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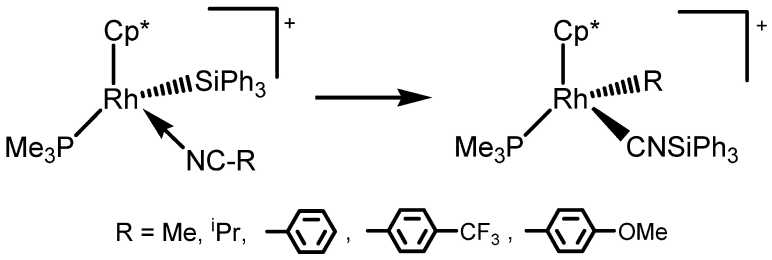

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A Mechanistic Investigation of the Carbon−Carbon Bond Cleavage of Aryl and Alkyl Cyanides Using a Cationic Rh(III) Silyl Complex

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Abstract: Cationic Rh(III) complex [Cp*(PMe$_3$)Rh(SiPh$_3$)(CH$_2$Cl$_2$)]BAr$_4'$ (**1**) activates the carbon−carbon bond of aryl and alkyl cyanides (R−CN, where R = Ph, (4-(CF$_3$)C$_6$H$_4$), (4-(OMe)C$_6$H$_4$), Me, ^{i}Pr, ^{t}Bu) to produce complexes of the general formula [Cp*(PMe$_3$)Rh(R)(CNSiPh$_3$)]BAr$_4'$. With the exception of the ^{t}BuCN case, every reaction proceeds at room temperature ($t_{1/2}$ < 1 h for aryl cyanides, $t_{1/2}$ < 14 h for alkyl cyanides). A general mechanism is presented on the basis of (1) an X-ray crystal structure determination of an intermediate isolated from the reaction involving 4-methoxybenzonitrile and (2) kinetic studies performed on the C−C bond cleavage of *para*-substituted aryl cyanides. Initial formation of an η^1-nitrile species is observed, followed by conversion to an η^2-iminoacyl intermediate, which was observed to undergo migration of R (aryl or alkyl) to rhodium to form the product [Cp*(PMe$_3$)Rh(R)(CNSiPh$_3$)]BAr$_4'$.

Introduction

The activation of carbon−carbon bonds by transition metal complexes in homogeneous media remains a challenge in the field of organometallic chemistry. Success has primarily been limited to systems in which strain relief or aromatization is a driving force, or where the C−C bond activation is promoted by chelation assistance or the presence of activating groups.[1] However, there are a handful of examples in which the unstrained C−C bonds of alkyl and aryl cyanides are cleaved by organometallic complexes. Parkin has shown that photolysis of an *ansa* molybdenocene, [Me$_2$Si(C$_5$Me$_4$)$_2$]MoH$_2$, in the presence of acetonitrile results in the reductive loss of H$_2$ and oxidative addition of the C−C bond of acetonitrile to form [Me$_2$Si(C$_5$Me$_4$)$_2$]Mo(Me)(CN).[2] Examples of the C−C cleavage of aryl cyanides are more common.[3] A recent example from Jones showed that reaction of [(dippe)NiH]$_2$ with benzonitrile leads to initial formation of an η^2-nitrile complex which then undergoes oxidative addition to form (dippe)Ni(Ph)(CN).[4] Both species were isolable and characterized by X-ray crystallography.

We have previously communicated results concerning the C−C bond activation of aryl and alkyl cyanides (R−CN, where R = Ph, (4-(CF$_3$)C$_6$H$_4$), (4-(OMe)C$_6$H$_4$), Me, ^{i}Pr, ^{t}Bu) using a cationic Rh(III) silyl complex, [Cp*(PMe$_3$)Rh(SiPh$_3$)(CH$_2$Cl$_2$)]BAr$_4'$ (**1**).[5] Herein, kinetic investigations of the cleavage of aryl cyanides are described, and an overall reaction mechanism is proposed. As further support for the proposed mechanism, the structure of an intermediate isolated from the reaction involving 4-methoxybenzonitrile has been characterized by X-ray crystallography.

Results and Discussion

Generation of [Cp*(PMe$_3$)Rh(SiPh$_3$)(CH$_2$Cl$_2$)]BAr$_4'$ (1; Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$). Rhodium silyl complex **1** was generated by addition of 1 equiv of triphenylsilane to a dichloromethane solution of [Cp*(PMe$_3$)Rh(Me)(CH$_2$Cl$_2$)]BAr$_4'$ (**2**).[6] This Si−H activation reaction occurred quantitatively as assessed by NMR spectroscopy and was complete within seconds at −80 °C.[7] Complex **1** was difficult to isolate as decomposition occurred upon removal of solvent even at low temperatures. Thus, to perform the C−C bond activation reactions described below, **1** was generated in-situ.

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[‡] University of California and Lawrence Berkeley National Laboratory.

(1) For examples, see: (a) Jun, C. H.; Moon, C. W.; Lee, D. Y. *Chem.-Eur. J.* **2002**, *8*, 2422. (b) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1975. For general reviews, see: (c) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (d) Murakami, M.; Ito, Y. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer-Verlag: New York, 1999. (e) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
(2) Churchill, D.; Shin, J. H.; Hascall, T.; Hahn, J. M.; Bridgewater, B. M.; Parkin, G. *Organometallics* **1999**, *18*, 2403.
(3) For examples, see: (a) Miller, J. A. *Tetrahedron Lett.* **2001**, 6991. (b) Abla, M.; Yamamoto, T. *J. Organomet. Chem.* **1997**, *532*, 267. (c) Favero, G.; Morvillo, A.; Turco, A. *J. Organomet. Chem.* **1983**, *241*, 251. (d) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360. (e) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543.
(4) (a) Garcia, J. J.; Jones, W. D. *Organometallics* **2000**, *19*, 5544. (b) Garcia, J. J.; Brunkan, N. M.; Jones, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 9547.
(5) Taw, F. L.; White, P. S.; Bergman, R. G.; Brookhart, M. *J. Am. Chem. Soc.* **2002**, *124*, 4192.
(6) Taw, F. L.; Mellows, H.; White, P. S.; Hollander, F. J.; Bergman, R. G.; Brookhart, M.; Heinekey, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 5100.
(7) Taw, F. L.; Bergman, R. G.; Brookhart, M., unpublished results.

10.1021/ja034468o CCC: $25.00

Scheme 1

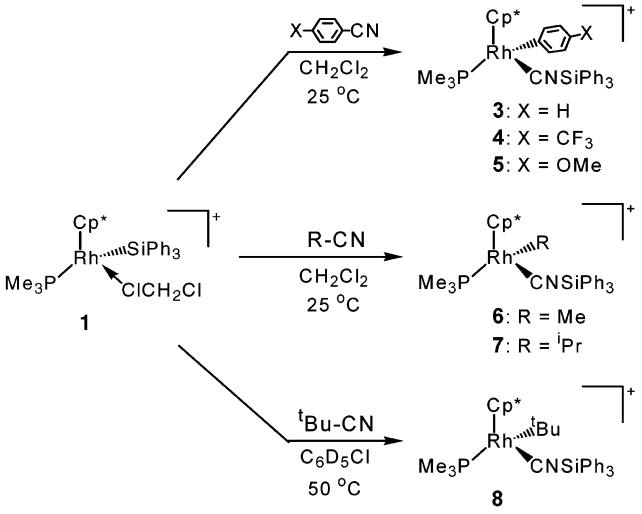


Table 1. Approximate $t_{1/2}$ Values for Activation of Aryl and Alkyl Cyanides

R–CN	$t_{1/2}$ (at 25 °C)
(4-(CF_3)C_6H_4)–CN	<5 min
Ph–CN	10 min
(4-(OMe)C_6H_4)–CN	1 h
Me–CN	3 h
^{i}Pr–CN	14 h
^{t}Bu–CN	[50% after 3 d @ 50 °C]

Carbon–Carbon Bond Activation of Alkyl and Aryl Cyanides. When 1.0 equiv of an aryl or alkyl cyanide (R–CN, where R = Ph, (4-(CF_3)C_6H_4), (4-(OMe)C_6H_4), Me, ^{i}Pr, ^{t}Bu) was added to a solution of complex **1**, C–C bond activation occurred to form the products shown in Scheme 1.[8] With the exception of the ^{t}BuCN case (see below), all of the reactions proceeded quantitatively at room temperature, as was monitored by NMR spectroscopy. As a qualitative comparison of the relative rates of reaction among the nitrile substrates studied, approximate $t_{1/2}$ values are listed in Table 1. An X-ray crystal structure of complex **7**, the product of C–C activation of isopropylcyanide, has been previously reported.[5]

Addition of 1.0 equiv of ^{t}BuCN to a solution of **1** resulted in the formation of the η^1-nitrile adduct, [Cp*(PMe_3)Rh($SiPh_3$)(NC^tBu)]BAr_4' (**9**), which was relatively stable at room temperature (trace amounts of C–C activation product **8** were observed after ~5 d). Heating a solution of **9** to 50 °C for 3 days resulted in approximately 50% conversion to [Cp*(PMe_3)Rh(^{t}Bu)($CNSiPh_3$)]BAr_4' (**8**). However, conversion to **8** was incomplete, and only a mixture of decomposition products was formed after prolonged heating. The sluggish reactivity observed in this case may be due to steric hindrance imposed by the bulky *tert*-butyl group of the substrate.

General Reaction Scheme for C–C Activation Reactions. In the C–C bond activation reactions discussed above, initial formation of an η^1-nitrile complex at low temperatures (<−40 °C) was observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.[9] Upon warming, variable amounts (depending on the nitrile substrate used) of a transient intermediate grew in as the reaction progressed and disappeared upon quantitative formation of product (Scheme 2).[10]

(8) Complete spectroscopic data have been reported for complexes **1**–**8** in the Supporting Information of ref 5.

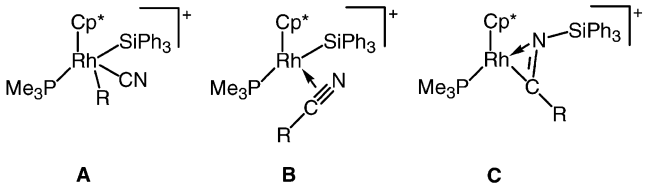
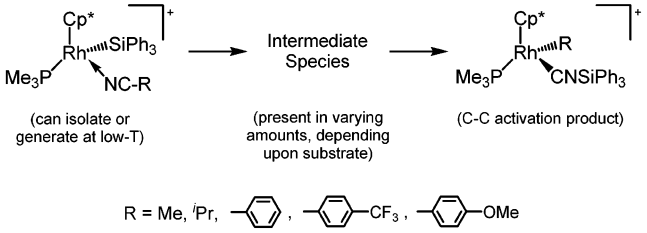


Figure 1. Possible structures for intermediate species.

Scheme 2



Possible structures for this intermediate are shown in Figure 1. The first possibility, **A**, is a Rh(V) species formed by oxidative addition of R–CN. Migration of the silyl group to nitrogen would result in the C–C activation product. Complex **B** is a Rh(III) η^2-nitrile complex which can then undergo oxidative addition of R–CN with subsequent or concerted silyl migration to form the product. Intermediate **B** is analogous to the previously reported nickel η^2-nitrile complex,[4] which was observed to undergo reversible cleavage of the C–C bond of benzonitrile. The last possibility, **C**, is a Rh(III) η^2-iminoacyl complex which can lead to the final product by migration of the R group to the Rh center.

Determination of the Structure of the Intermediate Species. Reactions involving aryl cyanides exhibited (as observed by variable-temperature NMR spectroscopy) initial formation of an η^1-nitrile complex at low temperatures (<−40 °C). Upon warming, significant build-up of the transient intermediate species was observed before complete conversion to product occurred. Thus, the η^1-nitrile complex and the intermediate could be generated at low temperatures and characterized by NMR spectroscopy. For example, addition of 1.0 equiv of 4-methoxybenzonitrile to a dichloromethane solution of **1** at −40 °C initially led to exclusive formation of the η^1-nitrile complex [Cp*(PMe_3)Rh($SiPh_3$)(NC(4-(OMe)C_6H_4))]BAr_4' (**10**; Scheme 3).

A ^{29}Si NMR spectrum of **10** (acquired at −20 °C) revealed a resonance at δ 17.52 ppm (t, $J_{Rh-Si} = J_{P-Si} = 20$ Hz), as shown in Table 2. Because the Si atom is bound directly to the Rh center, coupling to both ^{103}Rh and ^{31}P nuclei was observed. A spectrum of the product (**5**) revealed a silyl resonance at δ −19.54 ppm (s). Because the Si atom is three bonds removed from Rh, no coupling to either ^{103}Rh or ^{31}P was observed. If a solution of the η^1-nitrile complex was allowed to warm to

(9) An η^1 (versus η^2) coordination mode has been assigned to the nitrile in the [Cp*(PMe_3)Rh($SiPh_3$)(NCR)]BAr_4' complexes based upon the following observations: (a) we have obtained an X-ray crystal structure of [Cp*(PMe_3)Rh(Me)(NCMe)]BAr_4', which clearly shows that the nitrile is bound in an η^1 fashion (Taw, F. L.; Bergman, R. G.; Brookhart, M., unpublished results); (b) $^1J_{Rh-P}$ values (146–152 Hz) and $^3J_{P-C(nitrile)}$ values (6.5–7.0 Hz) for the silyl nitrile complexes are similar to the values obtained for [Cp*(PMe_3)Rh(Me)(η^1-NCMe)]BAr_4', $^1J_{Rh-P} = 151.1$ Hz, $^3J_{P-C} = 6.9$ Hz.

(10) For MeCN, ca. 1% of the intermediate species was observed in the ^{31}P-{^{1}H} NMR spectrum (δ −2.0 ppm, $J_{Rh-P} = 176.4$ Hz); for ^{i}PrCN, ca. 5% of the intermediate species was observed (δ −2.9 ppm, $J_{Rh-P} = 176.9$ Hz); for ^{t}BuCN, ca. 30% of the intermediate species was observed (δ −3.6 ppm, $J_{Rh-P} = 177.2$ Hz).

Scheme 3

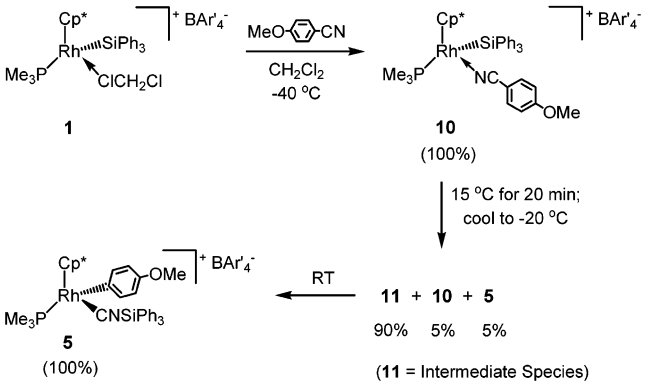


Table 2. ^{29}Si NMR Data for Complexes **5**, **10**, and **11**

complex	^{29}Si NMR data
10: η^1-nitrile	δ 17.52 (t, $J_{Rh-Si} = J_{P-Si} = 20$ Hz)
11: intermediate species	δ −21.76 (s)
5: product	δ −19.54 (s)

15 °C for 20 min, a mixture of the η^1-nitrile complex (**10**), the intermediate (**11**), and the product (**5**) was observed in an approximate ratio of 5:90:5 (by NMR spectroscopy; Scheme 3). Cooling this reaction to −20 °C to prevent further product formation and acquiring a ^{29}Si NMR spectrum allowed characterization of the intermediate. A singlet corresponding to the intermediate was observed at δ −21.76 ppm, indicating that the Si atom in the intermediate is not directly bound to the Rh center (Table 2). Thus, **C** is the only plausible choice among the three proposed intermediates. Additionally, a $^{13}C\{^1H\}$ NMR spectrum of the intermediate exhibited a resonance at 196.8 ppm (dd, $^1J_{Rh-C}$ = 12.8 Hz, $^2J_{P-C}$ = 18.6 Hz), diagnostic of the η^2-iminoacyl carbon.

X-ray Crystal Structure of [Cp*(PMe$_3$)Rh(η^2-C(4-(OMe)-C$_6$H$_4$)=N(SiPh$_3$))]BAr$_4'$ (11). X-ray quality crystals of the intermediate species, [Cp*(PMe$_3$)Rh(η^2-C(4-(OMe)C$_6$H$_4$)=N(SiPh$_3$))]BAr$_4'$ (**11**), were obtained from the reaction involving 4-methoxybenzonitrile. The ORTEP diagram of **11** is shown in Figure 2, with selected bond distances and bond angles listed in Table 3. The Rh(1)−C(2) bond distance of 1.963 Å and the Rh(1)−N(1) bond distance of 2.128 Å confirm the η^2-iminoacyl structure. η^2-Iminoacyl complexes have been previously reported;[11] however, none of these complexes exhibit reactivities similar to those of the systems described here.

Kinetic Studies of Aryl Cyanide Activation. On the basis of the evidence presented above, a general reaction mechanism may be proposed for the cleavage of aryl cyanides, as shown in Scheme 4.[12] Species **X** is produced by the addition of 1.0 equiv of aryl cyanide to a dichloromethane solution of rhodium silyl complex **1** at −40 °C. Upon warming to 0 °C, slow conversion to η^2-iminoacyl intermediate **Y** followed by C−C bond cleavage and formation of **Z** can be observed by NMR spectroscopy. The rate laws for this series of consecutive first-order reactions are as follows:

$$\frac{d[\mathbf{X}]}{dt} = -k_1[\mathbf{X}] \quad (1)$$

$$\frac{d[\mathbf{Y}]}{dt} = k_1[\mathbf{X}] - k_2[\mathbf{Y}] \quad (2)$$

$$\frac{d[\mathbf{Z}]}{dt} = k_2[\mathbf{Y}] \quad (3)$$

The concentrations of species **X**, **Y**, and **Z** as the reaction progresses may be monitored by integration of their respective signals in the $^{31}P\{^1H\}$ NMR spectra (Table 4). The concentration versus time plots of each of these species for the activation

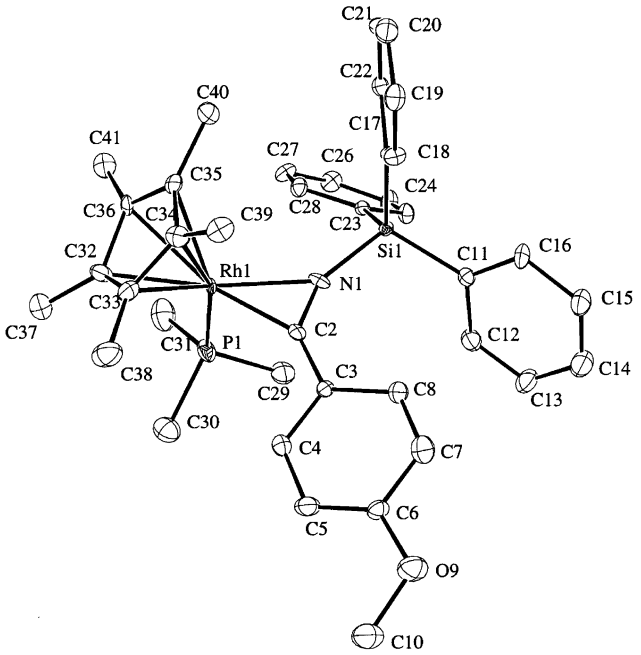
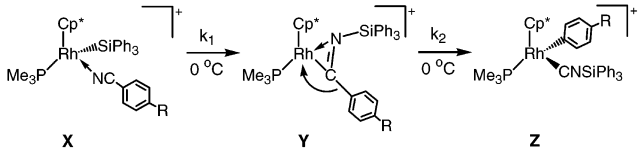


Figure 2. ORTEP diagram of [Cp*(PMe$_3$)Rh(η^2-C(4-(OMe)C$_6$H$_4$)=N(SiPh$_3$))]$^+$ (**11**, BAr$_4'^-$ counterion omitted for clarity).

Table 3. Selected Bond Distances and Bond Angles for Complex **11**

	bond distance (Å)		bond angle (deg)
Rh(1)−C(32)	2.163(12)	P(1)−Rh(1)−C(2)	90.3(3)
Rh(1)−P(1)	2.285(3)	P(1)−Rh(1)−N(1)	92.2(2)
Rh(1)−C(2)	1.963(10)	Rh(1)−C(2)−C(3)	142.1(8)
Rh(1)−N(1)	2.128(8)	Rh(1)−N(1)−Si(1)	142.6(5)
C(3)−C(2)	1.465(15)	C(3)−C(2)−N(1)	137.3(1)
C(2)−N(1)	1.255(14)	C(2)−N(1)−Si(1)	151.9(8)

Scheme 4



(11) For a few representative examples, see: (a) Shin, J. H.; Savage, W.; Murphy, V. J.; Bonanno, J. B.; Churchill, D. G.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2001**, *11*, 1732. (b) Sánchez-Nieves, J.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **2000**, *19*, 3161. (c) Wu, Z.; Diminnie, J. B.; Xue, Z. *Organometallics* **1999**, *18*, 1002. (d) Daff, P. J.; Monge, A.; Palma, P.; Poveda, M. L.; Ruiz, C.; Valerga, P.; Carmona, E. *Organometallics* **1997**, *16*, 2263. (e) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (f) Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 650. (g) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049.

(12) Kinetic analyses assume the first step is essentially irreversible ($k_{-1} < k_1$). This is clearly the case for 4-methoxybenzonitrile because the intermediate (complex **11**) builds up to over 90%. We assume this assumption is valid for the other aryl nitriles.

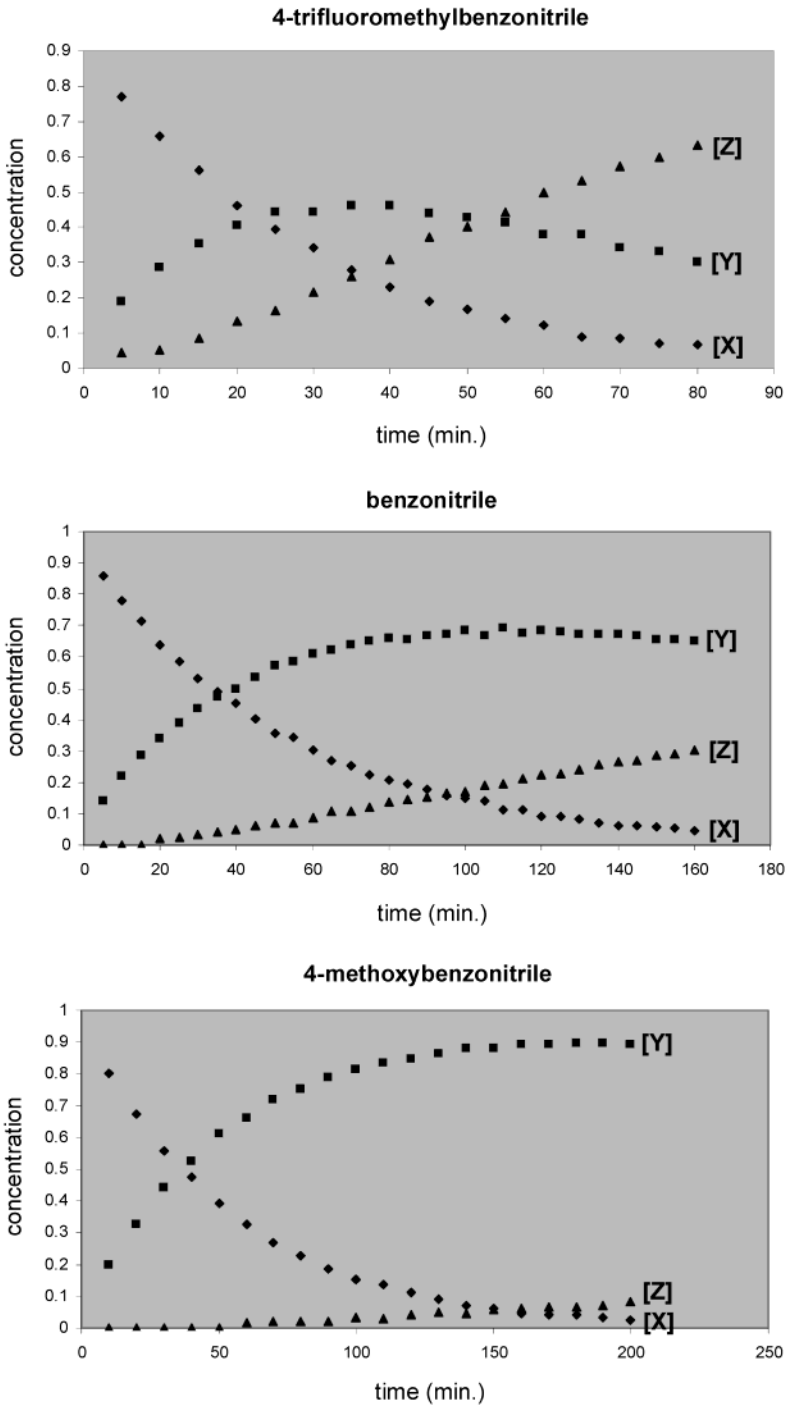


Figure 3. Concentration versus time plots for activation of aryl cyanides (at 0 °C).

Table 4. $^{31}P\{^{1}H\}$ NMR Data for Species **X**, **Y**, and **Z** Associated with Each Aryl Cyanide Studied

	X	Y	Z
4-trifluoromethyl-benzonitrile	δ −6.4 ppm $^{1}J_{Rh-P} = 147.0$ Hz	δ −2.3 ppm $^{1}J_{Rh-P} = 174.2$ Hz	δ 5.3 ppm $^{1}J_{Rh-P} = 129.9$ Hz
benzonitrile	δ −6.3 ppm $^{1}J_{Rh-P} = 146.3$ Hz	δ −2.0 ppm $^{1}J_{Rh-P} = 175.2$ Hz	δ 5.7 ppm $^{1}J_{Rh-P} = 132.6$ Hz
4-methoxy-benzonitrile	δ −6.1 ppm $^{1}J_{Rh-P} = 146.6$ Hz	δ −1.7 ppm $^{1}J_{Rh-P} = 176.0$ Hz	δ 5.9 ppm $^{1}J_{Rh-P} = 132.7$ Hz

reactions using 4-trifluoromethylbenzonitrile, benzonitrile, and 4-methoxybenzonitrile are shown in Figure 3. Analysis of these data as described below yields values of k_1 and k_2.

The following expressions[13] may be obtained by integration of the rate laws shown in eqs 1−3:

$$[\mathbf{X}] = [\mathbf{X}]_o e^{-k_1 t} \tag{4}$$

$$[\mathbf{Y}] = [\mathbf{X}]_o \frac{k_1}{k_1 - k_2} [e^{-k_2 t} - e^{-k_1 t}] \tag{5}$$

$$[\mathbf{Z}] = [\mathbf{X}]_o + \frac{[\mathbf{X}]_o}{k_1 - k_2} [k_2 e^{-k_1 t} - k_1 e^{-k_2 t}] \tag{6}$$

A plot of $-\ln[\mathbf{X}]$ versus time reveals a line whose slope is equal

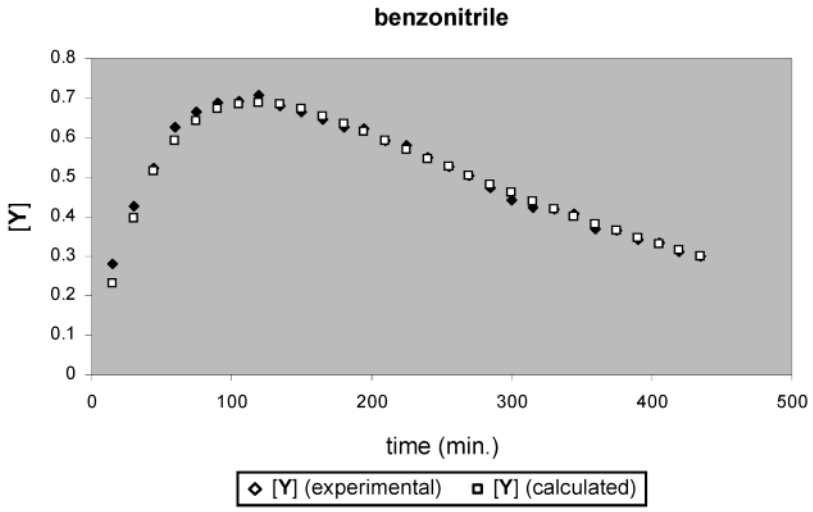


Figure 4. Concentration versus time plot comparing experimental and calculated curves for [**Y**].

Table 5. Values of k_1 for Activation of Aryl Cyanides

aryl cyanide	k_1 (at 0 °C)
4-trifluoromethylbenzonitrile	$5.6(3) \times 10^{-4}$ s^{-1}
benzonitrile	$3.1(2) \times 10^{-4}$ s^{-1}
4-methoxybenzonitrile	$3.0(2) \times 10^{-4}$ s^{-1}

Table 6. Values of k_2 for Activation of Aryl Cyanides

aryl cyanide	k_2 (at 0 °C)
4-trifluoromethylbenzonitrile	$3.8(3) \times 10^{-4}$ s^{-1}
benzonitrile	$5.6(3) \times 10^{-5}$ s^{-1}
4-methoxybenzonitrile	$8.5(1) \times 10^{-6}$ s^{-1}

to k_1 (as derived from eq 4). Table 5 lists values of k_1 determined from these plots for each aryl cyanide substrate. For the first step in which an η^1-nitrile species undergoes first-order logarithmic decay to an η^2-iminoacyl complex, the rate is slightly enhanced by the presence of an electron-withdrawing group (CF_3) in the *para* position of the aryl ring. Presumably, an electron-withdrawing substituent will render the nitrile carbon more electrophilic and thus encourage migration. However, there is essentially no difference in rate between benzonitrile and 4-methoxybenzonitrile; thus the sensitivity of k_1 to electronic effects is small.

Values of k_2 may be determined by using eq 5 or 6. Because the only unknown is k_2 for either of these equations, any standard mathematical software (such as MathCad) may be used to optimize for values of k_2 that provide the best theoretical fit for experimental curves. For example, for the reaction involving benzonitrile, a concentration versus time plot for experimental values of [**Y**] and calculated values of [**Y**] using an optimized value of k_2 is shown in Figure 4. Clearly, there is a good fit between the experimental and calculated curves, indicating a valid k_2 value.

Table 6 lists the values of k_2 associated with conversion of the η^2-iminoacyl complex to the final C−C activation product, for each aryl cyanide substrate studied. Unlike the first step of the activation mechanism, the substituent in the *para* position of the aryl ring has a large effect on the overall rate. The presence of the electron-withdrawing CF_3 group results in an increase in rate by an order of magnitude over the benzonitrile case, which in turn is an order of magnitude faster than when an electron-donating *para*-methoxy group is on the aryl ring. Destabilization of the Rh−N interaction due to the presence of an electron-withdrawing group in intermediate species **Y** as well as the formation of a stronger Rh−Ar bond in the transition state may account for enhanced rates of conversion to product. These substituent effects are consistent with previous reports that the migratory insertion in aryl carbonyl complexes is accelerated by electron-donating groups on the migrating aryl group.[14]

When the concentration of η^1-nitrile species **X** becomes zero, the value of k_2 may be determined directly from the first-order logarithmic decay of [**Y**]. As confirmation of the values of k_2 derived above, we calculated k_2 from a plot of $-\ln[\mathbf{Y}]$ versus time (measured when $[\mathbf{X}] = 0$). For the reaction involving benzonitrile, a value of 5.2×10^{-5} s^{-1} was determined for k_2, and for the reaction involving 4-methoxybenzonitrile, a value of 8.3×10^{-6} s^{-1} was determined. Accurate values for the case of 4-trifluoromethylbenzonitrile could not be obtained using this particular technique, as the concentration of species **Y** was less than 10% when species **X** was depleted from the reaction mixture.

Summary and Conclusions

We have shown that $[Cp^*(PMe_3)Rh(SiPh_3)(CH_2Cl_2)]BAr_4'$ (**1**), a cationic Rh(III) silyl complex, will activate the C−C bonds of a wide range of aryl and alkyl cyanides, including cases involving bond cleavage of a secondary or tertiary alkyl cyanide. With the exception of *tert*-butyl cyanide, facile cleavage of the C−CN bond occurred quantitatively at 25 °C. Activation of the aryl cyanides was facile, as evidenced by the short reaction times required for the reaction at room temperature. For the alkyl cyanides, an increase in the steric bulk of the R substituent led to increased reaction times.

From spectroscopic and kinetic data, a general reaction mechanism for the C−C bond cleavage of aryl and alkyl cyanides has been proposed (Scheme 5). An η^2-iminoacyl intermediate, $[Cp^*(PMe_3)Rh(\eta^2\text{-}C(4\text{-}(OMe)C_6H_4)\!=\!N(SiPh_3))]$-

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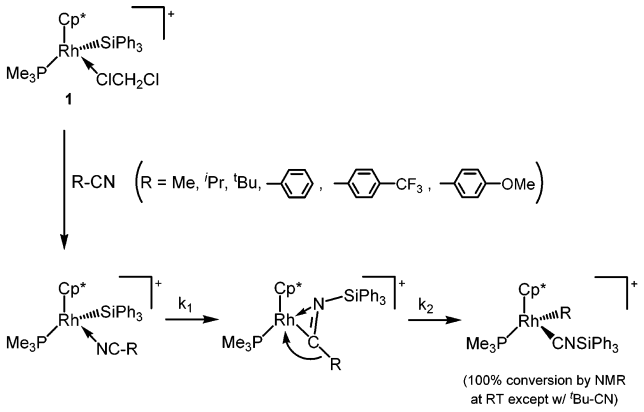
Scheme 5



BAr_4' (**11**), isolated from the activation reaction involving 4-methoxybenzonitrile, has been characterized by NMR spectroscopy and X-ray diffraction. Additionally, mechanistic studies of the activation of 4-trifluoromethylbenzonitrile, benzonitrile, and 4-methoxybenzonitrile revealed that the presence of electron-withdrawing substituents enhanced the overall rate and that the second step, consisting of the conversion of the η^2-iminoacyl species to the C−C activation product, exhibited a greater sensitivity to substituent effects, with acceleration by electron-withdrawing groups.

Experimental Section

General Considerations. Unless otherwise noted, all reactions and manipulations were performed using standard high-vacuum, Schlenk, or drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C NMR signals of the deuterated solvents, respectively. ^{31}P NMR chemical shifts were referenced to an 85% H_3PO_4 sample used as an external standard. ^{29}Si NMR chemical shifts were referenced to an external standard of TMS.

Materials. All solvents were deoxygenated and dried via passage over a column of activated alumina.[15] Deuterated solvents (Cambridge Isotope Laboratories) were purified by vacuum transfer from CaH_2 and stored over 4 Å molecular sieves. $NaBAr_4'$ was purchased from Boulder Scientific and used without further purification. Triphenylsilane and all nitrile substrates were purchased from Aldrich and used without further purification. The synthesis and characterization of complexes **1**,[5] **2**,[6] and **3**−**9**[5] have been previously reported.

Spectral Data for $BAr_4'^-$. The ^{1}H and ^{13}C NMR resonances of the BAr_4' ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) counteranion in CD_2Cl_2 were essentially invariant for all cationic complexes discussed here, and its spectroscopic data are not repeated for each compound. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.73 (s, 8H, H_o), 7.57 (s, 4H, H_p). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 161.9 (q, $^1J_{C-B} = 49.8$, C_{ipso}), 135.0 (s, C_o), 129.0 (q, $^2J_{C-F} = 31.4$, C_m), 124.7 (q, $^1J_{C-F} = 272.6$, CF_3), 117.7 (s, C_p).

[Cp*(PMe$_3$)Rh(SiPh$_3$)(NC(4-(OMe)C$_6$H$_4$))]BAr$_4'$ (10). An NMR tube was charged with a CD_2Cl_2 solution of **1** (0.025 mmol) and sealed with a septum. The tube was then placed in a −40 °C bath, and a CD_2Cl_2 solution of 1.0 equiv (3.3 mg, 0.025 mmol) of 4-methoxybenzonitrile was added via syringe. Complex **10** was formed within 5 s. ^{1}H NMR (400 MHz, CD_2Cl_2, −40 °C): δ 7.60 (d, $^3J_{H-H} = 8.8$ Hz, 2H, Ar of nitrile), 7.52 (m, 6H, $SiPh_3$), 7.33 (m, 9H, $SiPh_3$), 7.03 (d, $^3J_{H-H} = 8.8$ Hz, 2H, Ar of nitrile), 3.83 (s, 3H, OMe), 1.44 (d, $^4J_{P-H} = 2.7$ Hz, 15H, Cp*), 1.11 (d, $^2J_{P-H} = 10.0$ Hz, 9H, PMe_3). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, −40 °C): δ −6.0 (d, $^1J_{Rh-P} = 145.9$ Hz, PMe_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, −40 °C): δ 164.5 (s, Ar of nitrile), 136.6 (s, $SiPh_3$), 135.8 (s, Ar of nitrile), 135.6 (s, Ar of nitrile), 134.5 (s, $SiPh_3$), 128.9 (s, $SiPh_3$), 128.1 (s, Ar of nitrile), 127.5 (s, $SiPh_3$), 103.2 (s, Cp*−Ar), 55.99 (s, OMe), 17.36 (d, $^1J_{P-C} = 31.7$ Hz, PMe_3), 9.81 (s, Cp*−Me) [the nitrile carbon was not located due to overlap with broad aryl resonances]. ^{29}Si NMR (119 MHz, CD_2Cl_2, −20 °C): δ 17.52 (t, $^1J_{Rh-Si} = {}^2J_{P-Si} = 20$ Hz, $SiPh_3$).

[Cp*(PMe$_3$)Rh(η^2-C(4-(OMe)C$_6$H$_4$)=N(SiPh$_3$))]BAr$_4'$ (11). Letting an NMR tube containing a dichloromethane solution of **10** (see above procedures) warm to 15 °C for 20 min generated a 5:90:5 mixture of **10**, **11**, and **5**, respectively. To grow X-ray quality crystals of **11**, this solution was layered with pentane and placed in a freezer (−30 °C) in the glovebox. After ~4 weeks, orange crystals of **11** were isolated in 30% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, −20 °C): δ 7.50 (br m, 15H, $SiPh_3$), 7.50 (m, 2H, *Ar*−OMe, difficult to assign−overlaps with $SiPh_3$ resonance), 6.86 (d, $^3J_{H-H} = 8.5$ Hz, 2H, *Ar*−OMe), 3.82 (s, 3H, OMe), 1.58 (d, $^4J_{P-H} = 2.6$ Hz, 15H, Cp*), 0.98 (d, $^2J_{P-H} = 9.8$ Hz, 9H, PMe_3). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, −20 °C): δ −1.3 (d, $^1J_{Rh-P} = 175.4$ Hz, PMe_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, −20 °C): δ 196.8 (dd, $^2J_{P-C} = 18.6$ Hz, $^1J_{Rh-C} = 12.8$ Hz, η^2-*C*([4-OMe]-Ph)=N($SiPh_3$)), 165.4 (s, *Ar*−OMe), 135.9 (s, $SiPh_3$), 131.8 (s, $SiPh_3$), 130.9 (s, *Ar*−OMe), 129.0 (s, *Ar*−OMe), 128.8 (s, $SiPh_3$), 115.0 (s, *Ar*−OMe), 99.04 (dd, $^2J_{P-C} = 5.1$ Hz, $^1J_{Rh-C} = 2.8$ Hz, Cp*−Ar), 54.19 (s, OMe), 15.89 (d, $^1J_{P-C} = 29.8$ Hz, PMe_3), 10.00 (s, Cp*−Me). ^{29}Si NMR (119 MHz, CD_2Cl_2, −20 °C): δ −21.76 (s, $SiPh_3$).

Kinetic Studies. The following general procedures were used for kinetic studies of the C−C bond activation reactions involving each of the aryl cyanide substrates (4-trifluoromethylbenzonitrile, benzonitrile, and 4-methoxybenzonitrile): An NMR tube was charged with a CD_2Cl_2 solution of **1** (0.025 mmol) and sealed with a septum. The tube was then placed in a −78 °C bath, and a CD_2Cl_2 solution of 1.0 equiv of the appropriate nitrile was added via syringe. To monitor the activation reaction by NMR spectroscopy, the NMR tube was placed in the NMR probe at −20 °C. The probe temperature was then set to 0 °C, and the time at which this temperature was achieved was considered to be $t = 0$. Spectra were obtained at regular intervals (5, 10, 15, or 60 min), and integration of ^{31}P{^{1}H} NMR signals for each species provided their relative concentrations. See the Supporting Information for full details on these calculations.

Crystallographic Studies. Crystallographic studies were performed by Dr. Peter S. White at the University of North Carolina, Chapel Hill, Single-Crystal X-ray Facility. For complex **11**, data were collected at −100 °C on a Bruker SMART diffractometer, using the ω scan mode. Crystallographic data and collection parameters are reported in the Supporting Information. All computations were performed using the NRCVAX suite of programs.[16]

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Supporting Information Available: Details of the kinetic studies performed and crystallographic data for complex **11** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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