H_6 was heated in an ampule in an oil bath for 2 days. The solvent was evaporated under vacuum and the residue heated to 40 °C to remove free naphthalene. The yellow powder was then washed with a mixture of benzene and tetrahydrofuran and again evaporated to dryness on the high-vacuum line. Yield: 74 mg

Table 2. Crystallographic Data for Ru(H)(X)(dmpe)$_2$ Complexes

	X			
formula	trans 3-methylindole-*N*	trans 5-methoxyindole-*N*	trans 5-fluoroindole-*N*	cis *N*-methylindole-*C*[2]
formula	$RuP_4NC_{21}H_{41}$	$RuP_4NOC_{21}H_{41}\cdot{}^1/_2C_6H_6$	$RuP_4NFC_{20}H_{41}\cdot{}^1/_2C_6H_6$	$RuP_4NC_{21}H_{41}$
mol wt	532.53	548.53	575.55	532.53
space group (No.)	*Pnnm* (58)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
a, Å	17.263(10)	9.065(2)	8.854(4)	15.08(1)
b, Å	10.668(10)	16.379(3)	16.45(1)	10.173(8)
c, Å	13.524(10)	19.196(5)	18.873(8)	18.09(2)
β, deg	90	92.06(4)	93.95(4)	114.49(7)
V, Å^3	2490(6)	2848(2)	2743(5)	2526(8)
ρ_{calc}, g cm^{-3}	1.42	1.37	1.39	1.40
Z	4	4	4	4
temp, °C	−75	25	−70	−75
radiation (monochr)	Mo (graphite)	Mo (graphite)	Mo (graphite)	Mo (graphite)
μ, cm^{-1}	8.78	7.77	8.08	8.66
range of transm factors	0.74–1.48	0.91–1.05	0.83–1.35	0.77–1.42
$R(F_o)$	0.056	0.032	0.046	0.052
$R_w(F_o)$	0.070	0.034	0.054	0.060
goodness of fit	2.91	1.28	2.04	2.29

(84%). ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(pyrrole-*N*), δ: 6.703, s, 2 H; 6.397, s, 2 H; 1.552, m, 4 H; 1.228, m, 4 H; 1.188, s, 12 H; 1.114, s, 12 H. ^{31}P{^{1}H} NMR, δ: 18.44, s. ^{13}C{^{1}H} NMR, δ: 133.74, s, H_α; 128.02, s, H_β; 31.41, qnt, CH_2; 24.37, qnt, CH_3; 14.48, qnt, CH_3. Anal. Calcd (found) for $RuP_4C_{16}H_{37}N$: C, 41.03 (41.65); H, 7.95 (8.23); N, 2.99 (2.45).

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with Pyrazole. A mixture of 100 mg of Ru(dmpe)$_2$(H)(naphthyl) (0.189 mmol) and 12.8 mg of pyrazole (0.189 mmol) dissolved in 20 mL of C_6H_6 was heated to 130 °C in an ampule for 3 days. The solvent was evaporated under vacuum and free naphthalene sublimed from the crude product at 40 °C. The residue was then extracted with hexane and the solvent evaporated to give the pure cis N–H addition product. Yield: 69 mg (78%). ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(pyrazole-*N*), δ: 7.985, s, 1 H; 7.048, s, 1 H; 6.499, s, 1 H; 1.832, m, 4 H; 1.294, m, 4 H; 1.183, d, 24 H; −18.767, qnt, J = 22 Hz, 1 H. ^{31}P{^{1}H} NMR, δ: 45.97, s. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(pyrazole-*N*), δ: 8.007, s, 1 H; 7.828, s, 1 H; 6.531, s, 1 H; 1.384–0.888, m, 40 H; −7.915, dq, 1 H. ^{31}P{^{1}H} NMR, δ: 45.97, s. ^{13}C{^{1}H} NMR, δ: 141.20, s; 137.38, s; 101.31, s; 31.11, qnt; 23.56, qnt; 15.31, qnt. Anal. Calcd (found) for $RuP_4C_{15}H_{37}N_2$: C, 38.38 (38.86); H, 7.94 (7.93); N, 5.96 (5.94).

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with Indazole. A 10-mg sample of Ru(dmpe)$_2$(H)(naphthyl) and 2.2 mg of indazole were placed in an NMR tube and dissolved in 1 mL of C_6D_6. The sample was freeze–pump–thaw-degassed three times before flame-sealing. The reaction progress was monitored by ^{1}H NMR spectroscopy, as described under Results and Discussion. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(indazole-*N*), δ: 8.028, d, 1 H; 7.930, t, 1 H; 7.499, m, 1 H; 7.119, t, 1 H; 7.035, s, 1 H; 1.884, m, 4 H; 1.35, m, 4 H; 1.143, d, 24 H. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)-(indazole-*N*), δ: 8.064, d, 1 H; 7.941, d, 1 H; 7.499, m, 1 H; 7.370, t, 1 H; 7.009, s, 1 H; 0.75–1.46, m, 40 H; −7.723, qnt, 1 H.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with Pyrrolidine. A 10-mg sample of Ru(dmpe)$_2$(H)(naphthyl) and 1.34 mg of pyrrolidine were dissolved in 1 mL of C_6D_6 in an NMR tube, and the mixture was freeze–pump–thaw-degassed three times before flame-sealing. The progress of the reaction was monitored by ^{1}H NMR spectroscopy as described under Results and Discussion. The following hydride resonances were observed (the aliphatic region was unresolved). ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)-(pyrrolidine-*N*), δ: −19.804, qnt. ^{1}H NMR for *cis*-Ru(dmpe)$_2$-(H)(pyrrolidine-*N*), δ: −7.549, dq.

Reaction of Ru(dmpe)$_2$(naphthyl) with 7-Methylindole. A mixture of 10 mg of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 2.5 mg of 7-methylindole (0.0189 mmol) was dissolved in 1 mL of C_6D_6 in an NMR tube and the sample freeze–pump–thaw-degassed three times before flame-sealing. The sample was heated, and the reaction progress was monitored by ^{1}H NMR spectroscopy as described under Results and Discussion.

Reaction of Ru(dmpe)$_2$(H)(naphthyl) with 2-Methylindole. A mixture of 10 mg of Ru(dmpe)$_2$(H)(naphthyl) (0.0189 mmol) and 2.5 mg of 2-methylindole (0.0189 mmol) was dissolved in 1 mL of C_6D_6 in an NMR tube and the sample freeze–pump–thaw-degassed three times before flame-sealing. The reaction mixture was heated and the progress monitored by ^{1}H NMR spectroscopy as described under Results and Discussion. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(2-methylindole-*N*), δ: −20.072, qnt. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(2-methylindole-*N*), δ: −7.649, dq. ^{1}H NMR for *trans*-Ru(dmpe)$_2$(H)(2-methylindole-*C*[3]), δ: −13.310, qnt. ^{1}H NMR for *cis*-Ru(dmpe)$_2$(H)(2-methylindole-*C*[3]), δ: −8.449, dq.

X-ray Structural Determination of *trans*-Ru(dmpe)$_2$(H)-(3-methylindole-*N*). A colorless crystal of the complex measuring approximately 0.20 × 0.25 × 0.20 mm^3 was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer under a cold stream of nitrogen at −75 °C. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction revealed a primitive orthorhombic crystal system. Data were collected in accord with the parameters in Table 2. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The space group was assigned as *Pnnm* on the basis of the systematic absences, and the correctness of this choice was confirmed by successful solution of the Patterson map, showing the ruthenium atom on a crystallographic mirror plane. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure.[27] An empirical absorption correction was applied by using the program DIFABS following isotropic refinement. Anisotropic refinement of all non-hydrogen atoms allowed the use of a difference Fourier map for the location of the hydrogen atoms, the coordinates of which were subsequently idealized. Final anisotropic refinement was carried out on all non-hydrogen atoms with both the positional and thermal parameters "riding" on the atom to which they were attached. The hydride ligand was not located. Selected distances and angles are given in Table 3.

X-ray Structural Determination of *trans*-Ru(dmpe)$_2$(H)-(5-methoxyindole-*N*). A colorless crystal of the complex measuring approximately 0.22 × 0.24 × 0.28 mm^3 was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer under a cold stream of nitrogen at 25 °C. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction revealed a primitive monoclinic crystal system. Data were collected in accord with

(27) $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\sum wF_o^2$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birminghan, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Table 3. Selected Distances and Angles for Ru(H)(X)(dmpe)$_2$ Complexes

	X			
	trans 3-methy-lindole-*N*	trans 5-methoxy-indole-*N*	trans 5-fluoro-indole-*N*	cis *N*-methyl-indole-C^2
	Distances (Å)			
Ru–N1	2.266(7)	2.267(4)	2.265(5)	2.132(7)[a]
Ru–P1	2.328(2)	2.286(2)	2.296(2)	2.287(2)
Ru–P2	2.316(2)	2.290(2)	2.295(2)	2.289(3)
Ru–P3		2.301(2)	2.314(2)	2.294(2)
Ru–P4		2.304(2)	2.308(2)	2.343(3)
N1–C1	1.436(11)	1.357(7)	1.350(8)	1.410(8)
C1–C2	1.351(12)	1.381(8)	1.372(8)	1.399(8)
C2–C3	1.455(13)	1.396(8)	1.395(8)	1.431(9)
N1–C8	1.331(12)	1.394(7)	1.397(6)	1.388(8)
	Angles (deg)			
N1–Ru–P1	94.3(1)	98.7(1)	99.4(1)	85.0(2)[b]
N1–Ru–P2	97.8(1)	99.3(1)	98.8(1)	164.0(2)[b]
N1–Ru–P3		92.9(1)	93.3(1)	92.1(2)[b]
N1–Ru–P4		92.8(1)	93.4(1)	97.8(2)[b]

[a] Ru–C1. [b] C1–Ru–P.

the parameters in Table 2. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time showed a 25% decay in intensity. A linear decay correction was applied. The space group was uniquely assigned as $P2_1/c$ on the basis of the systematic absences, and the correctness of this choice was confirmed by successful solution of the Patterson map, showing the ruthenium atom in a general position. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure.[27] A benzene solvent molecule was located on a center of symmetry. An empirical absorption correction was applied by using the program DIFABS following isotropic refinement. Anisotropic refinement of all non-hydrogen atoms allowed the use of a difference Fourier map for the location of the hydrogen atoms, the coordinates of which were subsequently idealized. Final anisotropic refinement was carried out on all non-hydrogen atoms with both the positional and thermal parameters "riding" on the atom to which they were attached. The hydride ligand was located in the final difference map and was refined isotropically in the final model. Selected distances and angles are given in Table 3.

X-ray Structural Determination of *trans*-Ru(dmpe)$_2$(H)(5-fluoroindole-*N*). A colorless crystal of the complex measuring approximately 0.30 × 0.33 × 0.23 mm^3 was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer under a cold stream of nitrogen at −70 °C. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction revealed a primitive monoclinic crystal system. Data were collected in accord with the parameters in Table 2. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The space group was uniquely assigned as $P2_1/c$ on the basis of the systematic absences, and the correctness of this choice was confirmed by successful solution of the Patterson map, showing the ruthenium atom in a general position. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure.[27] A benzene solvent molecule was located on a center of symmetry. An empirical absorption correction was applied by using the program DIFABS following isotropic refinement. Anisotropic refinement of all non-hydrogen atoms allowed the use of a difference Fourier map for the location of the hydrogen atoms, the coordinates of which were subsequently idealized. Final anisotropic refinement was carried out on all non-hydrogen atoms with both the positional and thermal parameters "riding" on the atom to which they were attached. The hydride ligand was located in the final difference map and was refined isotropically in the final model. Selected distances and angles are given in Table 3.

X-ray Structural Determination of *cis*-Ru(dmpe)$_2$(H)(*N*-methylindole-C^2). A colorless crystal of the complex measuring approximately 0.23 × 0.31 × 0.35 mm^3 was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer under a cold stream of nitrogen at −75 °C. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction revealed a primitive monoclinic crystal system. Data were collected in accord with the parameters in Table 2. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The space group was uniquely assigned as $P2_1/c$ on the basis of the systematic absences, and the correctness of this choice was confirmed by successful solution of the Patterson map, showing the ruthenium atom on a crystallographic mirror plane. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure.[27] An empirical absorption correction was applied by using the program DIFABS following isotropic refinement. Anisotropic refinement of all non-hydrogen atoms allowed the use of a difference Fourier map for the location of the hydrogen atoms, the coordinates of which were subsequently idealized. Final anisotropic refinement was carried out on all non-hydrogen atoms with both the positional and thermal parameters "riding" on the atom to which they were attached. The hydride ligand was located in the final difference map and was refined isotropically in the final model. Selected distances and angles are given in Table 3.

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Supplementary Material Available: A textual presentation of the synthetic details and characterization data for the isocyanides used in this study and tables of crystallographic data, bond distances and angles, fractional atomic coordinates, and anisotropic thermal parameters (39 pages). Ordering information is given on any current masthead page.