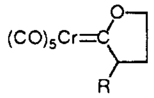
for proton transfer between 1 and the hydroxide ion. This value agrees satisfactorily with a value of 27 M^{-1} calculated from the kinetic data for the slower process[16] assuming that the curvilinear dependence on hydroxide ion concentration is a manifestation of coupling to the proton transfer equilibrium. From the equilibrium constant of 22 M^{-1} and pK_w (13.72 at 20 °C, $I = 0.5$ M) a pK_a of 12.3 is calculated for 1. This is 4.3 pK_a units higher than the pK_a of *p*-cyanophenol in water, while in THF the acidities of 1 and *p*-cyanophenol are about the same.[6b] From this comparison one may deduce that water provides much less solvational stabilization to 2 than to the *p*-cyanophenolate ion, indicating that the charge in 2 is highly dispersed.

Rate Constants. Our k_{OH} value of 135 $M^{-1}\,s^{-1}$ is much higher than k_{OD} reported for the deprotonation of **3a** (3.07 $M^{-1}\,s^{-1}$) and **3b** (1.97 $M^{-1}\,s^{-1}$) by OD^- in acetone-d_6/D_2O (3.6:1 by volume) at 38 °C.[7] However, a reevaluation of the kinetic data on these latter reactions suggests k_{OD} values in the order of 10^3 $M^{-1}\,s^{-1}$.[17] Since the acidities of **3a** and **3b** are comparable to that of 1,[7] this new estimate for k_{OD} is consistent with our result when the difference in solvent and temperature is taken into account.



3a: R = H
b: R = CH3

Intrinsic Rate Constant. On the basis of $k_{pip} = 69$ $M^{-1}\,s^{-1}$ and $pK_a^{pip} = 11.52$ an *intrinsic* rate constant[18] for deprotonation of 1 by secondary amines can be estimated as $\log k_0 = \log (k_{pip}/q) - \beta(\Delta pK + \log (p/q))$.[18,19] Assuming $\beta = 0.5$ affords $\log k_0 = 2.08$. Since $\Delta pK + \log (p/q) = -0.48$ is quite small, any error in the assumed Brønsted β value is of little consequence. Our $\log k_0$ is quite low, lower than for any carbon acid studied to date[18,21] except for nitroalkanes.[11] There is accumulating evidence of an inverse relationship between resonance stabilization of carbanions and the intrinsic rate constant for their formation,[18] which is the result of the resonance stabilization lagging behind bond changes in the transition state.[18] Our low $\log k_0$ value therefore suggests that 2 must derive much of its stabilization from a resonance rather than a polar effect, which is consistent with the solvent effect on the pK_a discussed above. Similar conclusions have been reached regarding the rather low intrinsic rate constants in the deprotonation of hydride transition-metal complexes.[22]

Acknowledgment. This research has been supported by Grant CHE-8617370 from the National Science Foundation.

Registry No. 1, 20540-69-6.

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Insertion of Ethylene into Zr–Si and Hf–Si Bonds

John Arnold, Mary P. Engeler, Frederick H. Elsner, Richard H. Heyn, and T. Don Tilley*

Chemistry Department, D-006
University of California at San Diego
La Jolla, California 92093-0506

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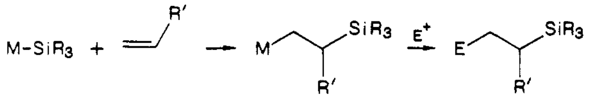
Summary: The zirconium and hafnium silyl derivatives $Cp^*Cl_2MSi(SiMe_3)_3$ and $CpCp^*Zr[Si(SiMe_3)_3]Cl$ (M = Zr, Hf; Cp* = η^5-C_5Me_5; Cp = η^5-C_5H_5) undergo clean insertion reactions with ethylene to give the β-silylalkyl complexes $[Cp^*Cl_2ZrCH_2CH_2Si(SiMe_3)_3]_2$ (**1a**), $Cp^*Cl_2HfCH_2CH_2Si(SiMe_3)_3$ (**1b**), and $CpCp^*Zr[CH_2CH_2Si(SiMe_3)_3]Cl$ (**2**), respectively. These reactions are photochemically and thermally induced. Complex **1a** is dimeric in both the solution and solid states, whereas **1b** is monomeric in solution. Crystals of **1a** are triclinic, $P\bar{1}$, with $a = 9.247$ (4) Å, $b = 12.643$ (6) Å, $c = 14.519$ (6) Å, $\alpha = 79.64$ (3)°, $\beta = 81.25$ (3)°, $\gamma = 75.33$ (4)°, $V = 1605$ (1) Å^3, $Z = 1$, $R_F = 4.46\%$, and $R_{wF} = 5.31\%$. The quantum yield for formation of **2** (λ = 380–470 nm, benzene-d_6) in the presence of excess ethylene is 2.5, implying a radical chain mechanism initiated by homolytic cleavage of a M–Si bond.

We have discovered transition-metal–silicon bonds that are reactive toward insertion of unsaturated substrates such as CO, CNR, and organic carbonyls.[1] These reactions involving d^0 metal silyl complexes represent new routes to Si–C bonds and therefore have potentially important synthetic applications. Insertion of alkenes into M–Si bonds are also of interest, since the resulting β-silylalkyls could provide β-functional organosilicon compounds via reaction chemistry analogous to that based on hydrozirconation[2] (eq 1). Also, it appears that such insertions may occur in some transition-metal-catalyzed hydrosilations.[3,4] Relevant investigations by Wrighton and co-workers have recently produced the first observation of insertion of an unactivated, monoalkene (C_2H_4) into the metal–silicon bond of photochemically activated $Cp^*(CO)_2FeSiMe_3$ (Cp* = η^5-C_5Me_5).[4] With the goal of developing chemistry based on "silylzirconation" (eq 1), we initially examined the behavior of d^0 silyls $Cp_2Zr(SiMe_3)Cl$ and $Cp_2Zr[Si(SiMe_3)_3]Cl$ toward ethylene.[5] However,



(1)

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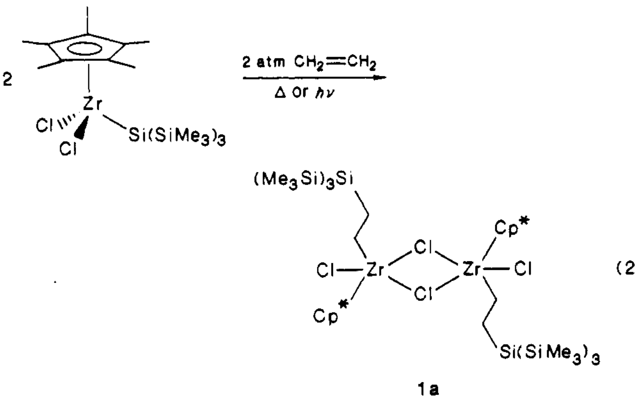
insertion products were not observed in these cases. Our investigations of early-transition-metal silyl complexes have since produced more reactive metal–silicon bonded species that do react with ethylene. In this report we describe facile, stoichiometric insertions of ethylene into the M–Si bonds of $CpCp^*Zr[Si(SiMe_3)_3]Cl$[1b] and $Cp^*Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf).[6] Related alkene insertions in analogous group 4 metal alkyl derivatives are of current interest with respect to the mechanism of alkene polymerizations.[7]

The zirconium silyl derivative $Cp^*Cl_2ZrSi(SiMe_3)_3$ combines rapidly with ethylene to give insertion product **1a** (eq 2). Under 2 atm of ethylene, dimeric **1a**[8] is formed cleanly in the dark ($t_{1/2} \approx 30$ min at 34 °C, benzene-d_6). This reaction is accelerated in the presence of ambient fluorescent room light, being complete within 5 min at 22 °C. Hafnium silyl $Cp^*Cl_2HfSi(SiMe_3)_3$ reacts more sluggishly with ethylene under analogous conditions ($t_{1/2} \approx 2$ days in the dark at 22 °C; complete conversion within 1 h in the presence of fluorescent room light at 22 °C) to give $Cp^*Cl_2HfCH_2CH_2Si(SiMe_3)_3$ (**1b**), which exists largely in monomeric form in benzene solution.[8] These insertion reactions are quantitative by ^1H NMR, and isolated yields approach 80%. Relevant to the observed photochemistry are UV–vis spectra for silyl complexes $Cp^*Cl_2MSi(SiMe_3)_3$ (M = Zr, Hf), which display absorptions that tail well into the visible region.[6a] These bands disappear upon formation of **1a** and **1b**,[8] and as expected the M–C bonds of these compounds are inert toward further insertions under 8 atm of ethylene in the presence of room light.



(2)

The ethylene group of **1a** and **1b** gives rise to AA′XX′ patterns in ^1H NMR spectra. For **1a**, this part of the spectrum was simulated (Figure 1). The crystal structure of **1a** consists of dimeric units that possess a crystallographic inversion center (Figure 2).[9] The inequivalent Zr–Cl (bridge) distances, 2.579 (2) and 2.692 (2) Å, suggest that the $Cp^*Cl_2ZrCH_2CH_2Si(SiMe_3)_3$ units are rather weakly associated. The three independent Zr–Cl distances agree closely with values observed for corresponding parameters in $[CpZrCl_3]_\infty$.[10] Distances and angles within the β-silylalkyl ligand are unexceptional and are inconsistent with the presence of an "agostic" interaction.[11]

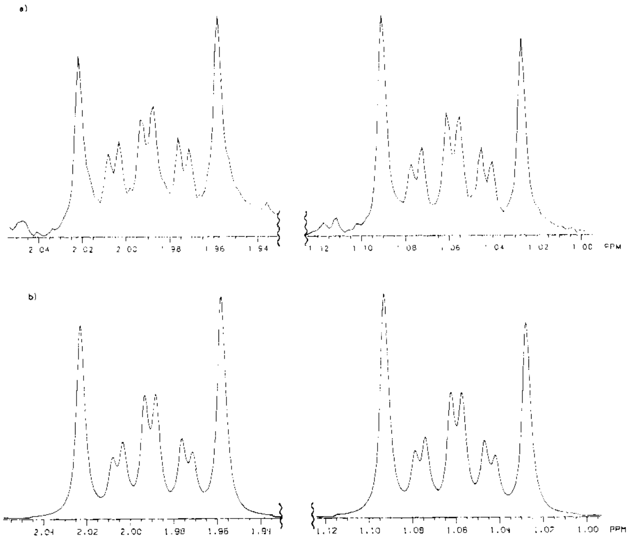


Figure 1. ^1H NMR resonances assigned to the ethylene hydrogens of **1a**: (a) measured. (b) simulated. Coupling constants ($ZrCH_2CH_2Si$, AA′XX′): $J_{AA'} = 13.0$ Hz; J_{AX}, $J_{A'X'} = 5.0$ Hz; $J_{AX'}$, $J_{A'X} = 14.5$ Hz; $J_{XX'} = 14.5$ Hz.

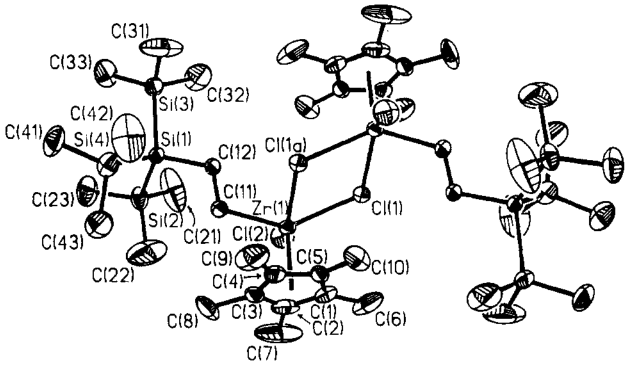


Figure 2. ORTEP view of **1a** with atom-labeling scheme. Selected bond distances (Å) and angles (deg): Zr(1)–Cl(1) 2.692 (2), Zr(1)–Cl(1A) 2.579 (2), Zr(1)–Cl(2) 2.410 (2), Zr(1)–C(11) 2.222 (6), C(11)–C(12) 1.539 (8), C(12)–Si(1) 1.907 (5), Zr(1)–C(11)–C(12) 111.4 (4), C(11)–C(12)–Si(1) 114.0 (4), Cl(1)–Zr(1)–Cl(1A) 73.8 (1), Zr(1)–Cl(1)–Zr(1A) 106.2 (1), Cl(1A)–Zr(1)–C(11) 83.8 (1), C(11)–Zr(1)–Cl(2) 91.0 (2), Cl(1)–Zr(1)–Cl(2) 83.6 (1), Cl(1)–Zr(1)–C(11) 139.7 (2), Cl(2)–Zr(1)–Cl(1A) 137.0 (1).

Upon exposure to fluorescent room light, the red zirconium silyl $CpCp^*Zr[Si(SiMe_3)_3]Cl$ reacts with 1 equiv of ethylene over ca. 3 days to afford β-silylalkyl derivative **2** (eq 3). Under 50 psi of ethylene, the reaction time is

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(8) For **1a**: Anal. C, H, Cl. Mol wt calcd: 1146. Found: 1113 (isothermal distillation in benzene). ^1H NMR (benzene-d_6, 22 °C, 300 MHz): δ 0.28 (s, 27 H, $SiMe_3$), 1.06 (m, 2 H, CH_2Si), 1.84 (s, 15 H, Cp*), 1.99 (m, 2 H, $ZrCH_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C, 75.5 MHz): δ 1.38 ($SiMe_3$), 4.39 (CH_2Si), 11.89 ($C_5\mathit{Me}_5$), 72.92 ($ZrCH_2$), 124.1 (C_5Me_5). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 22 °C): δ −71.58 ($\mathit{Si}(SiMe_3)_3$), −12.45 ($Si(\mathit{Si}Me_3)_3$). UV–vis (pentane, nm): 224 (ϵ = 11 000 M^{-1} cm^{-1}), 274 (ϵ = 9000 M^{-1} cm^{-1}). For **1b**: Anal. C, H, Cl. Mol wt calcd: 660. Found: 686 (isothermal distillation in benzene). ^1H NMR (benzene-d_6, 22 °C, 300 MHz): δ 0.27 (s, 27 H, $SiMe_3$), 0.93 (m, 2 H, CH_2Si), 1.80 (m, 2 H, $HfCH_2$), 1.87 (s, 15 H, Cp*). ^{13}C NMR (benzene-d_6, 22 °C, 75.5 MHz): δ 1.49 (q, $^1J_{CH}$ = 120 Hz, $SiMe_3$), 4.79 (t, $^1J_{CH}$ = 122 Hz, CH_2Si), 11.47 (q, $^1J_{CH}$ = 127 Hz, $C_5\mathit{Me}_5$), 75.36 (t, $^1J_{CH}$ = 123 Hz, $HfCH_2$), 122.6 (s, C_5Me_5). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 59.6 MHz, 22 °C): δ −71.49 ($\mathit{Si}(SiMe_3)_3$), −12.45 ($Si(\mathit{Si}Me_3)_3$). UV–vis (pentane, nm): 222 (ϵ = 15 000 M^{-1} cm^{-1}), 257 (ϵ = 14 000 M^{-1} cm^{-1}).

(9) $C_{42}H_{92}Cl_4Si_8Zr_2$: triclinic, $P\bar{1}$, a = 9.247 (4) Å, b = 12.643 (6) Å, c = 14.519 (6) Å, α = 79.64 (3)°, β = 81.25 (3)°, γ = 75.33 (4)°; V = 1605 (1) Å^3; Z = 1; μ = 6.58 cm^{-1}; Mo Kα radiation (λ = 0.710 73 Å). Of 6815 reflections collected ($3° \le 2\theta \le 50°$), 5666 were independent (R_{int} = 4.07%) and 3653 were considered observed ($F > 6.0\sigma(F)$); R_F = 4.46%, R_{wF} = 5.31%.

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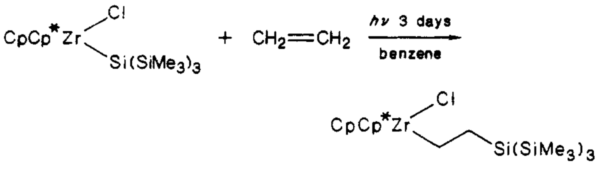

(3)

2

only ca. 10 h. This reaction is relatively clean (by ^{1}H NMR in benzene-d_6), and pure 2 can be isolated in ca. 50% yield as yellow crystals from pentane.[12] In the absence of light no product is formed after 5 days, indicating that insertion requires photochemical activation of CpCp*Zr[Si(SiMe$_3$)$_3$]Cl. The UV-vis spectrum of CpCp*Zr[Si(SiMe$_3$)$_3$]Cl exhibits an absorption at 461 nm (ϵ = 500 L mol^{-1} cm^{-1}), and use of cutoff filters has determined that the corresponding electronic transition gives rise to the observed photochemistry. The quantum yield for this reaction (λ = 380–470 nm, benzene-d_6) in the presence of excess ethylene is 2.5, suggesting a radical chain mechanism initiated by homolytic cleavage of a M–Si bond.[13]

Compound 1 is remarkably stable for an alkyl complex with β-hydrogens, very little decomposition being observed after 3 days at 80 °C (by ^{1}H NMR in benzene-d_6). Future work will involve further development and study of this insertion chemistry. Preliminary experiments show that Cp*Cl$_2$ZrSi(SiMe$_3$)$_3$ is unreactive toward styrene, propene, and Me$_3$SiCH=CH$_2$ and that Cp*Cl$_2$HfSi(SiMe$_3$)$_3$ is inert toward diphenylacetylene and 1-hexene.

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Supplementary Material Available: A listing of crystal, data collection, and refinement parameters and tables of positional and thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1a** (9 pages); a table of observed and calculated structure factors for **1a** (21 pages). Ordering information is given on any current masthead page.

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[12] For **2**: Anal. C, H. ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): δ 0.34 (s, 27 H, SiMe$_3$), 1.08 (m, 2 H, CH$_2$Si), 1.40 (m, 2 H, ZrCH$_2$), 1.71 (s, 15 H, Cp*), 5.90 (s, 5 H, Cp). UV-vis (pentane, nm): 225 (ϵ = 6000 M^{-1} cm^{-1}), 329 (ϵ = 1000 M^{-1} cm^{-1}).

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A Palladadigermetane: Palladium-Catalyzed Insertion Reactions of Digermiranes

Takeshi Tsumuraya and Wataru Ando*

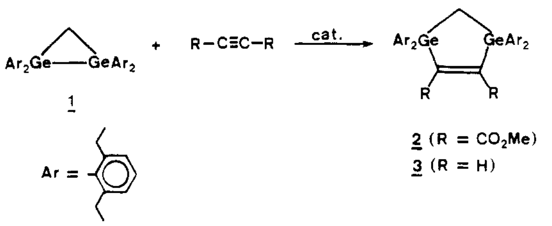
Department of Chemistry, The University of Tsukuba
Tsukuba, Ibaraki 305, Japan

Received May 1, 1989

Summary: The palladium-catalyzed reactions of digermirane **1** with dimethyl acetylenedicarboxylate and acetylene give the ring expansion products **2** and **3**. Reaction with methyl acrylate gives the rearranged product **4**. In the stoichiometric reaction of **1** with Pd(PPh$_3$)$_4$, palladadigermetane **6** is isolated as a stable compound. **6** reacts with dimethyl acetylenedicarboxylate, acetylene, and methyl acrylate to yield **2**, **3**, and **4**, respectively. The similar palladium-catalyzed reactions of thia- and selenadigermiranes **9** and **10** with acetylene give the ring expansion products **11** and **12**, respectively.

One of the most interesting reactions of the Si–Si bond of the reactive disilanes is the transition-metal-catalyzed insertion of unsaturated hydrocarbons, and numerous papers have been published so far.[1-7] In spite of these studies, no interest has been shown in the transition-metal-catalyzed insertion of unsaturated compounds into the Ge–Ge bond.[8] Recently, we reported the preparation and chemical properties of a digermirane and its heterocyclic analogues.[9,10] We report here the novel palladium-catalyzed ring-expansion reactions of a digermirane and thia- and selenadigermiranes. We also report the stoichiometric reaction of the digermirane with Pd(PPh$_3$)$_4$ to yield a palladadigermetane as stable red crystals.

When a benzene solution of digermirane 1,[9c] dimethyl acetylenedicarboxylate, and Pd(PPh$_3$)$_4$ (10 mol %) was heated to reflux for 45 h under an argon atmosphere, a crystalline product identified as digermacyclopentene 2,[11] a insertion product of the acetylene into the Ge–Ge bond, was obtained in 51% yield (eq 1). It was also found that



(1)

Pd(II) complexes such as PdCl$_2$(PPh$_3$)$_2$ and PdCl$_2$(PhCN)$_2$ and NiCl$_2$(PPh$_3$)$_2$ catalyzed the insertion of the acetylene into the Ge–Ge bond of the digermirane 1 equally, giving the adduct 2. Unsubstituted acetylene also reacted with

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[11] Compound **2**: colorless crystals; mp 173–174 °C; ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.87 (t, J = 7 Hz, 24 H, CH$_3$), 1.30 (s, 2 H, GeCH$_2$Ge), 2.50 (q, J = 7 Hz, 16 H, CH$_2$), 3.53 (s, 6 H, OMe), 6.9–7.4 (m, 12 H, Ar); ^{13}C NMR (25 MHz, CDCl$_3$) δ 11.5 (t, GeCH$_2$Ge), 15.1 (q, CH$_3$), 30.3 (t, CH$_2$), 51.8 (q, OMe), 125.9 (d, Ar), 128.8 (d, Ar), 141.2 (s, Ar), 147.8 (s, Ar), 157.9 (s, Ar), 169.9 (s, C=C).

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