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Insertions of nitriles and pyridine into the Zr–Si bond of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr[Si(SiMe_3)_3]Me$

Hee-Gweon Woo and T. Don Tilley *

Chemistry Department, D-006, University of California–San Diego, La Jolla, CA 92093-0506 (U.S.A.)

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Abstract

The zirconium silyl complex $CpCp^{\star}Zr[Si(SiMe_3)_3]Me$ (**1**; $Cp = \eta^5\text{-}C_5H_5$; $Cp^{\star} = \eta^5\text{-}C_5Me_5$) reacts with nitriles RCN (R = Me, $CH{=}CH_2$, Ph) to form the azomethine derivatives $CpCp^{\star}Zr[N{=}C(R)Si(SiMe_3)_3]Me$ (**2**, R = Me; **3**, R = $CH{=}CH_2$; **4**, R = Ph). Pyridine reacts with **1** to give a 75% yield of $CpCp^{\star}Zr[NC_5H_5Si(SiMe_3)_3]Me$ (**5**), which results from 1,2-addition of the Zr–Si bond of **1** to pyridine. These reactions provide the first examples of nitrile and pyridine insertions into a transition metal–silicon bond. The related silyl complexes $Cp_2Zr[Si(SiMe_3)_3]Me$ and $CpCp^{\star}Zr[Si(SiMe_3)_3]Cl$ are much less reactive toward nitriles and pyridine.

Early transition-metal (d^0) silyl complexes have provided a number of reactivity modes that were previously unobserved in transition-metal silicon chemistry. In particular our group has explored the reactivity of d^0 metal–silicon bonds toward insertion of unsaturated substrates [1], and toward "σ-bond metathesis" processes [2]. We have observed that this reaction chemistry is influenced strongly by the nature of the d^0 metal center, and by substituents at both the metal and silicon. For example, whereas $Cp_2Zr[Si(SiMe_3)_3]Me$ ($Cp = \eta^5\text{-}C_5H_5$) undergoes insertion of CO into the Zr–Me bond, $CpCp^{\star}Zr[Si(SiMe_3)_3]Me$ (**1**, $Cp^{\star} = \eta^5\text{-}C_5Me_5$) reacts with CO via insertion into the Zr–Si bond [1c]. Here we report the first clean insertions of nitriles and pyridine into a transition metal–silicon bond, which have been observed for **1**. This insertion chemistry for **1** differs markedly from that of the closely related silyl complexes $Cp_2Zr[Si(SiMe_3)_3]X$ (X = Cl, Me) [1a] and $CpCp^{\star}Zr[Si(SiMe_3)_3]Cl$ [1c].

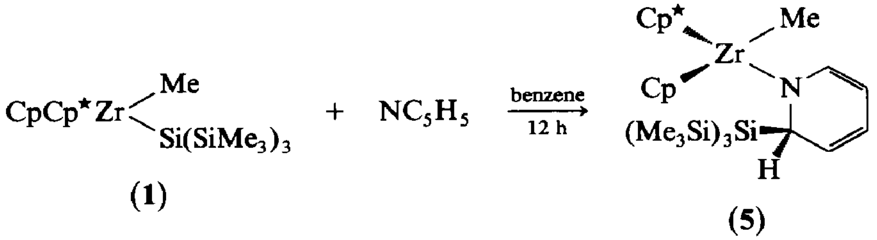
Insertion of nitriles into the Zr–Si bond of **1** [1c] occurs readily at room temperature to form the azomethine derivatives **2**–**4** in 60-78% isolated yields (eq. 1).

$$\underset{(1)}{\mathrm{CpCp^{\star}Zr[Si(SiMe_3)_3]Me}} + \mathrm{RCN} \xrightarrow[6\ \mathrm{h}]{\text{benzene}} \mathrm{CpCp^{\star}Zr[N{=}C(R)Si(SiMe_3)_3]Me} \quad \begin{array}{l}(\mathbf{2},\ \mathrm{R} = \mathrm{Me}\\ \mathbf{3},\ \mathrm{R} = \mathrm{CH{=}CH_2}\\ \mathbf{4},\ \mathrm{R} = \mathrm{Ph})\end{array} \qquad (1)$$

In each case exclusive insertion into the Zr–Si bond is indicated by the ^{1}H NMR spectrum, which contains high-field resonances assigned to the Zr–Me ligands [3*]. Complexes **2**–**4** display characteristic ν(C=N) stretching frequencies in the infrared spectra at 1555–1600 cm^{-1}. These values are somewhat lower than those found in the analogous zirconium azomethine complexes $\mathrm{Cp^{\star}_2Zr[N{=}C(H)C_6H_4Me]H}$ (1660 cm^{-1}) and $\mathrm{Cp^{\star}_2Zr[N{=}C(H)C_6H_4Me]_2}$ (1670 cm^{-1}) [4]. Silyl substitution has the same effect in lowering the ν(C=O) stretching frequencies of ketones [5].

Interestingly, no insertion of MeCN was observed for $\mathrm{Cp_2Zr[Si(SiMe_3)_3]Me}$, $\mathrm{Cp_2Zr[Si(SiMe_3)_3]Cl}$, or $\mathrm{CpCp^{\star}ZrMe_2}$, although $\mathrm{CpCp^{\star}Zr[Si(SiMe_3)_3]Cl}$ appears to react with MeCN slowly over several days to form an insertion product (as observed by ^{1}H NMR spectroscopy). These observations suggest that the greater reactivity of **1** toward nitriles may be explained by: (1) the absence of π-donor ligands, which provides a good Lewis acid center for coordination of the nitrile, and (2) weakening of the Zr–Si bond by steric repulsions between the bulky Cp* and $\mathrm{Si(SiMe_3)_3}$ ligands. Nitrile exchange between **2** and excess acrylonitrile, and between **3** or **4** and excess MeCN, was not observed even with prolonged heating at 80 °C. In contrast, exchange of nitriles was observed in the reaction of $\mathrm{Cp^{\star}_2ScNC(H)CMe_3}$ and *p*-anisonitrile [4].

When a mixture of **1** and 1.2 equivalents of pyridine in benzene is stirred for 12 h, the initial orange color of the solution is gradually replaced by an intense red. Subsequent work-up of the mixture provides deep red microcrystals of a new compound, **5**, crystallized from a toluene-pentane solvent mixture (eq. 2).



(2)

Spectroscopic and analytical data clearly characterize **5** as an adduct of **1** with pyridine [6*]. Furthermore, the NMR data show that the aromaticity of the pyridine group of **5** has been disrupted via intramolecular migration of $\mathrm{(Me_3Si)_3Si}$ to the *ortho* position of the pyridine ring. Resonances assigned to the pyridine-derived ring carbons of **5** indicate that 1,2-insertion of pyridine into the Zr–Si bond of **1** has occurred. Assignment of these resonances is based on ^{1}H-decoupling experiments, and on analysis of NMR spectra for the products of *o*-D-$\mathrm{NC_5H_4}$ and 4-picoline insertion. The NMR spectra provide evidence for the presence of only one diastereomer of **5**, which we assume to be the less sterically hindered isomer shown in eq. 2. Related transformations have been observed in reactions of

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* Reference number with asterisk indicates a note in the list of references.

$Cp^{\star}{}_2Th(\eta^4\text{-}C_4H_6)$ [7] and $Cp^{\star}Cl_2Hf[\eta^2\text{-}COSi(SiMe_3)_3]$ [1b] with pyridine, and of $Zr(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(CH_2Ph)_2$ with bipyridine [8]. Also, for comparison, the formally 12-electron silyl complexes $Cp^{\star}Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf) readily add pyridine in solution to form the adducts $Cp^{\star}Cl_2MSi(SiMe_3)_3(py)$ [9].

Compound **1** is less reactive toward substituted pyridines. Thus, no reaction was observed between **1** and 2-picoline, 3-picoline, bipyridine, 1,10-phenanthroline, or pyrazine. However, insertions of 4-picoline (16 h) and 4-(dimethylamino)pyridine (3 days) into the Zr–Si bond of **1** were observed by ^1H NMR spectroscopy. Consistent with previous results, the closely related silyl complex $Cp_2Zr[Si(SiMe_3)_3]Me$ is unreactive toward insertion of pyridine, and $CpCp^{\star}Zr[Si(SiMe_3)_3]Cl$ reacts very sluggishly with pyridine (ca. 10% reaction over 24 h, by ^1H NMR spectroscopy). Mechanistic details for this pyridine insertion reaction are presently unknown, but we note that coordination of pyridine to zirconium should activate the pyridine ring toward nucleophilic attack [10].

Finally, we have also observed that compound **1** does not react with acetylene (excess, benzene-d_6, 1 day), carbon dioxide (excess, benzene-d_6, 1 day), carbon disulfide (excess, benzene-d_6, 1 day), ethylene (100 psi, benzene, 2 days), styrene (1 equivalent, benzene-d_6, 1 day), trimethylsilylazide (1 equivalent, benzene-d_6, 1 day), or *p*-tolylisocyanate (1 equivalent, benzene-d_6, 1 day).

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3 Selected data for **2**: Yellow crystals (m.p. 151–153 °C) from diethyl ether in 65% yield. Anal. Found: C, 54.2; H, 8.82. $C_{27}H_{53}NSi_4Zr$ calcd.: C, 54.5; H, 8.97%. IR (nujol, CsI, cm^{-1}): $\nu(CN) = 1600$. ^1H NMR (benzene-d_6, 22 °C, 300 MHz): δ −0.19 (ZrMe), 0.30 ($Si(SiMe_3)_3$), 1.75 ($Cp^{\star}$), 1.97 (N=CMe), 5.66 (Cp). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C, 75.5 MHz): δ 1.81 ($Si(SiMe_3)_3$), 11.95 ($Cp^{\star}$), 19.16 (ZrMe), 41.74 (N = C*Me*), 108.61 (Cp), 115.37 ($Cp^{\star}$), 188.45 (N = *C*Me). For **3**: Orange crystals (m.p. 161–163 °C) from diethyl ether in 60% yield. Anal. Found: C, 55.4; H, 8.82. $C_{28}H_{53}NSi_4Zr$ calcd.: C, 55.4; H, 8.80%. IR (nujol, CsI, cm^{-1}): $\nu(CN) = 1555$. ^1H NMR (benzene-d_6, 22 °C, 300 MHz): δ −0.11 (ZrMe), 0.33 ($Si(SiMe_3)_3$), 1.74 ($Cp^{\star}$), 5.20 (d, $J = 10.2$ Hz, N=CCHCH_2), 5.42 (d, $J = 17.1$ Hz, N=CCHCH_2), 5.88 (dd, $J = 10.2$, 17.1 Hz, NCC*H*CH_2), 5.67 (Cp). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C, 75.5 MHz): δ 1.30 ($Si(SiMe_3)_3$), 11.00 ($Cp^{\star}$), 19.25 (ZrMe), 108.11 (Cp), 117.67 ($Cp^{\star}$), 114.86, 146.86 ($CHCH_2$), 187.55 (N=*C*$CHCH_2$). For **4**: Yellow crystals (m.p. 173–175 °C) from pentane in 78% yield. Anal. Found: C, 58.5; H, 8.58. $C_{32}H_{55}NSi_4Zr$ calcd.: C, 58.5; H, 8.43%. IR (nujol, CsI, cm^{-1}): $\nu(CN) = 1570$. ^1H NMR (benzene-d_6, 22 °C, 300 MHz): δ −0.08 (ZrMe), 0.28 ($Si(SiMe_3)_3$), 1.63 ($Cp^{\star}$), 5.71 (Cp), 7.05, 7.13, 7.28 (Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C, 75.5 MHz): δ 1.36 ($Si(SiMe_3)_3$), 11.05 ($Cp^{\star}$), 20.57 (ZrMe), 108.44 (Cp), 114.94 ($Cp^{\star}$), 124.42, 126.68, 128.00, 149.82 (Ph), 191.87 (N=*C*Ph).

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6 Selected data for **5**: Yield 75%, m.p. 127–129 °C. Anal. Found: C, 56.6; H, 8.76. $C_{30}H_{55}NSi_4Zr$ calcd.: C, 56.9; H, 8.75%. ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): δ 0.00 (ZrMe), 0.34 (Si(SiMe$_3$)$_3$), 1.76 (Cp*), 3.34 (br, 1 H, *para*-H of pyridyl ring), 4.29 (m, 2 H, *meta*-H of pyridyl ring), 5.40 (d, 1 H, $J = 8.1$ Hz, NC(H)Si(SiMe$_3$)$_3$ of pyridyl ring), 5.66 (d, 1H, $J = 7.8$ Hz, *ortho*-H of pyridyl ring), 5.75 (Cp). ^{13}C{^{1}H} NMR (benzene-d_6, 22 °C, 75.5 MHz): δ 1.23 (Si(SiMe$_3$)$_3$), 10.81 (Cp*), 21.71 (ZrMe), 111.48 (Cp), 118.08 (Cp*), 31.13, 101.39, 102.93, 131.43, 134.02 (pyridyl ring).

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