Organometallics **2004,** *23,* 6097−6098

Oxidative Addition of Silyl Cyanides to Rhodium Porphyrin Radical: Isocyanide or Cyanide Transfer Mechanism

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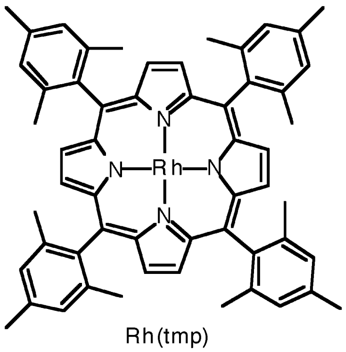
Received September 26, 2004

Summary: Rhodium porphyrin radical, coordinated with pyridine, activated the carbon−silicon bond of silyl cyanides to yield rhodium porphyrin silyls and cyanide. The reaction with Me_3SiCN exhibited second-order kinetics, rate = k_{obsd}[Rh(tmp)][Me_3SiCN], at a sufficiently high concentration of pyridine, and the mechanism was interpreted to involve a cyanide or isocyanide group transfer to rhodium radical.

Activation of silicon−carbon bonds by transition- and lanthanide-metal complexes is fundamentally interesting and industrially important with potential applications in the catalytic synthesis and modification of new organosilicon polymers (eq 1).[1] The application of this

$$2M + SiCN \rightarrow MSi + MCN \qquad (1)$$

method in organic synthesis has been reported in insertion reactions with alkynes.[2] Most reported examples of carbon−silicon bond activation involve classical oxidative addition at a metal center by a two-electron process,[3,4] electrophilic aromatic substitution,[5] and σ-bond metathesis.[6] We have recently reported that (tetramesitylporphyrinato)rhodium(II) [Rh(tmp)] (Figure 1),[7] a metal-centered radical, activates nonstrained aliphatic carbon−carbon bonds of nitroxides to yield rhodium porphyrin alkyls.[8,9] Expanding the scope of substrates, we have found that Rh(tmp) undergoes a formal carbon−silicon bond activation[10] with silyl cyanides[11,12] and now report the results of our kinetic studies in identifying a novel radical type isocyanide or cyanide transfer process.



Rh(tmp)

Figure 1.

A solution of Rh(tmp)[7,8] in benzene reacted with 10 equiv of Me_3SiCN at 110 °C for 10 h to give Rh(tmp)-$SiMe_3$[13] and Rh(tmp)CN[14] in 16 and 14% ^1H NMR yields, respectively (eq 1). The carbon−silicon bond has been activated, but the yields were rather poor.

When pyridine was added to Rh(tmp) to form the electron-rich five-coordinate complex pyRh(tmp),[15,16] the rate of carbon−silicon bond activation (CSA) was much faster. The yields of Rh(tmp)$SiMe_3$ and *trans*-pyRh-(tmp)CN also increased significantly (eq 2; Table 1, entries 1−4). The product Rh(tmp)$SiMe_3$ did not coordinate with pyridine either in solution or in the solid state after isolation, presumably due to the stronger trans effect of the silyl group.[17] The rates and yields increased slightly from 70 to 130 °C. When the sterically

$$2Rh(tmp) + RMe_2SiCN + py \xrightarrow{C_6H_6,\ N_2} Rh(tmp)SiRMe_2 + pyRh(tmp)CN \qquad (2)$$

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10.1021/om049253h CCC: $27.50

Table 1. Reaction of Silyl Cyanides with PyRh(tmp)

entry	substrate[a]	temp/°C	time	product (% yield)	
1	Me_3SiCN	70	3 h	Rh(tmp)$SiMe_3$ (71)	pyRh(tmp)CN (72)
2	Me_3SiCN	90	1 h	Rh(tmp)$SiMe_3$ (73)	pyRh(tmp)CN (70)
3	Me_3SiCN	110	1 h	Rh(tmp)$SiMe_3$ (88)	pyRh(tmp)CN (81)
4	Me_3SiCN	130	1 h	Rh(tmp)$SiMe_3$ (82)	pyRh(tmp)CN (84)
5	$^tBuMe_2SiCN$	110	1 day	Rh(tmp)Si^tBuMe_2 (18)	pyRh(tmp)CN (85)
6	$^tBuMe_2SiCN$	130	1 day	Rh(tmp)Si^tBuMe_2 (22)	pyRh(tmp)CN (80)

[a] Conditions: 10 equiv of silyl cyanide with 2 equiv of pyridine.

more hindered $^tBuMe_2SiCN$ was used, a lower yield of Rh(tmp)Si^tBuMe_2 was observed, while pyRh(tmp)CN still was isolated in high yield. Since Rh(tmp)Si^tBuMe_2 in benzene either with or without excess pyridine added was thermally stable at 110 °C for at least 1 day, its poor isolated yield is ascribed to a sterically hindered reaction.

Kinetic measurements of reaction 2 with Me_3SiCN carried out spectrally at 538 nm under the conditions 70.0 °C, initial concentrations $(3.28-9.06) \times 10^{-5}$ M Rh(tmp), $(0.61-6.21) \times 10^{-2}$ M Me_3SiCN, and $(0.01-4.80) \times 10^{-3}$ M pyridine yielded the rate law shown in eq 3. Under the conditions of the measurements with Me_3SiCN always in at least 10-fold excess, the rate becomes pseudo first order, in accord with eq 4. The rate was independent of pyridine at sufficiently high concentration ($\geq 5.0 \times 10^{-4}$ M) and exhibited saturation kinetics in pyridine. The mechanistic scheme shown in eqs 5−7 conforms to the rate law, with reaction 5 attaining a fast preequilibrium and the formal cyanide group transfer step to rhodium in reaction 6 being the rate-determining step. The rates were also measured from 60 to 90 °C.

$$\text{rate} = k'_{\text{obsd}}[\text{Rh(tmp)}]_0[\text{Me}_3\text{SiCN}] \quad (3)$$

$$= k_{\text{obsd}}[\text{Rh(tmp)}]_0 \quad (4)$$

$$\text{Rh(tmp)} + \text{py} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{pyRh(tmp)} \quad (5)$$

$$\text{pyRh(tmp)} + \text{Me}_3\text{SiCN} \underset{k_{-2}}{\overset{k_2\,(\text{rds})}{\rightleftharpoons}} \text{pyRh(tmp)CN} + \text{Me}_3\text{Si} \quad (6)$$

$$\text{Me}_3\text{Si} + \text{pyRh(tmp)} \xrightarrow{\text{k}_3} \text{Rh(tmp)SiMe}_3 + \text{py} \quad (7)$$

$$-\text{d}[\text{Me}_3\text{Si}]/\text{d}t = 0 \text{ (under steady-state conditions)}$$

$$\text{rate} = \text{d}[\text{Me}_3\text{SiRh(tmp)}]/\text{d}t = \frac{k_2K_1[\text{py}]}{1 + K_1[\text{py}]}[\text{Rh(tmp)}]_0[\text{Me}_3\text{SiCN}] \quad (8)$$

Rh(tmp) is known to coordinate with pyridine, and pyRh(tmp) has been characterized by ESR.[15] The stoichiometry and binding constants of reaction 5 were measured spectrophotometrically at $\lambda = 536$ nm from 20 to 40 °C. Analyses of the data confirmed a 1:1 adduct and yielded the binding constant at 30.0 °C; K_1 ($=k_1/k_{-1}$) $= 2.95 \times 10^4$ M^{-1}, $\Delta H_1 = -10 \pm 1$ kcal mol^{-1}, and $\Delta S_1 = -12 \pm 2$ cal mol^{-1} K^{-1}. Substitution of extrapolated values of K_1 at 60 to 90 °C in eq 8 allows the estimation of k_2. Evaluation of the activation parameters concerning k_2 from 60 to 90 °C then yielded $\Delta H_2^{\ddagger} = 13.1 \pm 1.3$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -26.3 \pm 3.7$ cal mol^{-1} K^{-1}.

A few possibilities exist for the the oxidative addition of the Si−CN bond. (1) An electron-transfer mechanism via disproportionation of pyRh(py) occurs to yield [pyRh^{III}(tmp)]$^+$ and [pyRh^{I}(tmp)]$^-$,[15,16] which may react either by an electrophilic or a nucleophilic manner, respectively, with Me_3SiCN. The pathways involving [pyRh^{III}(tmp)]$^+$ and [pyRh^{I}(tmp)]$^-$ existing in preequilibrium or being involved in the rate-controlling step are ruled out, since neither [pyRh^{III}(tmp)]$^+$ nor [pyRh^{I}(tmp)]$^-$ reacted with Me_3SiCN to yield Rh(tmp)$SiMe_3$. Therefore, pyRh(tmp) radical is the reacting species. (2) A two-electron oxidative addition process occurs with the involvement of a formal, neutral cis-silyl Rh(IV) cyanide intermediate, which then yields Rh(tmp)CN and a silyl radical. This mechanism is less preferred, as a crowded side-on cis coordination[18] of silyl cyanide to rhodium is necessary. Furthermore, this pathway requires an uncommon seven-coordinated Rh(IV)[19] organometallic species. (3) A one-electron oxidative addition occurs with the formal cyanide transfer. The mechanism is consistent with the small $\Delta H_2^{\ddagger} = 13.1$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -26.1$ cal mol^{-1} K^{-1}, typical of a bimolecular atom transfer reaction in cobalt(II) chemistry.[20] In this mechanism, SiCN can coordinate to Rh(tmp) in a linear, kinetically indistinguishable N- or C-bound form. As Me_3SiNC is also present in Me_3SiCN in small amounts and the proportion increases at elevated temperature,[21] the C-bound (i.e., isonitrile) form may be the more preferred coordination mode, in view of the reported facile reactions of MeNC and BuNC with Rh(tmp).[14,22]

In conclusion, we have discovered the novel bond activation of silyl cyanide by rhodium porphyrin metal-centered radical. The mechanism has been identified to be a bimolecular reaction with the isocyanide or cyanide group transfer to rhodium in the rate-controlling step. Bond activation by Rh(tmp) and mechanistic studies are being continued.

Acknowledgment. We thank the Research Grants Council of Hong Kong of the SAR of China for financial support (No. 400203).

Supporting Information Available: Text, tables, and figures giving experimental data for the products, kinetic studies, and derivation of rate law. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049253H

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