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Elimination of bis(trimethylsilyl)stannylene from tris(trimethylsilyl)stannylated zirconocene and hafnocene chlorides

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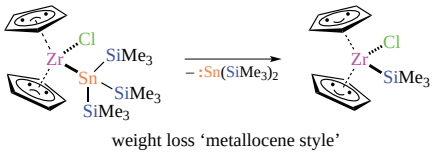
Reactions of $(Me_3Si)_3SnK$ with Cp_2MCl_2 (M = Zr, Hf) give the respective stannylated metallocene chlorides. These complexes display a tendency to eliminate bis(trimethylsilyl)-stannylene under $Cp_2M(Cl)SiMe_3$ formation.

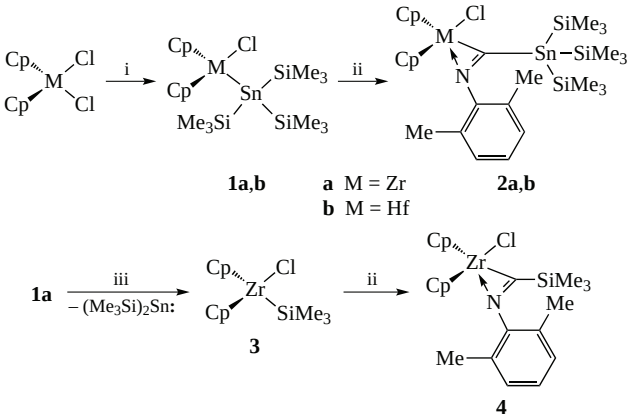


Keywords: stannylated compounds, group 4 elements, metallocenes, stannylene, tin, silicon, zirconium, hafnium.

More than 30 years ago, Harrod and co-workers reported the first example of the dehydrocoupling polymerization of phenylsilane by the action a titanocene catalyst.[1] In the course of mechanistic work, Tilley and co-workers studied the chemistry of silylated zirconocenes and hafnocenes to come to the conclusion that that reaction proceeded *via* σ-bond metathesis.[2,3] For their studies they used tris(trimethylsilyl)silylated zirconocene and hafnocene chlorides.[4,5] The related germanium compounds, $Cp_2M(Cl)Ge(SiMe_3)_3$ (M = Zr, Hf), have received considerably less attention. Tilley and co-workers obtained $Cp_2Zr(Cl)Ge(SiMe_3)_3$ by the reaction of Cp_2ZrCl_2 with $LiGe(SiMe_3)_3$.[6] Alternatively, this compound was also formed in the reaction with $KGe(SiMe_3)_3$.[7] The analogous hafnium compound is still unknown. Once we move down group 14 to analogous tin compounds, neither $Cp_2Zr(Cl)Sn(SiMe_3)_3$ nor $Cp_2Hf(Cl)Sn(SiMe_3)_3$ were known so far. This is somewhat unexpected because Tilley and co-workers have reported the dehydrocoupling polymerization of phenylstannanes. However, it seems they were more interested in arylated stannyl complexes of group 4 metallocenes. Synthesis of $Cp_2M(Cl)SnPh_3$ (M = Zr, Hf) was published already in 1972 by Kingston and Lappert.[8] Later, Tilley reported the preparation of $CpCp^*M(Cl)SnPh_3$ (M = Zr, Hf) and $Cp^*_2Zr(Cl)SnPh_3$,[9] followed by a study showing that complexes of the type $Cp'M(X)SnPh_3$ (M = Zr, Hf; Cp′ = Cp, Cp*; X = Cl, H) can undergo α-elimination of diphenylstannylene.[10] In the current account, we wish to report the preparation of $Cp_2M(Cl)Sn(SiMe_3)_3$ (M = Zr, Hf), the observation of bis(trimethylsilyl)stannylene elimination from these complexes and the trapping of $Cp_2M(Cl)Sn(SiMe_3)_3$ and $Cp_2Zr(Cl)SiMe_3$ with *N*-(2,6-dimethylphenyl)isonitrile.

Following an established reaction pattern,[4–7] we reacted zirconocene and hafnocene dichlorides with potassium tris(trimethylsilyl)stannide[11] (Scheme 1). The reactions proceeded smoothly and tris(trimethylsilyl)stannylated zirconocene **1a** and hafnocene **1b** chlorides were obtained.

^{119}Sn NMR spectroscopic analysis of **1a** and **1b** revealed resonances at δ −415 and −392 ppm, respectively, shifted substantially down-field compared to $(Me_3Si)_3SnK$ (δ −897 ppm) and $(Me_3Si)_4Sn$ (δ −664 ppm). This follows a similar behavior of the central silicon ^{29}Si NMR resonances of $Cp_2M(Cl)Si(SiMe_3)_3$ (M = Zr, Hf)[4], which resonate at δ −85.5 (Zr) and −79.7 (Hf) ppm[12] compared to δ −135.6 ppm for $(Me_3Si)_4Si$ and δ −195.8 $(Me_3Si)_3SiK$.[13] Both compounds were subjected to single crystal XRD analysis (Figure 1).†



Scheme 1 *Reagents and conditions*: i, $(Me_3Si)_3SnK$·18-crown-6, toluene, −35 °C → room temperature, 3 h; ii, 2,6-$Me_2C_6H_3N{\equiv}C$, toluene, room temperature, 30 min; iii, C_6D_6, room temperature, 12 h.

† *Crystal data for* **1a**. $C_{19}H_{37}ClSi_3SnZr$ (*M* = 595.12 g mol^{-1}), triclinic, space group $P\bar{1}$ (no. 2), *T* = 100(2) K, *a* = 9.0594(7), *b* = 10.8512(5) and *c* = 14.6361(13) Å, α = 87.408(2)°, β = 87.667(3)°, γ = 67.375(2)°, *Z* = 2, *V* = 1326.30(17) Å^3, μ = 1.573 mm^{-1}, d_{calc} = 1.490 g cm^{-3}, *F*(000) = 600. An orange block shaped single crystal (0.29 × 0.24 × 0.16 mm) was selected and 48532 reflections measured using a Bruker APEX-2 CCD diffractometer (ω and ϕ scans, sealed tube, λ[MoK$_\alpha$] = 0.71073 Å, 4.06° ⩽ 2θ ⩽ 60.2°). 7778 unique reflections (R_{int} = 0.0280, R_σ = 0.0179) were used in all calculations. The final R_1 was 0.0149 [>2σ(*I*)] and wR_2 was 0.0375 (all data), GOF = 0.993.

Crystal data for **1b**. $C_{19}H_{37}ClHfSi_3Sn$ (*M* = 682.39 g mol^{-1}), triclinic, space group $P\bar{1}$ (no. 2), *T* = 100(2) K, *a* = 9.0437(2), *b* = 10.8396(2) and *c* = 14.5907(3) Å, α = 87.3860(10)°, β = 87.6970(10)°, γ = 67.3120(10)°, *Z* = 2, *V* = 1317.88(5) Å^3, μ = 5.123 mm^{-1}, d_{calc} = 1.720 g cm^{-3}, *F*(000) = 664. A red orange block shaped single crystal (0.24 × 0.21 × 0.17 mm) was selected and 26970 reflections measured using a Bruker APEX-2 CCD diffractometer (ω and ϕ scans, sealed tube, λ[MoK$_\alpha$] = 0.71073 Å, 2.8° ⩽ 2θ ⩽ 61.1°), 8024 unique (R_{int} = 0.0295,

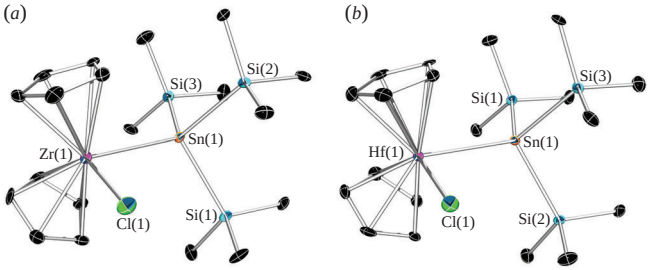


Figure 1 Molecular structures of (*a*) tris(trimethylsilyl)stannylated zircorocene **1a** and (*b*) relative hafnocene **1b** in the solid state.

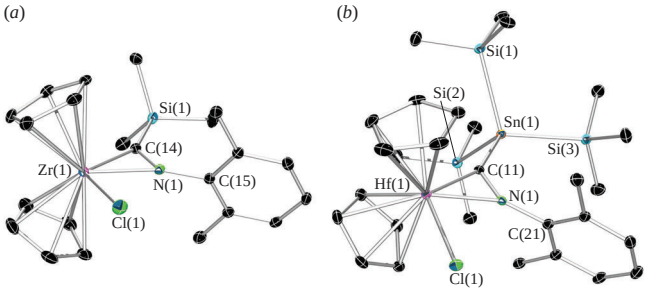


Figure 2 Molecular structures of (*a*) the isonitrile insertion product **4** and (*b*) its analogue **2b** in the solid state. The structure of **2a** (see Online Supplementary Materials, Figure S1) is isostructural to that of **2b**.

While NMR samples of complexes **1a** and **1b** were both found to eliminate $(Me_3Si)_2Sn$: to form $Cp_2M(Cl)SiMe_3$, solutions of hafnocene complex **1b** were substantially more stable. This is consistent with Tilley's observation of hafnocene silyl complexes reacting much slower than the related zirconocene complexes.[2] For complex **1a**, such a facile decomposition reaction to trimethylsilyl zirconocene chloride **3** was complete within 12 h (see Scheme 1). Synthesis of **3** was reported 35 years ago by Tilley who reacted zirconocene dichloride with tris(trimethylsilyl)aluminum.[14] To provide structural confirmation of the identity of **3**, we reacted it with *N*-(2,6-dimethylphenyl)isonitrile and obtained the known insertion product **4**,[4] which was subjected to single crystal XRD analysis (see Scheme 1, Figure 2).†

The facile insertion of **3** into the isonitrile suggested to subject also **1a** and **1b** to the same conditions. Despite a lack of previous examples for isonitrile insertion into Zr/Hf–Sn bonds, we found that both complexes reacted smoothly to afford the corresponding η^2-stannaiminoacyl complexes **2a**,**b** (see Scheme 1). Single crystal XRD analysis of these complexes (see Figure 2) showed structures similar to **4**. ^{119}Sn NMR spectra of compounds **2a** and **2b** feature tin resonances at a slightly higher field at δ −431 and −339 ppm, respectively.

The observed α-elimination of the bis(trimethylsilyl)-stannylene fragment from **1a** is not entirely unexpected as Tilley described related elimination reactions of diarystannylenes.[10,18,19] In attempts to obtain distannene complexes of group 4 metallocenes, we have previously reacted tetrakis(trimethylsilyl)-1,2-distannadiide with Cp_2MCl_2 (M = Zr, Hf) and observed the formation of metallatristannacyclobutanes, which presumably were formed by bis(trimethylsilyl)stannylene insertion into the initially formed metalladistannacyclopropane.[20]

R_σ = 0.0282) which were used in all calculations. The final R_1 was 0.0196 [>2$\sigma(I)$] and wR_2 was 0.0483 (all data), GOF = 1.054.

Crystal data for **2a**. $C_{28}H_{46}ClNSi_3SnZr$ (M = 726.29 g mol^{-1}), triclinic, space group $P\bar{1}$ (no. 2), T = 100(2) K, a = 10.0358(2), b = 10.9185(4) and c = 17.0175(7) Å, α = 99.882(2)°, β = 99.860(2)°, γ = 111.5420(10)°, Z = 2, V = 1651.94(10) Å^3, μ = 1.278 mm^{-1}, d_{calc} = 1.460 g cm^{-3}, F(000) = 740. A yellow block shaped single crystal (0.19 × 0.18 × 0.17 mm) was selected and 17585 reflections measured using a Bruker APEX-2 CCD diffractometer (ω and ϕ scans, sealed tube, λ[MoK$_\alpha$] = 0.71073 Å, 2.52° ⩽ 2θ ⩽ 56.04°), 7710 unique (R_{int} = 0.0511, R_σ = 0.0613) which were used in all calculations. The final R_1 was 0.0289 [>2$\sigma(I)$] and wR_2 was 0.0870 (all data), GOF = 0.939.

Crystal data for **2b**. $C_{28}H_{46}ClHfNSi_3Sn$ (M = 813.56 g mol^{-1}), triclinic, space group $P\bar{1}$ (no. 2), T = 100(2) K, a = 13.0292(10), b = 15.2417(11) and c = 18.1548(14) Å, α = 80.267(4)°, β = 69.091(3)°, γ = 84.941(2)°, Z = 4, V = 3317.9(4) Å^3, μ = 4.086 mm^{-1}, d_{calc} = 1.629 g cm^{-3}, F(000) = 1608. A yellow block shaped single crystal (0.28 × 0.11 × 0.10 mm) was selected and 114123 reflections measured using a Bruker APEX-2 CCD diffractometer (ω and ϕ scans, sealed tube, λ[MoK$_\alpha$] = 0.71073 Å, 2.42° ⩽ 2θ ⩽ 55.9°), 15795 unique (R_{int} = 0.0499, R_σ = 0.0421) which were used in all calculations. The final R_1 was 0.0335 [>2$\sigma(I)$] and wR_2 was 0.0949 (all data), GOF = 1.078.

Crystal data for **4**. $C_{22}H_{28}ClNSiZr$ (M = 461.21 g mol^{-1}), monoclinic, space group $P2_1/c$ (no. 14), T = 100(2) K, a = 16.523(3), b = 9.2278(18) and c = 15.326(3) Å, β = 112.99(3)°, Z = 4, V = 2151.3(7) Å^3, μ = 0.697 mm^{-1}, d_{calc} = 1.424 g cm^{-3}, F(000) = 952. An orange block shaped single crystal (0.40 × 0.22 × 0.18 mm) was selected and 16604 reflections measured using a Bruker Smart APEX CCD diffractometer (ω and ϕ scans, sealed tube, λ[MoK$_\alpha$] = 0.71073 Å, 5.16° ⩽ 2θ ⩽ 52.74°), 4391 unique (R_{int} = 0.0349, R_σ = 0.0372) which were used in all calculations. The final R_1 was 0.0284 [>2$\sigma(I)$] and wR_2 was 0.0705 (all data), GOF = 1.032.

All structures were solved by direct methods (SHELXT)[15] and refined by full matrix least-squares procedures on F^2 using SHELXL 2018/3.[16] WinGX[17] was used to prepare material for publication.

CCDC 2106836–2106840 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.016.

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