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Published on Web 03/28/2002

Carbon−Carbon Bond Activation of R−CN (R = Me, Ar, ^{i}Pr, ^{t}Bu) Using a Cationic Rh(III) Complex

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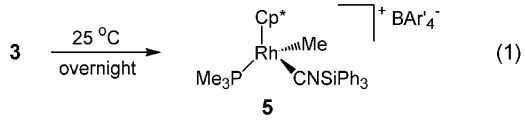
Received January 2, 2002

Activation of carbon−carbon bonds by 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 directing or activating groups.[2] We report here the C−C bond activation of R−CN (R = Me, Ph, (4-CF_3)Ph, (4-MeO)Ph, ^{i}Pr, ^{t}Bu) using a cationic Rh(III) complex.

Addition of 1.0 equiv of Ph_3SiH to the previously reported complex $[Cp^*(PMe_3)Rh(Me)(CH_2Cl_2)]^+BAr'_4{}^-$ (**1,** Ar′ = 3,5-$C_6H_3(CF_3)_2$) resulted in release of methane and quantitative formation of $[Cp^*(PMe_3)Rh(SiPh_3)(CH_2Cl_2)]^+BAr'_4{}^-$ (**2**, Scheme 1).[3] At room temperature, this reaction was complete within seconds and is analogous to the Si−H activation reaction reported by Bergman for the corresponding Ir(III) system.[4] Addition of 1.0 equiv of MeCN to **2** caused immediate displacement of dichloromethane to form the η^1-nitrile adduct $[Cp^*(PMe_3)Rh(SiPh_3)(NCMe)]^+BAr'_4{}^-$ (**3**). Alternately, addition of MeCN to **1** resulted in formation of $[Cp^*(PMe_3)Rh(Me)(NCMe)]^+BAr'_4{}^-$ (**4**). Subsequent addition of Ph_3SiH to **4** resulted in Si−H activation and release of methane to form **3** (Scheme 1).

Complex **2** is difficult to isolate as decomposition occurred upon removal of solvent even at −40 °C. However, the η^1-nitrile complex (**3**) can be isolated as a thermally sensitive, orange solid. In solution, **3** is stable below −20 °C for prolonged periods of time. However, upon standing in solution at room temperature overnight, complex **3** converted quantitatively to another product which we have characterized as the C−C activation product, $[Cp^*(PMe_3)Rh(Me)(CNSiPh_3)]^+BAr'_4{}^-$ (**5,** eq 1).



(1)

5

Complex **5** exhibited in the ^{1}H NMR spectrum resonances attributable to Cp*, PMe_3, $SiPh_3$, and Me moieties. Assignment of these resonances was supported by $^{13}C\{^1H\}$ NMR data.[5] Of note is the appearance of a signal at δ 173.4 ppm (dd, $^1J_{Rh-C}$ = 23.1 Hz, $^2J_{P-C}$ = 65.7 Hz),which is diagnostic of the isonitrile carbon. An alternate structure for **5** is the Rh(V) species $[Cp^*(PMe_3)Rh(SiPh_3)(Me)(CN)]^+BAr'_4{}^-$ resulting from direct oxidative addition of Me-CN. However, this possibility was ruled out by the ^{29}Si NMR spectrum of **5** which revealed a singlet at −17.95 ppm, indicating that $SiPh_3$ is not directly bound to the Rh center. Use of CD_3CN instead of CH_3CN resulted in exclusive formation of $[Cp^*(PMe_3)Rh(CD_3)(CNSiPh_3)]^+BAr'_4{}^-$.

In light of these results, we examined other nitrile substrates to determine the scope of this C−C activation reaction. Since complex

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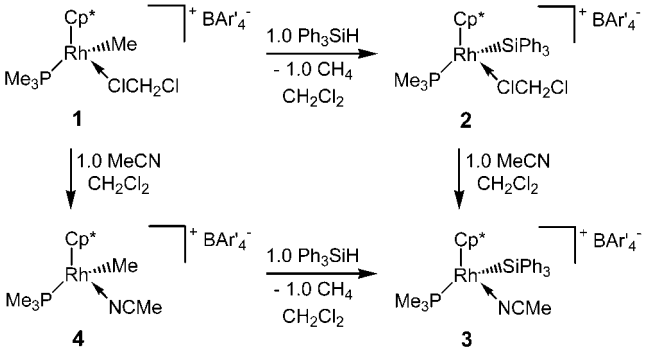
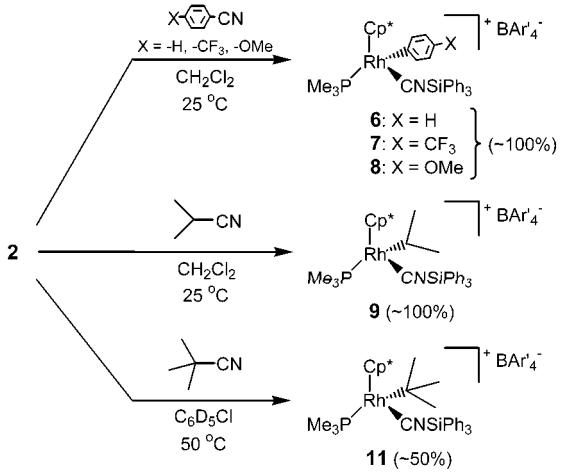
Scheme 1



Scheme 2



2 was not isolable, it was generated in-situ by adding 1.0 equiv of Ph_3SiH to a dichloromethane solution of **1** (as in Scheme 1). Adding 1.0 equiv of PhCN to a solution of **2** resulted in quantitative formation of $[Cp^*(PMe_3)Rh(Ph)(CNSiPh_3)]^+BAr'_4{}^-$ (**6**) within 1 h at room temperature (Scheme 2). Similarly, adding 1.0 equiv of 4-trifluoromethylbenzonitrile or 4-methoxybenzonitrile to **2** resulted in the corresponding C−C activation products (**7** and **8**, Scheme 2). Complete conversion to complex **7** occurred within 15 min, and complete conversion to **8** occurred within 4 h.

Addition of 1.0 equiv of ^{i}PrCN to a solution of **2** also resulted in formation of the C−C activation product, $[Cp^*(PMe_3)Rh(^{i}Pr)(CNSiPh_3)]^+BAr'_4{}^-$ (**9,** Scheme 2). This reaction was complete within 2.5 days at room temperature. We were able to grow yellow-orange crystals of **9** in 75% isolated yield (quantitative yield by NMR). The X-ray crystal structure of **9** is shown in Figure 1.[6] This structure confirmed the Rh−C−N−Si bond linkage and that cleavage of the ^{i}Pr−CN bond occurred.

10.1021/ja0255094 CCC: $22.00

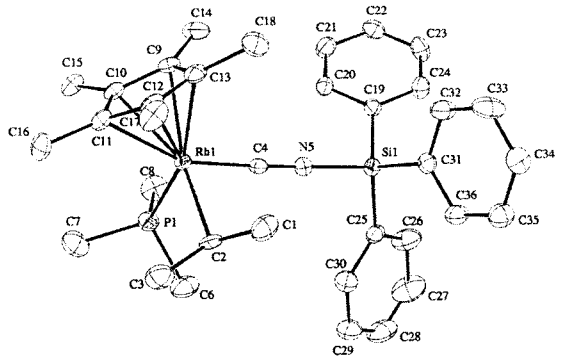


Figure 1. ORTEP diagram of $[Cp^*(PMe_3)Rh(^iPr)(CNSiPh_3)]^+$ (**9**).

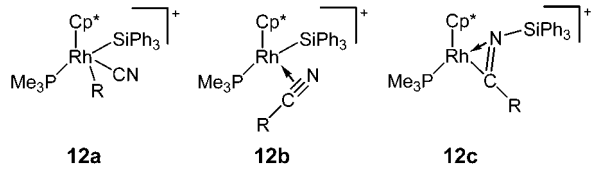


Figure 2. Possible structures for intermediate.

Addition of 1.0 equiv of ^{t}BuCN to a solution of **2** resulted in immediate formation of the η^1-nitrile adduct $[Cp^*(PMe_3)Rh(SiPh_3)(NC^tBu)]^+BAr'_4{}^-$ (**10**). Complex **10** is relatively stable, and small amounts of the C−C activation product were observed only after several days at room temperature. Heating a solution of **10** to 50 °C for 3 days resulted in approximately 50% conversion to $[Cp^*(PMe_3)Rh(^tBu)(CNSiPh_3)]^+BAr'_4{}^-$ (**11,** Scheme 2). However, conversion to **11** was incomplete and only a mixture of decomposition products were formed after prolonged heating.

In the course of our studies on the C−C activation reactions discussed above, we observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy the appearance of variable amounts (depending on the nitrile substrate used) of a transient intermediate which grew in as the reaction progressed and disappeared upon quantitative formation of product. Possible structures for this intermediate are shown in Figure 2. The first possibility, **12a**, 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 **12b** 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. The last possibility, **12c**, is a Rh(III) η^2-iminoacyl complex which can form the final product by migration of the R group to the Rh center.

Reactions involving aryl cyanides exhibited significant build-up of the transient intermediate species before complete conversion to product. Thus, we could generate the intermediate at low temperatures and completely characterize it by NMR spectroscopy. For example, addition of 4-methoxybenzonitrile to **2** at −40 °C led to exclusive formation of the η^1-nitrile complex $[Cp^*(PMe_3)Rh(SiPh_3)(NC(4\text{-}OMe)Ph)]^+BAr'_4{}^-$ (**13**). A ^{29}Si NMR spectrum of **13** (at −20 °C) revealed a resonance at δ 17.52 ppm (dd, $J_{Rh-Si} = J_{P-Si} = 20$ Hz), corresponding to the silyl group. Since 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 (**8**) revealed a resonance at δ −19.54 ppm (s) corresponding to the silyl group. Since the Si atom is three bonds away from Rh, no coupling to either ^{103}Rh or ^{31}P was observed. If a solution of the η^1-nitrile complex is allowed to warm to 15 °C for 20 min, a mixture of the η^1-nitrile complex (**13**), the intermediate (**14**), and the product (**8**) is observed in an approximate ratio of 5:90:5 (by NMR). 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. Thus, **12c** is the only plausible intermediate. Precedent for this type of η^2-iminoacyl complex exists in the literature.[7] However, none of the examples exhibit reactivity similar to the system described here.

Parkin has shown that photolysis of an *ansa* molybdenocene, $[Me_2Si(C_5Me_4)_2]MoH_2$, in the presence of MeCN results in the loss of H_2 and oxidative addition of the C−C bond of MeCN to form $[Me_2Si(C_5Me_4)_2]Mo(Me)(CN)$.[8] Examples of C−C cleavage of aryl cyanides are more common.[9] A recent example from Jones showed that reaction of $[(dippe]NiH]_2$ with PhCN leads to initial formation of an η^2-nitrile complex which then undergoes oxidative addition to form (dippe)Ni(Ph)(CN).[10]

In this work we have shown that a cationic Rh(III) complex will C−C activate the bonds of a wide range of nitriles, including cases involving cleavage of a secondary or tertiary carbon center. With the exception of ^{t}BuCN, facile cleavage of the C−CN bond occurred quantitatively at 25 °C. Studies are currently underway to extend the scope and establish full mechanistic details of this reaction.

Acknowledgment. Research performed at UNC was supported by the NSF (CHE-0107810). Research performed at UCB was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098. We thank Professor Joseph L. Templeton, Dr. Peter J. Alaimo, and Dr. Olafs Daugulis for helpful discussions and Dr. Marc ter Horst for NMR technical assistance.

Supporting Information Available: Synthesis and characterization of new compounds, including all crystallographic data for complex **9** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0255094