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Isonitrile Insertion into the Ru−O Bond and Migratory C−C Bond Formation. Novel Organoruthenium Imidic Ester and Acyl Species

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Organometallics of type [Ru(C_6H_2O-2-CHNHC_6H_4R-3-Me-5)(PPh_3)$_2$(CO)(Cl)], **3** (R = H, Me, OMe, Cl), incorporating a four-membered C,O chelate ring smoothly react with CNBu^t in benzene solution affording the yellow-colored organoruthenium imidic ester hydrochloride system [Ru(C_6H_2OCN(Bu^t)HCl-2-CHNC_6H_4R-3-Me-5)(PPh_3)$_2$(CO)(CNBu^t)], **4**, in which a five-membered C,C chelate ring is present. While stable in the solid state, **4** is spontaneously reactive in solution, furnishing the red-colored chelate [Ru(C_6H_2(CO-1)O-2-CHNHC_6H_4R-3-Me-5)(PPh_3)$_2$(CNBu^t)(Cl)], **5**, incorporating five-membered acyl-phenolato C,O chelation. Chloride elimination from **5** by excess CNBu^t furnishes [Ru(C_6H_2(CO-1)O-2-CHNHC_6H_4R-3-Me-5)(PPh_3)$_2$(CNBu^t)$_2$]Cl, [**6**]Cl. Characteristic spectral features of the families are reported. A notable electrochemical feature is that the Ru(III)/Ru(II) reduction potential increases with increasing number of carbon atoms in the coordination sphere: $\mathbf{5} < \mathbf{6}^+ < \mathbf{4}$. The X-ray structures of **4**(Me), **5**(H), and [**6**(Me)]Cl·2CH_2Cl_2 are reported. The equatorial coordination planes are RuC_4, RuC_2OCl, and RuC_3O, respectively, the axis being uniformly defined by the *trans* RuP_2 fragment. Both **5**(H) and **6**(Me)$^+$ display iminium-phenolato N−H···O hydrogen bonding, while in **4**(Me), N−H···Cl and C−H···O hydrogen bondings are present. In the transformation $\mathbf{3} \rightarrow \mathbf{4}$, one CNBu^t molecule displaces the chloride ligand and another inserts into the Ru−O bond, generating a chelated imidic ester function. In **4**(Me) the Ru−CO bond (1.891(8) Å) lying *trans* to the imidic ester carbon is ~0.1 Å longer than that in the precursor complex **3**(Me). The Ru−C(aryl) distance is also longer in **4**(Me) by 0.04 Å. Thus both the bonds are activated by isonitrile insertion and the transformation $\mathbf{4} \rightarrow \mathbf{5}$ occurs spontaneously with C−C bond formation via aryl migration attended with isonitrile elimination, the reaction following first-order kinetics. The activation parameters determined for the **4**(Cl) → **5**(Cl) reaction are $\Delta H^{\ddagger}$, 18.72(1.00) kcal mol^{-1}, and $\Delta S^{\ddagger}$, −17.89(3.20) eu, implying that the transition state is ordered but with an excess of net bond breaking over net bond formation. Logarithmic rate constants are found to vary linearly with the Hammett constant of the R substituent, consistent with nucleophilic aryl migration.

Introduction

The insertion of unsaturated moieties into metal−ligand bonds is an important reaction type in chemistry.[1] In the particular case of the isonitrile function, insertion was first observed in an organometallic nickel(II) system.[2] Isonitriles are now recognized as potent reagents, more reactive than the isoelectronic CO molecule, and their insertion chemistry spans several metal−ligand bond types including M−H,[3] M−C,[4] M−N,[5] M−O,[6] M−P,[7] and M−S.[8] In this work we explore the reactivity of the isonitrile function toward the four-membered metallacycle **1**.[9] Several factors encouraged us to do so. First, the alkyne function, −C≡C−, which is generally less reactive than C≡N−, has been shown to undergo facile insertion into the Ru−C bond of **1**,

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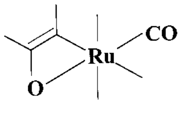
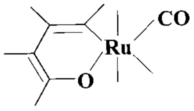
furnishing the six-membered metallacycle **2**.[10] Second, with two available reactive sites, Ru−O and Ru−C, **1** has the potential of displaying a rich insertion chemistry. Third, authentic instances of isonitrile insertion into Ru−ligand bonds are sparse.[11]



1



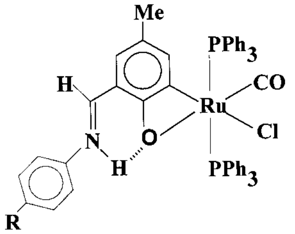
2

The metallacycle **1** has indeed been found to react smoothly with *tert*-butyl isonitrile ($CNBu^t$), which is found to insert exclusively into the Ru−O bond and also to displace a halide ligand present in the coordination sphere. The imidic ester organometallics so formed are themselve reactive and undergo spontaneous C−C bond formation via aryl migration, leading to acylruthenium species which include one or two isonitrile ligands in the coordination sphere. The variable-temperature rates and thermodynamics of the transformation are scrutinized. The new organometallics have been characterized.

Results and Discussion

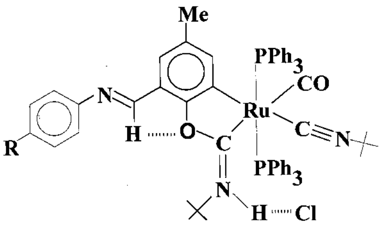
A. Synthetic Studies. a. Organoruthenium Imidic Ester Hydrochlorides.

The substrates incorporating metallacycle **1** used in the present work are of the type $Ru(RL^1)(PPh_3)_2(CO)Cl$, **3**.[9] The R groups used are H, Me, OMe, and Cl. Specific compounds will be identified as **3**(R). Thus **3**(Me) means **3** with R = Me. This identification protocol will be followed also for the other organometallics reported in this work.



$Ru(RL^1)(PPh_3)_2(CO)Cl$

3



$Ru(RL^2Cl)(PPh_3)_2(CO)(CNBu^t)$

4

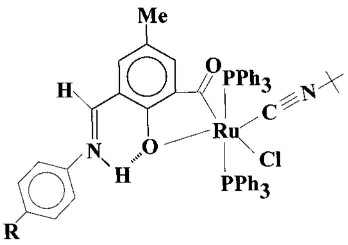
Upon reacting **3** with $CNBu^t$ in benzene solution, a rapid color reaction (violet to yellow) occurs and from the solution crystalline yellow species of type $Ru(RL^2Cl)(PPh_3)_2(CO)(CNBu^t)$, **4**, are isolated in excellent yields. In the reaction, eq 1,

$$\mathbf{3} + 2CNBu^t \rightarrow \mathbf{4} \tag{1}$$

one isocyanide molecule inserts into the Ru−O bond and the other displaces the chloride ligand. The latter, however, remains hydrogen bonded within the structure. In effect an imidic ester hydrochloride,[12] RL^2Cl, chelated to the metal at the imidic and aryl carbanionic sites is produced.

$$\mathbf{4} \xrightarrow{k} \mathbf{5} + CNBu^t \tag{2}$$

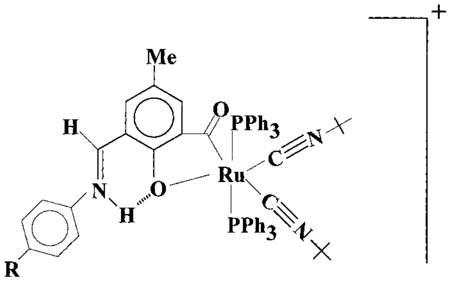
b. An Acyl Ruthenium Family. The imidic ester complexes of type **4** are stable in the solid state, but in benzene solution they undergo a spontaneous transformation, eq 2, furnishing the red-colored acyl organometallics of type $Ru(RL^3)(PPh_3)_2(CNBu^t)Cl$, **5**. The formation of the coordinated acyl function is attended with isonitrile elimination, regenerating the Ru−O(phenolato) and the Ru−Cl bonds and the hydrogen-bonded iminium-phenolato function.



$Ru(RL^3)(PPh_3)_2(CNBu^t)Cl$

5

In benzene solution **5** reacts further with $CNBu^t$, if available in excess, furnishing the orange-colored bis(isonitrile) acylruthenium cation of type $[Ru(RL^4)(PPh_3)_2(CNBu^t)_2]^+$, $\mathbf{6}^+$, eq 3, isolated as the chloride salt. It is the stable end product of the reaction between **3** and



$[Ru(RL^4)(PPh_3)_2(CNBu^t)_2]^+$

$\mathbf{6}^+$

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excess $CNBu^t$ and is directly accessible from **3** and **4** as well.

$$\mathbf{5} + CNBu^t \rightarrow \mathbf{6}^+ + Cl^- \qquad (3)$$

B. Characterization. All the organometallics reported here are diamagnetic, corresponding to t_{2g}^6 metal configuration. In acetone solution, [**6**]Cl acts as a 1:1 electrolyte with Λ_M in the range 114−130 Ω^{-1} cm^2 mol^{-1}. On the other hand **5** is a nonconductor, while **4** is very weakly conducting ($\Lambda_M < 20\ \Omega^{-1}$ cm^2 mol^{-1}), implying the presence of strong N−H···Cl association even in acetone solution.

a. Spectra. An allowed band near 500 nm due to the $t_{2g} \rightarrow \pi^*$(azomethine) charge transfer transition is diagnostic of the coordinated iminium-phenolato function of **3**.[9,10] This function is also present in **5** and **6**$^+$, and here the MLCT band is observed in the range 500−540 nm. This band is expectedly absent in the yellow-colored imidic ester species **4**, where the lowest energy band occurs only near 380 nm. The characteristic spectral difference between **4** and **5** has been utilized to study the rate of the **4** → **5** transformation, vide infra.

Two strongly π-acidic ligands ($CNBu^t$, CO) are present in the coordination sphere of **4**, while **5** has only one ($CNBu^t$). Accordingly the C≡N stretching frequency in **4** (~2150 cm^{-1}) is significantly higher than that in **5** (2050 cm^{-1}). In **6**$^+$ two $CNBu^t$ ligands are present and two C≡N stretches occur near 2150 and 2120 cm^{-1}. The aldimine C=N stretch lies near 1580 cm^{-1} (**4**) or 1630 cm^{-1} (**5** and **6**$^+$). This shift to higher frequency in the latter species occurs because the nitrogen atom is protonated in the iminium-phenolato moiety $C{=}N^+(Ar)H\cdots O$.[9,13,14] In **4** the imidic ester C=N stretch occurs at 1600 cm^{-1}, corresponding to the $C{=}N^+(Bu^t)H\cdots Cl$ moiety.

The $N^+{-}H$ moiety is present in all three systems, and its stretching vibration is observed in the 3400−3440 cm^{-1} region. In ^1H NMR the $N^+{-}H$ proton resonates near 12.3, 15.3, and 14.0 ppm in **4**, **5**, and **6**$^+$, respectively. The signal that "disappears" upon shaking with D_2O is a relatively broad singlet in **4** and **5**, but in **6**$^+$ it is split into a doublet (J ~12 Hz) due to *trans* coupling with the azomethine proton (which also has a doublet structure).

b. Metal Redox. All the organometallics are electroactive in dichloromethane solution and display a quasireversible one-electron cyclic voltammetric response assignable to the Ru(III)/Ru(II) couple. Representative Ru(III)/Ru(II) $E_{1/2}$ values are as follows: **4**(Me), 1.08 V; **5**(Me), 0.56 V; **6**(Me)$^+$, 0.93 V vs SCE. A notable feature is that the reduction potential increases with increasing number of carbon atoms in the coordination sphere (RuC_4 in **4**, RuC_3O in **6**$^+$, and RuC_2OCl in **5**). The relatively large increase between **5**(Me) and **6**(Me)$^+$ can however be attributed to the cationic nature of the latter. We note that the precursor **3**(Me) ($E_{1/2}$, 0.65 V)[9] like **5**(Me) has two coordinating carbon atoms and the two species has comparable $E_{1/2}$ values.

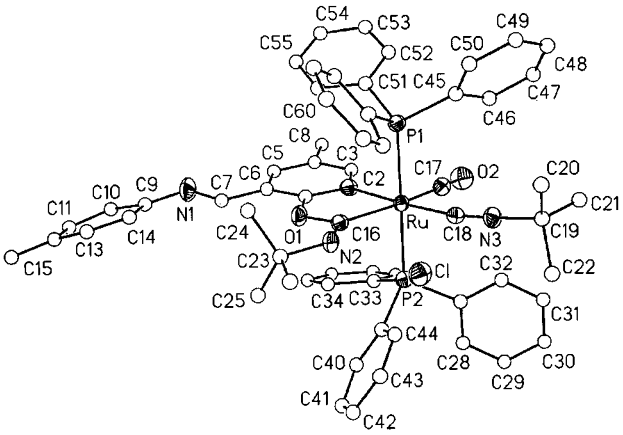

Figure 1. Perspective view and atom-labeling scheme for **4**(Me).

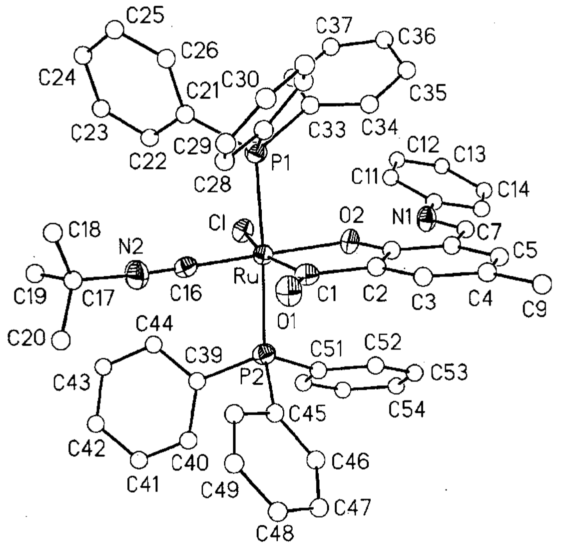

Figure 2. Perspective view and atom-labeling scheme for **5**(H).

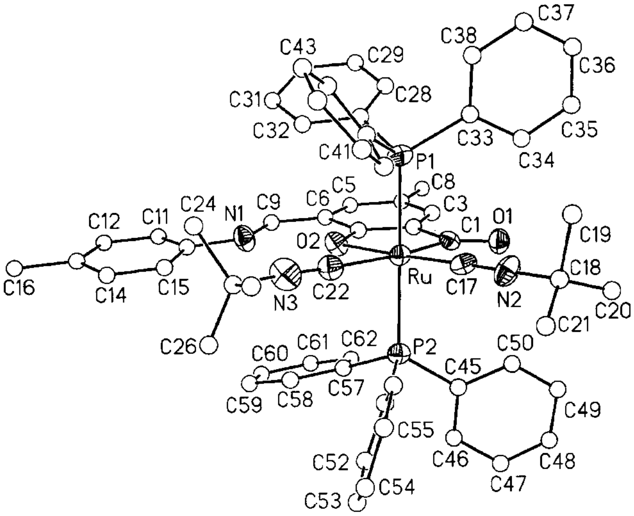

Figure 3. Perspective view and atom-labeling scheme for [**6**(Me)]$^+$.

C. Structure. The X-ray structures of three representative compounds, viz., **4**(Me), **5**(H), and [**6**(Me)]Cl·$2CH_2Cl_2$, have been determined. Molecular views are shown in Figures 1−3, and selected bond parameters are listed in Tables 1−3. To our knowledge, no other

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Table 1. Selected Bond Lengths [Å] and Angles [deg] for Ru(MeL^{2}Cl)(PPh$_3$)$_2$(CO)(CNBu^t), 4(Me)

Distances

Ru−C(2)	2.075(7)	C(7)−N(1)	1.243(10)
Ru−C(16)	2.107(7)	C(7)...O(1)	2.781(8)
Ru−C(17)	1.891(8)	C(1)−O(1)	1.397(8)
Ru−C(18)	2.047(8)	C(16)−N(2)	1.292(8)
C(18)−N(3)	1.147(8)	Ru−P(1)	2.410(2)
Ru−P(2)	2.393(2)	C(17)−O(2)	1.135(8)
C(16)−O(1)	1.356(8)	N(2)...Cl	3.327(7)

Angles

C(17)−Ru−C(18)	93.1(3)	C(2)−Ru−C(16)	78.1(3)
C(17)−Ru−P(1)	93.7(2)	C(2)−Ru−C(18)	176.3(3)
C(17)−Ru−P(2)	86.9(2)	C(16)−Ru−P(1)	90.1(2)
C(17)−Ru−C(2)	87.2(3)	C(16)−Ru−P(2)	89.1(2)
C(17)−Ru−C(16)	164.7(3)	C(16)−Ru−C(18)	101.9(3)
C(2)−Ru−P(1)	89.4(2)	C(18)−Ru−P(1)	86.9(2)
C(2)−Ru−P(2)	90.1(2)	C(18)−Ru−P(2)	93.6(2)
P(1)−Ru−P(2)	179.18(7)	O(2)−C(17)−Ru	172.6(6)
N(3)−C(18)−Ru	167.7(6)	C(1)−C(2)−Ru	113.5(5)
O(1)−C(16)−Ru	114.8(5)	N(2)−C(16)−Ru	134.6(5)
C(3)−C(2)−Ru	131.5(6)		

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Ru(HL^3)(PPh$_3$)$_2$(CNBu^t)(Cl), 5(H)

Distances

Ru−C(1)	1.979(5)	Ru−P(1)	2.357(2)
Ru−C(16)	1.882(6)	Ru−P(2)	2.365(2)
Ru−O(2)	2.122(3)	C(1)−O(1)	1.266(6)
Ru−Cl	2.635(1)	C(1)−C(2)	1.531(8)
C(7)−N(1)	1.288(7)	C(16)−N(2)	1.167(7)
N(1)⋯O(2)	2.543(8)		

Angles

C(16)−Ru−C(1)	93.4(2)	C(1)−Ru−P(1)	90.4(2)
C(16)−Ru−O(2)	176.1(2)	C(1)−Ru−P(2)	91.1(2)
C(16)−Ru−Cl	104.1(2)	C(16)−Ru−P(1)	88.4(2)
C(1)−Ru−O(2)	82.8(2)	C(16)−Ru−P(2)	88.7(2)
C(1)−Ru−Cl	162.4(2)	P(1)−Ru−P(2)	176.75(5)
O(2)−Ru−Cl	79.75(10)	O(2)−Ru−P(1)	91.02(11)
O(2)−Ru−P(2)	92.01(11)	Cl−Ru−P(1)	92.22(5)
Cl−Ru−P(2)	87.17(5)	C(8)−O(2)−Ru	112.6(3)
C(2)−C(1)−Ru	109.7(4)	N(2)−C(16)−Ru	178.2(5)

Table 3. Selected Bond Lengths [Å] and Angles [deg] for [Ru(MeL^4)(PPh$_3$)$_2$(CNBu^t)$_2$]Cl.2CH$_2$Cl$_2$, [6(Me)]Cl·2CH$_2$Cl$_2$

Distances

Ru−C(1)	2.080(12)	Ru−P(1)	2.360(3)
Ru−O(2)	2.151(8)	Ru−P(2)	2.361(3)
Ru−C(22)	2.080(14)	C(9)−N(1)	1.28(2)
Ru−C(17)	1.884(14)	C(1)−C(2)	1.51(2)
C(17)−N(2)	1.19(2)	C(22)−N(3)	1.17(2)
N(1)...O(2)	2.628(10)	C(1)−O(1)	1.216(13)

Angles

C(1)−Ru−O(2)	81.1(4)	C(1)−Ru−P(2)	92.5(3)
C(1)−Ru−C(17)	94.7(5)	O(2)−Ru−P(1)	92.0(3)
C(1)−Ru−C(22)	166.4(5)	O(2)−Ru−P(2)	90.9(2)
O(2)−Ru−C(22)	85.3(4)	C(17)−Ru−P(1)	87.3(4)
O(2)−Ru−C(17)	175.7(5)	C(17)−Ru−P(2)	90.0(4)
C(1)−Ru−P(1)	91.3(3)	C(22)−Ru−P(1)	88.8(4)
C(22)−Ru−P(2)	88.1(4)	P(1)−Ru−P(2)	175.52(13)
C(2)−C(1)−Ru	109.6(8)	C(7)−O(2)−Ru	111.4(7)
N(2)−C(17)−Ru	177.1(11)	N(3)−C(22)−Ru	172.3(12)
C(17)−Ru−C(22)	98.9(5)		

organoruthenium imidic ester structure is known, and structurally characterized acylruthenium species are rare.[15]

a. Geometrical Features. In the distorted octahedral coordination sphere the equatorial plane (mean deviation 0.02−0.05 Å) is defined by RuC$_4$, RuC$_2$OCl, and RuC$_3$O fragments in **4**(Me), **5**(H), and **6**(Me)$^+$, respectively. In each case the nearly linear *trans*-RuP$_2$ fragment defines the axis. The five-membered metalated chelate ring is planar (mean deviation 0.01−0.03 Å) in all three species. Indeed, the fragments RuMeL^2 in **4**(Me), RuHL^3 in **5**(H), and RuMeL^4 in **6**(Me)$^+$ excluding the aryl group pendant from the azomethine nitrogen (and the Bu^t methyl carbons in the case of **4**(Me)) are planar (mean deviation 0.02−0.03 Å). The pendant aryl group is inclined to this plane by 18.9°, 21.4°, and 4.8° in **4**(Me), **5**(H), and **6**(Me)$^+$, respectively. In **4**(Me) the chloride ion is displaced from the plane by 0.10 Å.

b. Bond Lengths. In **4**(Me) the Ru−CO bond (1.891(8) Å) lying *trans* to the imidic ester carbon is longer than that (1.800(7) Å) in the precursor complex **3**(Me).[9b] The Ru−C(aryl) distance is also longer in the former compound (2.075(7) vs 2.043(6) Å). The weakening of these two bonds in **4**(Me) is significant in the context of its spontaneous reactivity.

In both **5**(H) and **6**(Me)$^+$ an isonitrile ligand lies *trans* to the phenolato oxygen, and the corresponding Ru−CNBu^t distances are virtually equal in these two compounds, 1.882(6) and 1.884(14) Å, respectively. In **6**(Me)$^+$ the second isonitrile molecule lies *trans* to the acyl group, and here the Ru−CNBu^t bond is lengthened to 2.080(14) Å. The corresponding position in **5**(H) is occupied by the chloride ligand, and a relatively long Ru−Cl distance, 2.635(1) Å, is observed. These findings are consistent with the strong *trans* influence[16] of the metalated acyl group. The Ru−C(acyl) distance is lengthened by 0.1 Å as the *trans* ligand changes from chloride to CNBu^t on going from **5**(H) to **6**(Me)$^+$.

c. Hydrogen Bonding. Like the **3**(Me) precursor,[9b] **5**(H) and **6**(Me)$^+$ involve phenolato coordination to the metal and incorporate the hydrogen-bonded planar six-membered zwitterionic iminium-phenolato ring, the N⋯O distance being 2.543(8) and 2.628(10) Å, respectively; the distance in **3**(Me) is 2.665(12) Å.[9b] In **4**(Me) the iminium proton is shifted to the imidic ester nitrogen and N−H⋯Cl hydrogen bonding is established, the N2⋯Cl distance being 3.327(7) Å. The planarity of the $O_1C_1C_6C_7N_1$ fragment and the rotameric conformation of the aldimine fragment are believed to be due to the presence of C−H⋯O hydrogen bonding in the five-membered imine-ester ring. The C7⋯O distance of 2.781(8) Å provides ample opportunity for such bonding.[16,17]

D. Nature of Reactions. a. Isonitrile Insertion into the Ru−O Bond. The Ru−O bond in **3**(Me) has been shown[9b] to be quite long, 2.235(4) Å, and the phenolato oxygen is subject to facile displacement from the coordination sphere by anions such as carboxylate,[18a] nitrite, and nitrate[18b] as well as by coordinating solvents such as methanol. Solvolysis of the latter kind is crucial for alkyne insertion (**1** → **2**) into the Ru−C bond of **3**.[10b] In the present reaction (**3** → **4**), which occurs smoothly in a nonpolar solvent like benzene, the Ru−O bond is cleaved by the polar isonitrile reagent itself. This

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(15) Chawdhury, S. A.; Dauter, Z.; Mawby, R. J.; Reynolds, C. D.; Saunders, D. R.; Stephenson, M. *Acta Crystallogr.* **1983**, *C39*, 985.

(16) Pattanayak, S.; Chattopadhyay, S.; Ghosh, K.; Ganguly, S.; Ghosh, P.; Chakravorty, A. *Organometallics* **1999**, *18*, 1486.

(17) (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Raymo, F. M.; Bartberger, M. D.; Houk, K. N.; Stoddart, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 9264, and references therein.

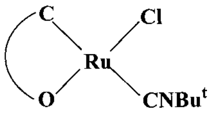
(18) (a) Ghosh, P.; Pramanik, A.; Chakravorty, A. *Organometallics* **1996**, *15*, 4147. (b) Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 64.

reagent is also well-suited to bridge the metal and the displaced phenolato oxygen, and we have insertion as in **4** instead of mere substitution.

Authentic instances of isonitrile insertion into the M−O bond are rare,[6] and to our knowledge **4** represents the first example of such an insertion into the Ru−O bond and more generally into the M−O(phenolato) bond.

b. Carbon−Carbon Bond Formation by Aryl Migration. As noted earlier, the transformation **3** → **4** weakens both the Ru−C(aryl) and the Ru−CO bonds. In effect, these bonds are activated and the spontaneous C−C bond-forming reaction **4** → **5** occurs in solution. The reaction is necessarily attended with cleavage of the imidic ester C−O bond, the liberated phenolato oxygen along with the acyl carbon completing five-membered chelation in **5**. The coordination position vacated by aryl/CO migration accommodates the incoming chloride ligand. Ironically the inserted isonitrile molecule which was at least partly responsible for the activation of **4** gets eliminated.

Upon comparing the geometrical disposition of coordinated atoms in the equatorial plane of **4** (CNBu^t *cis* to CO and *trans* to C(aryl)) with that of **5** (CNBu^t *cis* to C(acyl) and *trans* to O(phenolato)), it emerges that it is the aryl group that actually migrates in the reaction **4** → **5**. Carbonyl migration would have given rise to the *unobserved* disposition **7**, where CNBu^t lie *trans* to C(acyl) and *cis* to O(phenolato) atoms.



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c. Rates and Activation Parameters. The rate of the transformation **4**(Cl) → **5**(Cl) has been determined spectrophotometrically as a function of temperature. Spectra are characterized by well-defined isosbestic points (Figure 4). The plot of $-\ln(A_\alpha - A_t)$ vs t is highly linear, consistent with a first-order process (A_t is the absorbance at time t and A_α is the absorbance at the end of the reaction). Rate data are collected in Table 4. The activation parameters (Table 4) determined from a linear Eyring plot are $\Delta H^{\ddagger}$, 18.72(1.00) kcal mol^{-1}, and $\Delta S^{\ddagger}$, −17.89(3.20) eu. On going from **4** to **5** four covalent bonds are broken (two Ru−C, O−C, N−H in **4**) and four are formed (Ru−O, Ru−Cl, C−C, N−H in **5**). The magnitude of the total enthalpy change associated with either breaking or forming will be large (several hundred kcal). The moderately positive enthalpy of activation implies that in the transition state the balance is tilted toward bond breaking. To smoothly achieve the major changes in bonding pattern as well as other associated changes such as aldimine conformation, an ordered transition state will be required. The negative entropy of activation is consistent with this.

The rate of the reaction was also studied for **4**(H), **4**(Me), and **4**(OMe) (Table 4) at 313 K, and the log k values of the four species display a linear (correlation factor 0.9935) relationship with the Hammett constant[19] (σ_R) of the R group (Figure 5). The reaction becomes slower with increasing electron-withdrawing character of R, consistent with nucleophilic aryl migration.

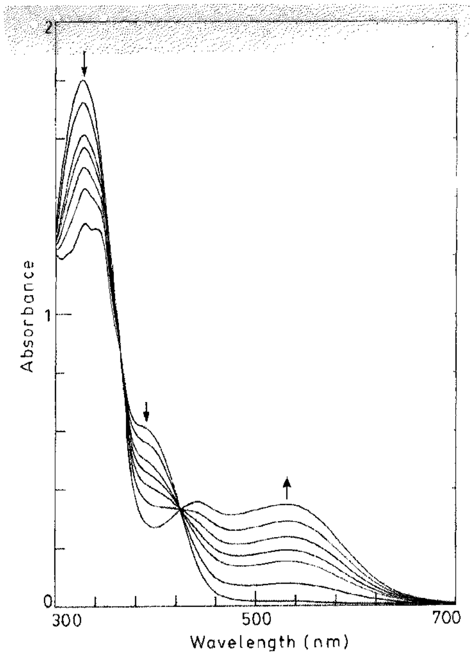


Figure 4. Spectral time evolution for the transformation of **4**(Cl) (1.53×10^{-4} M) → **5**(Cl) in benzene solution at 313 K.

Table 4. Rate Constants[a,b] and Activation Parameters[c] for the Reaction 4 → 5 in Benzene

T, K	compound	$10^3\,k$ min^{-1}
298	**4**(Cl)	1.20(1)
303	**4**(Cl)	1.78(1)
308	**4**(Cl)	3.14(1)
313	**4**(Cl)	4.95(1)
318	**4**(Cl)	9.24(1)
313	**4**(H)	5.62(1)
313	**4**(Me)	6.19(1)
313	**4**(OMe)	6.82(1)

[a] Concentration of the solute in each case was 1.89×10^{-4} M. [b] Least-squares deviation are given in parentheses. [c] $\Delta H^{\ddagger}$, 18.72(1.00) kcal mol^{-1}; $\Delta S^{\ddagger}$, −17.89(3.20) eu.

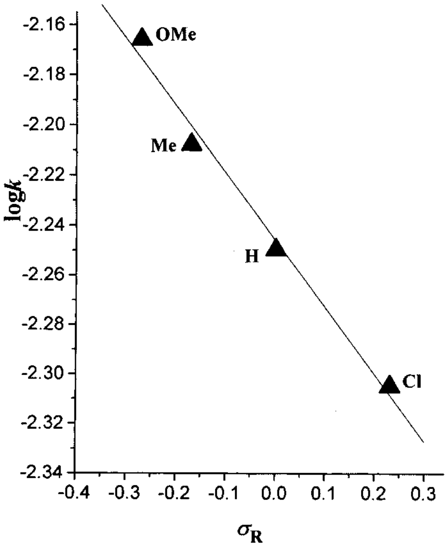
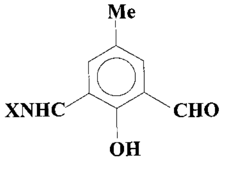


Figure 5. Plot of log k vs σ_R for the transformation of **4** → **5** in benzene solution at 313 K.

d. Synthesis of 3 Revisited. The stable acylruthenium species of this work has prompted us to revisit the synthesis of **3** from Ru(PPh$_3$)$_3$Cl$_2$ and the Schiff mono base **8** ($X = C_6H_4R$). It was postulated[9a] that oxidative aldehyde addition furnishes an acylruthenium(IV) intermediate such as **9** (Cl^- and PPh_3 ligands not shown), which undergoes aryl migration attended with C−CO bond scission and reductive proton elimination, generating the moiety **10** present in **3**. The intermediacy of **9** was indirectly supported by the isolation of stable acylrhodium(III) species[16] from **8**. Strong and elegant support is now provided by the isonitrile-promoted generation of the acylruthenium(II) species **5** from **3** via **4**. In essence, we have here a reversal of the aryl migration protocol noted above leading to C−CO bond formation.



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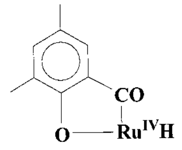

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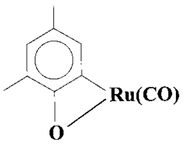

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Concluding Remarks

The main finding of this work will now be summarized. It is demonstrated that the polar $CNBu^t$ molecule undergoes facile insertion into the Ru−O bond of **3** in benzene solution, furnishing the novel organoruthenium imidic ester hydrochloride **4**. Alkynes were earlier shown to insert into the Ru−C bond of **3** but only after anchoring to the metal following solvolysis of the Ru−O bond by a polar solvent like methanol. The Ru−O bond is the prime active site of **3** toward both isonitrile and alkyne reagents. The reactions, however, take very different courses depending on the reagents.

In **4** the Ru−C(aryl) and Ru−CO bonds are in a state of activation, and spontaneous intramolecular C−C bond formation occurs via migratory insertion of the aryl group onto CO and this is attended with isonitrile elimination. The net effect is the generation of the acyl system **5**, in which the zwitterionic iminium-phenolato ring is reestablished. The activation parameters of the first-order transformation (**4** → **5**) suggest the presence of a significant degree of net order and bond breaking in the transition state.

In **5**, **6**$^+$, and **4** the coordination spheres are respectively RuC_2OClP_2, RuC_3OP_2, and RuC_4P_2, in each case the two phosphine ligands lying in *trans* positions. The Ru(III)/Ru(II) reduction potential increases with increase in the number of carbon ligands in the equatorial plane: **5** < **6**$^+$ < **4**.

Experimental Section

Materials. The compounds $Ru(PPh_3)_3Cl_2$[20] and $Ru(RL^1)(PPh_3)_2(CO)Cl$[9] were prepared as reported. Tertiary butyl isocyanide was obtained from Aldrich. The purification of dichloromethane for electrochemical work was done as described before.[21] All other chemicals and solvents were of analytical grade and were used as received.

Physical Measurements. Electronic and IR spectra were recorded with a Shimadzu UV-1601 PC spectrophotometer (thermostated cell compartment) and Perkin-Elmer 783 IR spectrometer, while ^1H NMR spectra were obtained using a Bruker 300 MHz FT NMR spectrometer (tetramethylsilane internal standard). Microanalyses (C,H,N) were done by using a Perkin-Elmer 240C elemental analyzer. Solution electrical conductivity was measured in acetone with a Philips PR 9500 bridge using a platinized electrode (cell constant of 1.05). The magnetic behavior of the complexes was examined by a PAR 155 vibrating sample magnetometer. All electrochemical measurements were performed under a nitrogen atmosphere in dichloromethane solution using a PAR 370-4 electrochemistry system. The supporting electrolyte was tetraethylammonium perchlorate, and potentials are referenced to the saturated calomel electrode (SCE) without junction correction.

Preparation of Complexes. a. Synthesis of $Ru(RL^2Cl)(PPh_3)_2(CO)(CNBu^t)$ (4). These were synthesized in excellent (~85%) yield by reacting $Ru(RL^1)(PPh_3)_2(CO)Cl$ in benzene solution with *tert*-butyl isocyanide in 1:2.5 molar ratio. Details of a representative case are given below.

$Ru(HL^2Cl)(PPh_3)_2(CO)(CNBu^t)$ (4(H)). To a stirred solution of 50 mg (0.056 mmol) of $Ru(HL^1)(PPh_3)_2(CO)Cl$ in 30 mL of benzene was added 12 mg (0.145 mmol) of $CNBu^t$. The color of the solution changed from violet to yellow within a few minutes. The yellow solution was then evaporated under reduced pressure, and the yellow solid thus obtained was washed thoroughly with hexane and finally dried in vacuo. Yield: 48 mg (81%). Anal. Calcd for $RuC_{61}H_{60}N_3O_2P_2Cl$: C, 68.75; H, 5.67; N, 3.94. Found: C, 68.69; H, 5.72; N, 3.88. ^1H NMR (C_6D_6, δ): 6.58 (s, 1H, arom), 7.20 (s, 1H, arom), 7.82 (s, 1H, $-CH{=}N^+$), 12.29 (s, 1H, $=N^+-H$), 1.86 (s, 3H, CH_3), 7.25−7.79 (m, 35H, arom), 1.29 and 1.60 (2s, 18H, $2Bu^t$). IR (KBr, cm^{-1}): $\nu(C{\equiv}O)$ 1955; $\nu(C{\equiv}N)$ 2150; $\nu(C{=}N)$ 1600, 1580; ν(N−H, hexachlorobutadiene) 3445. UV−vis (C_6H_6, λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$): 322(13544), 385(5020). $E_{1/2}$ (vs SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 1.10 V ($\Delta E_p = 130$ mV). $\Lambda_M = 19\ \Omega^{-1}\,cm^2\,mol^{-1}$.

$Ru(MeL^2Cl)(PPh_3)_2(CO)(CNBu^t)$ (4(Me)). The yield was 86%. Anal. Calcd for $RuC_{62}H_{62}N_3O_2P_2Cl$: C, 68.97; H, 5.79; N, 3.89. Found: C, 69.02; H, 5.70; N, 3.95. ^1H NMR (C_6D_6, δ): 6.57 (s, 1H, arom), 7.19 (s, 1H, arom), 7.89 (s, 1H, $-CH{=}N^+$), 12.28 (s, 1H, $=N^+-H$), 1.88 and 2.20 (2s, 6H, $2CH_3$), 7.23−7.76 (m, 34H, arom), 1.33 and 1.61 (2s, 18H, $2Bu^t$). IR (KBr, cm^{-1}): $\nu(C{\equiv}O)$ 1950; $\nu(C{\equiv}N)$ 2150; $\nu(C{=}N)$ 1600, 1580; ν(N−H, hexachlorobutadiene) 3440. UV−vis (C_6H_6, λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$): 320(11780), 370(4480). $E_{1/2}$ (vs SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 1.08 V ($\Delta E_p = 140$ mV). $\Lambda_M = 16\ \Omega^{-1}\,cm^2\,mol^{-1}$.

$Ru(MeOL^2Cl)(PPh_3)_2(CO)(CNBu^t)$ (4(OMe)). The yield was 90%. Anal. Calcd for $RuC_{62}H_{62}N_3O_3P_2Cl$: C, 67.97; H, 5.70; N, 3.84. Found: C, 67.87; H, 5.63; N, 3.89. ^1H NMR (C_6D_6, δ): 6.57 (s, 1H, arom), 7.20 (s, 1H, arom), 7.79 (s, 1H, $-CH{=}N^+$), 12.26 (s, 1H, $=N^+-H$), 1.86 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 7.25−7.74 (m, 34H, arom), 1.28 and 1.59 (2s, 18H, $2Bu^t$). IR (KBr, cm^{-1}): $\nu(C{\equiv}O)$ 1940; $\nu(C{\equiv}N)$ 2150; $\nu(C{=}N)$ 1600, 1580; ν(N−H, hexachlorobutadiene) 3440. UV−vis (C_6H_6, λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$): 325(14670), 380(5220). $E_{1/2}$ (vs SCE, CH_2Cl_2, scan rate, 50 mV s^{-1}): 0.92 V ($\Delta E_p = 180$ mV). $\Lambda_M = 14\ \Omega^{-1}\,cm^2\,mol^{-1}$.

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(19) (a) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970. (b) Finar, I. L. *Organic Chemistry*, Vol. 1: Fundamental Principles, 6th ed.; ELBS, Longman Group: Essex, England, 1990; p 605.

(20) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

(21) Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; ELBS and Longman Group: Harlow, England, 1965; p 176.

Table 5. Crystal, Data Collection, and Refinement Parameters for 4(Me), 5(H), and [6(Me)]Cl·2CH$_2$Cl$_2$

	4(Me)	**5**(H)	[**6**(Me)]Cl.2CH$_2$Cl$_2$
mol formula	$C_{62}H_{62}ClN_3O_2P_2Ru$	$C_{56}H_{51}ClN_2O_2P_2Ru$	$C_{64}H_{66}Cl_5N_3O_2P_2Ru$
mol wt	1079.61	982.45	1249.46
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a, Å	17.183(11)	16.028(5)	14.902(5)
b, Å	15.182(7)	14.445(3)	20.570(7)
c, Å	22.861(13)	21.263(7)	21.407(7)
β, deg	111.64(5)	92.18(3)	
V, Å^3	5544(5)	4919(2)	6562(4)
Z	4	4	4
λ, Å	0.71073	0.71073	0.71073
μ, cm^{-1}	4.34	4.81	5.33
D_{calcd}, g cm^{-3}	1.294	1.328	1.265
R^a, w$R2^b$ [$I > 2\sigma(I)$]	4.99, 12.87	5.08, 14.66	6.62, 16.39

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$.

Ru(ClL^{2}Cl)(PPh$_3$)$_2$(CO)(CNBu^t) (4(Cl)). It was obtained in 84% yield. Anal. Calcd for $RuC_{61}H_{59}N_3O_2P_2Cl_2$: C, 66.60; H, 5.41; N, 3.82. Found: C, 66.68; H, 5.45; N, 3.78. ^{1}H NMR (C_6D_6, δ): 6.57 (s, 1H, arom), 7.20 (s, 1H, arom), 7.79 (s, 1H, $-CH{=}N^+$), 12.29 (s, 1H, $=N^+-H$), 1.86 (s, 3H, CH$_3$), 7.25−7.75 (m, 34H, arom), 1.28 and 1.59 (2s, 18H, 2Bu^t). IR (KBr, cm^{-1}): ν(C≡O) 1940; ν(C≡N) 2140; ν(C=N) 1590, 1570; ν(N−H, hexachlorobutadiene) 3440. UV−vis (C_6H_6, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 328(12940), 380(4730). $E_{1/2}$ (vs SCE, CH$_2$Cl$_2$, scan rate, 50 mV s^{-1}): 1.14 V (ΔE_p = 190 mV). Λ_M = 23 Ω^{-1} cm^2 mol^{-1}.

b. Synthesis of Ru(RL^3)(PPh$_3$)$_2$(CNBu^t)(Cl) (5). These were synthesized in excellent yield (~80%) by stirring a benzene solution of **4** for 12 h. Details of a representative case are given below.

Ru(HL^3)(PPh$_3$)$_2$(CNBu^t)(Cl) (5(H)). A solution of 50 mg (0.047 mmol) of Ru(HL^{2}Cl)(PPh$_3$)$_2$(CO)(CNBu^t) in 40 mL of benzene was stirred for 12 h at room temperature (25 °C). The solution, whose color changed from yellow to red, was evaporated under reduced pressure, and the red crystalline solid thus obtained was washed with hexane and dried in vacuo. Yield: 36 mg (78%). Anal. Calcd for $RuC_{56}H_{51}O_2P_2N_2Cl$: C, 68.46; H, 5.23; N, 2.85. Found: C, 68.51; H, 5.19; N, 2.91. ^{1}H NMR (CDCl$_3$, δ): 6.58 (s, 1H, arom), 7.03 (s, 1H, arom), 7.84 (s, 1H, $-CH{=}N^+$), 15.23 (s, 1H, $=N^+-H$), 2.09 (s, 3H, CH$_3$), 7.10−7.78 (m, 35H, arom), 1.23(s, 9H, Bu^t). IR (KBr, cm^{-1}): ν(C≡N) 2050; ν(C=N) 1620; ν(N−H, hexachlorobutadiene) 3420. UV−vis (C_6H_6, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 340(9079), 424(2659), 517(5183). $E_{1/2}$ (vs SCE, CH$_2$Cl$_2$, scan rate, 50 mV s^{-1}): 0.55 V (ΔE_p = 210 mV).

Ru(MeL^3)(PPh$_3$)$_2$(CNBu^t)(Cl) (5(Me)). The yield was 80%. Anal. Calcd for $RuC_{57}H_{53}O_2P_2N_2Cl$: C, 68.70; H, 5.36; N, 2.81. Found: C, 68.65; H, 5.40; N, 2.78. ^{1}H NMR (CDCl$_3$, δ): 6.56 (s, 1H, arom), 7.01 (s, 1H, arom), 7.81 (s, 1H, $-CH{=}N^+$), 15.23 (s, 1H, $=N^+-H$), 2.08 and 2.39 (2s, 6H, 2CH$_3$), 7.09−7.70 (m, 34H, arom), 1.23 (s, 9H, Bu^t). IR (KBr, cm^{-1}): ν(C≡N) 2050; ν(C=N) 1625; ν(N−H, hexachlorobutadiene) 3420. UV−vis (C_6H_6, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 340(13220), 439(4678), 522(6743). $E_{1/2}$ (vs SCE, CH$_2$Cl$_2$, scan rate, 50 mV s^{-1}): 0.56 V (ΔE_p = 110 mV).

Ru(MeOL^3)(PPh$_3$)$_2$(CNBu^t)(Cl) (5(OMe)). It was obtained in 84% yield. Anal. Calcd for $RuC_{57}H_{53}O_3P_2N_2Cl$: C, 67.62; H, 5.28; N, 2.77. Found: C, 67.68; H, 5.23; N, 2.80. ^{1}H NMR (CDCl$_3$, δ): 6.56 (s, 1H, arom), 7.01 (s, 1H, arom), 15.47 (s, 1H, $=N^+-H$), 2.08 (s, 3H, CH$_3$), 7.09–7.78 (m, 35H, arom), 1.24 (s, 9H, Bu^t), 3.83 (s, 3H, OCH$_3$). IR (KBr, cm^{-1}): ν(C≡N) 2055; ν(C=N) 1625; ν(N−H, hexachlorobutadiene) 3420. UV−vis (C_6H_6, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 349(13429), 433(5233), 520(7514). $E_{1/2}$ (vs SCE, CH$_2$Cl$_2$, scan rate, 50 mV s^{-1}): 0.55 V (ΔE_p = 150 mV).

Ru(ClL^3)(PPh$_3$)$_2$(CNBu^t)(Cl) (5(Cl)). The yield was 80%. Anal. Calcd for $RuC_{56}H_{50}O_2P_2N_2Cl_2$: C, 66.14; H, 4.96; N, 2.75. Found: C, 66.09; H, 4.92; N, 2.79. ^{1}H NMR (CDCl$_3$, δ): 6.57 (s, 1H, arom), 7.05 (s, 1H, arom), 15.33 (s, 1H, $=N^+-H$), 2.08 (s, 3H, CH$_3$), 7.10−7.70 (m, 35H, arom), 1.23 (s, 9H, Bu^t). IR (KBr, cm^{-1}): ν(C≡N) 2055; ν(C=N) 1625; ν(N−H, hexachlorobutadiene) 3420. UV−vis (C_6H_6, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 343(12813), 442(4695), 532(4796). $E_{1/2}$ (vs SCE, CH$_2$Cl$_2$, scan rate, 50 mV s^{-1}): 0.57 V (ΔE_p = 140 mV).

c. Synthesis of [Ru(RL^4)(PPh$_3$)$_2$(CNBu^t)$_2$]Cl ([6]Cl). These were synthesized in excellent yield (~85%) by stirring a benzene solution of **3** with CNBu^t (mol ratio 1:5) for 16 h. Details of a representative case are given below. The [**6**]Cl species could also be prepared in similar yields by reacting **4** with CNBu^t (mol ratio 1:2.5) for 6 h or **5** with CNBu^t (mol ratio 1:2.5) for 3 h in stirred benzene solution. The general procedure for isolation is similar to what is described below.

[Ru(MeL^4)(PPh$_3$)$_2$(CNBu^t)$_2$]Cl ([6(Me)]Cl). To a stirred solution of 50 mg (0.054 mmol) of Ru(MeL^1)(PPh$_3$)$_2$(CO)Cl in 30 mL of benzene was added 22 mg (0.266 mmol) of CNBu^t. After stirring for 16 h an orange solution was obtained. It was then evaporated, and the orange crystalline solid thus obtained was filtered, washed with hexane, and dried in vacuo. Yield: 50 mg (85%). Anal. Calcd for $RuC_{62}H_{62}N_3O_2P_2Cl$: C, 68.97; H, 5.79; N, 3.89. Found: C, 68.91; H, 5.85; N, 3.82. ^{1}H NMR (CDCl$_3$, δ): 7.03 (s, 1H, arom), 9.48 (d, 1H, $-CH{=}N^+$, J_{HH} 12.0), 13.97(d, 1H, $=N^+-H$, J_{HH} 12.0), 2.05 and 2.41 (2s, 6H, 2CH$_3$), 1.29 and 1.02 (2s, 18H, 2Bu^t), 7.11−7.47 (m, 35H, arom). IR (KBr, cm^{-1}): ν(C≡N) 2110, 2150; ν(C=N) 1630; ν(N−H, hexachlorobutadiene) 3400. UV−vis (CH$_2$Cl$_2$, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 335(11300), 505(8220). $E_{1/2}$ (vs SCE, CH$_2$Cl$_2$, scan rate, 50 mV s^{-1}): 0.93 V (ΔE_p = 210 mV). Λ_M = 114 Ω^{-1} cm^2 mol^{-1}.

[Ru(MeOL^4)(PPh$_3$)$_2$(CNBu^t)$_2$]Cl ([6(MeO)]Cl). The yield was 82%. Anal. Calcd for $RuC_{62}H_{62}N_3O_3P_2Cl$: C, 67.97; H, 5.70; N, 3.84. Found: C, 67.90; H, 5.75; N, 3.79. ^{1}H NMR (CDCl$_3$, δ): 6.99 (s, 1H, arom), 9.65 (d, 1H, $-CH{=}N^+$, J_{HH} 12.0), 14.04 (d, 1H, $=N^+-H$, J_{HH} 12.0), 2.06 (s, 3H, CH$_3$) 3.89 (s, 3H, OCH$_3$), 7.06−7.64 (m, 35H, arom), 1.29 and 1.01 (2s, 18H, 2Bu^t). IR (KBr, cm^{-1}): ν(C≡N) 2120, 2160; ν(C=N) 1630; ν(N−H, hexachlorobutadiene) 3410. UV−vis (CH$_2$Cl$_2$, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 351(12840), 502(11590). $E_{1/2}$ (vs SCE, CH$_2$Cl$_2$, scan rate, 50 mV s^{-1}): 0.92 V (ΔE_p = 160 mV). Λ_M = 126 Ω^{-1} cm^2 mol^{-1}.

[Ru(ClL^4)(PPh$_3$)$_2$(CNBu^t)$_2$]Cl ([6(Cl)]Cl). The yield was 83%. Anal. Calcd for $RuC_{61}H_{59}N_3O_2P_2Cl_2$: C, 66.60; H, 5.41; N, 3.82. Found: C, 66.66; H, 5.37; N, 3.84. ^{1}H NMR (CDCl$_3$, δ): 7.03 (s, 1H, arom), 9.82 (d, 1H, $-CH{=}N^+$, J_{HH} 12.6), 13.91 (d, 1H, $=N^+-H$, J_{HH} 12.3), 2.05 (s, 3H, CH$_3$), 7.17−7.64 (m, 35H, arom). 1.30 and 1.02 (2s, 18H, 2Bu^t). IR (KBr, cm^{-1}): ν(C≡N) 2120, 2150; ν(C=N) 1630; ν(N−H, hexachlorobutadiene) 3400. UV−vis (CH$_2$Cl$_2$, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 338(13770), 507(9230). $E_{1/2}$ (vs SCE, CH$_2$Cl$_2$, scan rate, 50 mV s^{-1}): 0.98 V (ΔE_p = 240 mV). Λ_M = 132 Ω^{-1} cm^2 mol^{-1}.

Rate Measurements. Measurements were carried out in benzene solution by observing the change in absorbance at 532 nm. The k_{obs} values were calculated from a linear plot (correlation factor 0.9999) of $-\ln(A_\alpha - A_t)$ vs t, where A_α and A_t are the absorbances at the end of the reaction, 24 h, and at time *t*, respectively. The activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) were calculated from the variable-temperature rate constant, using the Eyring equation, eq 4 (K_B and *h* are the Boltzmann constant and Planck's constant, respectively). The plot of $-\ln(Kh/K_BT)$ vs $1/T$ was linear (correlation factor of 0.9957). The curve fit and all other calculations were done with the Microcal Origin, version 4.0, software package.

$$k = K_B T/h[\exp(-\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R)] \qquad (4)$$

X-ray Structure Determination. Single crystals of Ru(MeL^{2}Cl)(PPh$_3$)$_2$(CO)(CNBu^t), **4**(Me) (0.40 × 0.35 × 0.30 mm^3), were grown by slow diffusion of hexane into benzene solution at low temperature (refrigerator), and those of Ru(HL^3)(PPh$_3$)$_2$(CNBu^t)Cl, **5**(H) (0.40 × 0.35 × 0.20 mm^3), and [Ru(MeL^4)(PPh$_3$)$_2$(CNBu^t)$_2$]Cl·2CH$_2$Cl$_2$, [**6**(Me)]Cl·2CH$_2$Cl$_2$ (0.30 × 0.35 × 0.25 mm^3), by slow diffusion of hexane into dichloromethane solutions at room temperature. Cell parameters were determined by a least-squares fit of 30 machine-centered reflections ($2\theta = 14-28°$). Data were collected with the ω-scan technique in the range $3° \le 2\theta \le 45°$ for **4**(Me) and **5**(H) and $3° \le 2\theta \le 48°$ for [**6**(Me)]Cl·2CH$_2$Cl$_2$ on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Two check reflections measured after every 198 reflections showed no significant intensity reduction in any case. All data were corrected for Lorentz polarization effects, and an empirical absorption correction[22] was done on the basis of an azimuthal scan of six reflections for each crystal.

The metal atom was located in each case from Patterson maps, and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were refined by a full-matrix least-squares procedure. All non-hydrogen atoms were refined anisotropically and hydrogen atoms added at calculated positions. Calculations were performed using the SHELXTL vs 5.03[23] program package. Significant crystal data are listed in Table 5.

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Supporting Information Available: X-ray crystallography files, in CIF format, for the structure determination of **4**(Me), **5**(H), and [**6**(Me)]Cl·2CH$_2$Cl$_2$. These materials are available free of charge via the Internet at http://pubs.acs.org.

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