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Activation of Homolytic Si–Zn and Si–Hg Bond Cleavage, Mediated by a Pt^0 Complex, via Novel Pt–Zn and Pt–Hg Compounds

Yosi Kratish, Gregory Molev, Arseni Kostenko, Dennis Sheberla, Boris Tumanskii, Mark Botoshansky†, Shigeru Shimada, Dmitry Bravo-Zhivotovskii, and Yitzhak Apeloig**

In memory of Paul von Ragué Schleyer

Abstract: *The thermally stable [(tBuMe$_2$Si)$_2$M] (M = Zn, Hg) generate R$_3$Si$^•$ radicals in the presence of [(dmpe)Pt(PEt$_3$)$_2$] at 60–80 °C. The reaction proceeds via hexacoordinate Pt complexes, (M = Zn (**2a** and **2b**), M = Hg (**3a** and **3b**)) which were isolated and characterized. Mild warming or photolysis of **2** or **3** lead to homolytic dissociation of the Pt–MSiR$_3$ bond generating silyl radicals and novel unstable pentacoordinate platinum paramagnetic complexes (M = Zn (**5**), Hg (**6**)) whose structures were determined by EPR spectroscopy and DFT calculations.*

The vigorously developing chemistry of heterometallic complexes containing two or more different metals is of considerable contemporary interest with a variety of applications in synthesis, catalysis, and materials chemistry.[1] More specifically, recently heterometallic complexes containing Pt and Zn atoms attracted attention and several were isolated.[2–4] Several methodologies are available for their synthesis. One involves the formation of Pt–Zn heteronuclear dative linkages from Lewis basic and Lewis acidic metals (termed metal-only Lewis pairs (MOLPs)).[1a] For example, recently a MOLP Pt–Zn complex was isolated from the reaction of [Pt(PCy$_3$)$_2$] (Cy = cyclohexyl) and ZnBr$_2$.[2] Fischer et al. reported a number of novel {Pt–ZnCp*} (Cp* = pentamethylcyclopentadienyl) complexes in which a divalent zinc is bonded directly to platinum.[3] Complexes in which Pt and Zn are bridged by ligands were also isolated and characterized.[4]

Herein we report that thermally stable Si–Zn and Si–Hg bonds are activated towards homolytic cleavage by a Pt^0 complex, [(dmpe)Pt(PEt$_3$)$_2$] (**1**) dmpe = 1,2-bis(dimethylphosphanyl)ethane, yielding hexacoordinate Pt isomers **2a** and **2b** (M = Zn) or **3a**, **3b** (M = Hg), respectively, having a Pt–MSiR$_3$ moiety [Eq. (1)]. These novel hexacoordinate Pt–MSiR$_3$ compounds were isolated and characterized by X-ray crystallography and their photolysis and thermolysis is reported. Photolysis of **2** (i.e., the obtained 63:37 mixture of **2a** + **2b**, respectively) or of **3** (i.e., the obtained 26:74 mixture of **3a** + **3b**, respectively) yields quantitatively the tetracoordinate platinum complex **4** and the EPR spectra of the intermediate pentacoordinate platinum paramagnetic species, **5** (M = Zn) or **6** (M = Hg), respectively, are observed [Eq. (2)].

Bis(silyl)zincs and bis(silyl)mercuries are good precursors for the photochemical generation of R$_3$Si radicals.[5] For example, upon day-light exposure for 30 min [(tBuMe$_2$Si)$_2$Zn] (**7**) or [(tBuMe$_2$Si)$_2$Hg] (**8**) undergo quantitative demetallation forming short-lived [tBuMe$_2$Si]$^•$ radicals which dimerize to disilane **9** (95 %) or abstract an hydrogen (5 %) to form silane **10** [Eq. (3)].

In contrast to their facile photolysis, bis(silyl)zincs and bis(silyl)mercuries are generally thermally stable; for example no decomposition of [(tBuMe$_2$Si)$_2$Zn] (**7**), [(tBuMe$_2$Si)$_2$Hg] (**8**), [(tBu$_2$MeSi)$_2$Zn] (**11**), or [(tBu$_2$MeSi)$_2$Hg] (**12**) is observed after their heating at 120 °C for several days. However, in the presence of a stoichiometric amount of [(dmpe)Pt(PEt$_3$)$_2$] (**1**), **7** and **8** undergo dezincation (at 80 °C) or demercuration (at 60 °C) respectively, producing silane **10** (90 %) and disilane **9** (10 %) [Eq. (4)]. In contrast, the more sterically crowded [(tBu$_2$MeSi)$_2$Zn] (**11**) and [(tBu$_2$MeSi)$_2$Hg] (**12**) are thermally stable in the presence of **1** even at 140 °C. It is reasonable to assume that in Equation (4), **10** and **9** are formed from R$_3$Si$^•$ radicals by hydrogen abstraction or dimerization, respectively. The same products are also obtained in the photolysis of **7** and **8**, but the **10**:**9** ratio of 5:95 [Eq. (3)] is nearly inverse to that obtained in Equation (4).[6] Formation of **9** + **10** from **7** or **8** in the presence of **1** indicates that **1** activates the formation of R$_3$Si$^•$ radicals. This suggestion is supported by the fact that addition of **1** lowers the temperature required for silyl radical formation in the thermolysis reactions of ([tBuMe$_2$Si)$_2$Zn] (**7**) or [(tBuMe$_2$Si)$_2$Hg] (**8**) in the presence of (Me$_3$Si)$_3$SiH.[7]

To probe the presence of silyl radicals in the reaction in Equation (4) we used TEMPO ((2,2,6,6-tetramethyl-piperi-

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[*] Y. Kratish,[+] Dr. G. Molev,[+] A. Kostenko, Dr. D. Sheberla, Dr. B. Tumanskii, Dr. M. Botoshansky, Dr. D. Bravo-Zhivotovskii, Prof. Dr. Y. Apeloig
Schulich Faculty of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry
Technion-Israel Institute of Technology
Haifa 32000 (Israel)
E-mail: chrbrzh@tx.technion.ac.il
apeloig@technion.ac.il
Dr. S. Shimada
Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST)
Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565 (Japan)

[+] These authors contributed equally to this work.

[†] Deceased.

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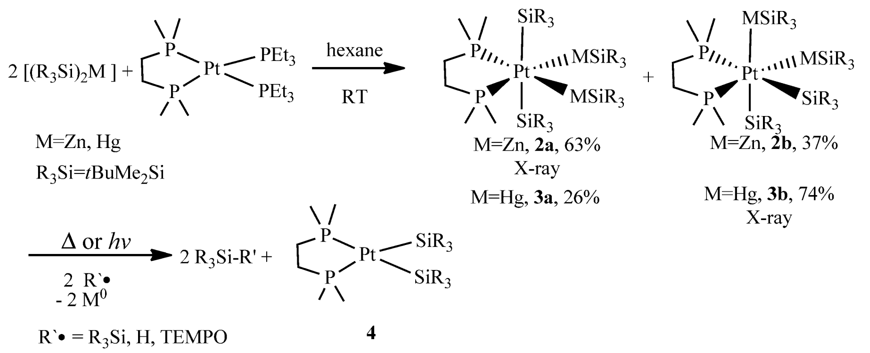
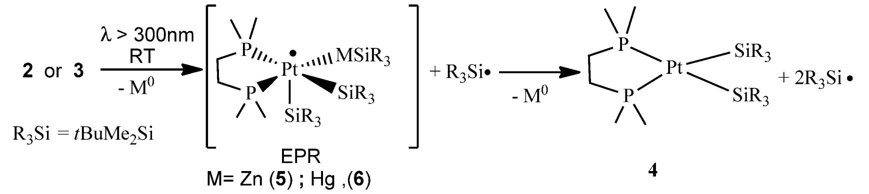


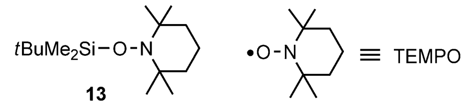
(1)



(2)

$$\underset{\text{M= Zn }(\mathbf{7})\text{ ; Hg }(\mathbf{8})}{(t\text{BuMe}_2\text{Si})_2\text{M}} \xrightarrow[-\text{M}^0]{h\nu} 2\,t\text{BuMe}_2\text{Si}^{\bullet} \xrightarrow{\text{hexane, RT}} \underset{\mathbf{9}\ (95\%)}{t\text{BuMe}_2\text{Si-SiMe}_2t\text{Bu}} + \underset{\mathbf{10}\ (5\%)}{t\text{BuMe}_2\text{SiH}} \quad (3)$$

$$\underset{\text{M= Zn }(\mathbf{7})\text{ ; Hg }(\mathbf{8})}{[(t\text{BuMe}_2\text{Si})_2\text{M}]} \xrightarrow[\substack{\text{Hexane}\\ 80^\circ\text{C (M=Zn)}\\ 60^\circ\text{C (M=Hg)}}]{[(\text{dmpe})\text{Pt}(\text{PEt}_3)_2]\ (\mathbf{1}),\ 2.5\text{ h}} \underset{\mathbf{10}\ (90\%)}{t\text{BuMe}_2\text{SiH}} + \underset{\mathbf{9}\ (10\%)}{t\text{BuMe}_2\text{Si-SiMe}_2t\text{Bu}} \quad (4)$$



din-1-yl)oxyl) as a silyl-radical scavenger. [(tBuMe$_2$Si)$_2$Hg] (**8**) reacts relatively slowly with TEMPO yielding only 20% of the expected radical adduct **13** after 2 h at 60 °C. However, in the presence of **1**, **8** produces **13** in 92% yield indicating that **1** enhances the production of silyl radicals. Unfortunately TEMPO reacts instantaneously (even at room temperature) with **7** yielding **13**, thus, precluding its use to probe the presence of silyl radicals in Equation (4), with M = Zn. However, analogy with **8** supports the generation of silyl radicals in reaction 4 also for **7**.

To understand how **1** generates silyl radicals in thermolysis of [(R$_3$Si)$_2$M] we studied their reactions in more detail. Addition of 1 mole equivalent of **1** to 2 mole equivalents of [(tBuMe$_2$Si)$_2$Zn] (**7**) at room temperature in hexane yields instantaneously and quantitatively two isomeric hexacoordinate octahedral Pt^{IV}[8] complexes, **2a** and **2b**, in a 63:37 ratio [Eq. (1), M = Zn]. Colorless crystals of the major isomer **2a**, which has two equatorial ZnSiR$_3$ ligands (the equatorial plane is defined by the dmpe ligand and the two ligands *trans* to it), were isolated and its structure was determined by X-ray crystallography (Figure 1 a).[9] Similarly **1** reacts with **8** yielding the analogous Pt–Hg isomeric complexes **3a** and **3b** in a ratio of 26:74, a nearly reversed isomeric ratio compared to the reaction with **7** [Eq. (1), M = Hg].[10] The brown-orange crystals of the major isomer **3b**, which has one axial and one equatorial HgSiR$_3$ ligand, were isolated from hexane and analyzed by X-ray crystallography (Figure 1 b).[9] Compounds **2** and **3** are formally products of a double insertion of the {(dmpe)Pt} fragment into the Si–Zn and Si < C- < Hg bonds of **7** and **8**, respectively, yielding octahedral hexacoordinate Pt^{IV} complexes. Compounds **2a** and **3b** have regular bond lengths and bond angles and their detailed structures are given in the Supporting Information.

Compounds **2** and **3** undergo complete thermal (60–80 °C, 2.5 h) and photolytic ($\lambda > 300$ nm, 25 °C, 0.5 h) conversion into a mixture of the tetracoordinate Pt^{II} complex **4**, tBuMe$_2$SiH (**10**), tBuMe$_2$Si-SiMe$_2t$Bu (**9**), and metallic zinc or mercury, respectively. Thermolysis or photolysis of mercury species **3** in the presence of 2 mole equivalent of TEMPO yields the silyl-TEMPO adduct **13** in 92% yield, indicating that tBuMe$_2$Si• radicals are generated from **3**. The absence of **9** and **10** in the presence of TEMPO indicates that the tBuMe$_2$Si$^{\bullet}$ radicals produced from **3** are trapped faster by TEMPO than they dimerizes or abstract a hydrogen atom.

Additional strong support for the suggestion that **2** and **3** fragment to give radical intermediates is the observation by EPR spectroscopy of paramagnetic species. When a hexane solution at 25 °C of **2** or **3** is irradiated ($\lambda > 300$ nm) within the EPR spectrometer cavity, metallic zinc or mercury precipitates and an intensive broad EPR signals (line-width

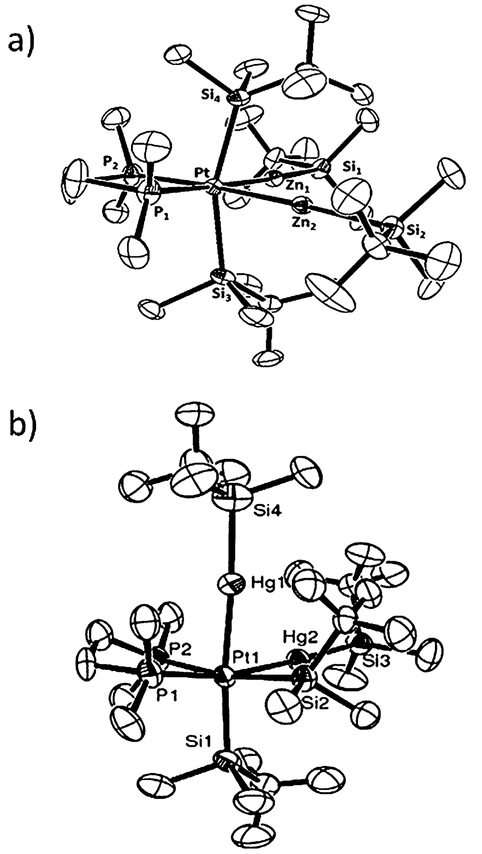


Figure 1. a) ORTEP drawing of the molecular structure of **2a**. b) ORTEP drawing of the molecular structure of **3b**. Thermal ellipsoids are set at 20% probability and hydrogen atoms are omitted for clarity.[9]

≈ 50.0 G) with g_{iso} values of 2.061 for **2** (Figure 2a) and 2.055 for **3** (Figure 2c) are observed. These *g*-factors are strongly shifted to low field relative to a free electron ($g = 2.002$), which is typical for heavy-element-centered radicals owing to strong spin-orbit coupling.[11] In frozen hexane or toluene solutions these EPR spectra exhibit a three-axis anisotropy (Figure 2b,d), indicating a rhombic molecular symmetry.[12] We conclude that the observed paramagnetic intermediates are Pt^{III} complexes **5** (M = Zn) and **6** (M = Hg), having a square-pyramidal geometry formed by cleavage of one of the Pt–$MSiR_3$ bonds [Eq. (2)]. Analysis of the EPR spectra of **5** and **6** (a detailed analysis is presented in the Supporting Information) leads to the conclusion that most of the spin is localized on the Pt atom. This situation is in contrast to that in most other Pt^{III} complexes in which most of the spin is delocalized to the ligands.[13] The good agreement between the simulated EPR spectra[14a,b] and the experimental spectrum strongly support the proposed square-pyramidal structures of radicals **5** and **6**.[15] The square-pyramidal structure of radicals **5** and **6** is also supported by quantum mechanics calculations[14b,c] at the ZORA (zero order regular approximation) B3LYP[16]/TZVP[17] level of theory for model systems in which the $tBuMe_2Si$ groups in **5** and **6** are substituted by Me_3Si groups (referred to as **5a** and **6a**, respectively). The calculated coupling constants and *g*-factors for **5a** and **6a** are in good agreement with the experimental values for **5** and **6**, respectively; the maximal experimental–calculated deviation in the *g* factor values is 1.4%.[14b]

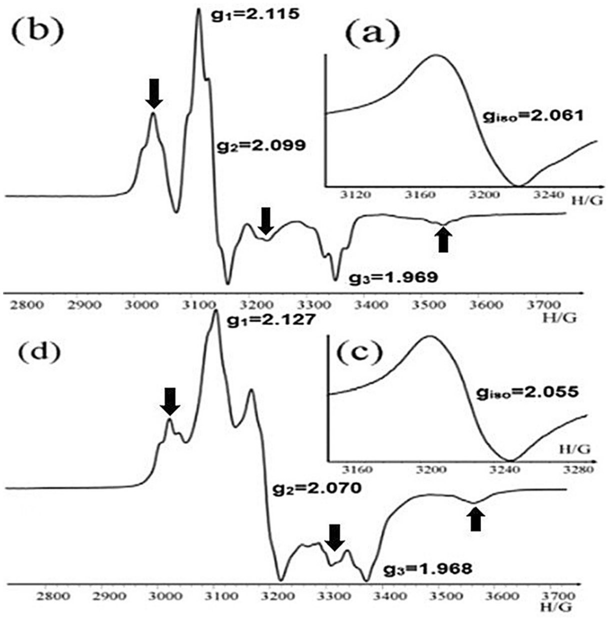
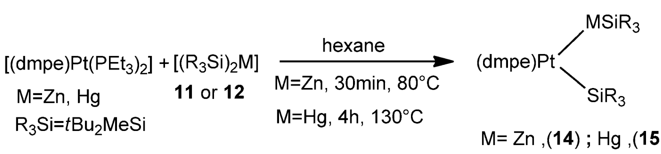


Figure 2. EPR spectra of **5** in hexane solution: a) at 25 °C; b) at −143 °C (frozen solution); EPR spectra of **6** in hexane solution: c) at 25 °C; d) at −143 °C (frozen solution). Arrows indicate the ^{195}Pt satellites.

The zinc-substituted Pt radical **5** is persistent at 25 °C ($\tau_{1/2} \approx 15$ h) while the analogous mercury-substituted Pt radical **6** has a $\tau_{1/2}$ of only 20 min at 25 °C. The observed first-order decay of **5** and **6**,[18] suggests that it occurs by cleavage of the equatorial R_3SiM–Pt bond to yield **4** [Eq. (2)]. The decay rates of **5** and **6** as a function of temperature, yield activation energies of 32.0 kcal mol^{-1} for **5** and 24.1 kcal mol^{-1} for **6**.[18] The calculated R_3SiM–Pt dissociation energies, at ZORA B3LYP-D3/TZVP,[14b,c] of 35.9 kcal mol^{-1} for **5a** and 28.6 kcal mol^{-1} for **6a**, in particular the difference of 7.3 kcal mol^{-1} (7.9 kcal mol^{-1}, exp.) are in good agreement with the experimental values.

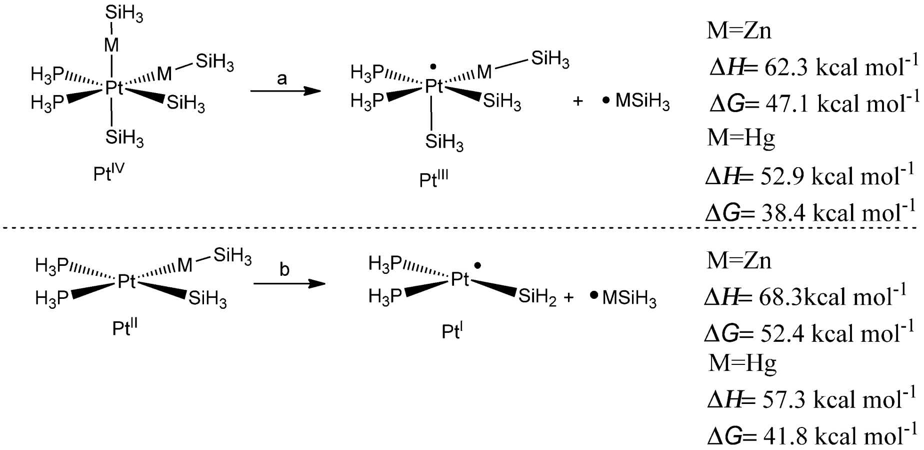
Thermolysis of the more bulky substituted $[(tBu_2MeSi)_2M]$ (M = Zn (**11**), 80 °C, M = Hg (**12**), 130 °C) with $[(dmpe)Pt(PEt_3)_2]$ (**1**) [Eq. (5)], yields the corresponding square-planar Pt^{II}–M complexes **14** and **15**, respectively.[19] However, in contrast to Equation (1) octahedral complexes similar to **2** and **3** are not observed with **11** or **12**.

The tetracoordinate **14** and **15** are thermally and photolytically highly stable in contrast to the thermally and photochemically reactive hexacoordinate **2** and **3**. The higher thermal and photolytic reactivity of **2** and **3** (R_3Si =



$$\underset{\substack{M=Zn,\ Hg\\ R_3Si=tBu_2MeSi}}{[(dmpe)Pt(PEt_3)_2]} + \underset{\textbf{11 or 12}}{[(R_3Si)_2M]} \xrightarrow[\substack{M=Zn,\ 30min,\ 80^{\circ}C\\ M=Hg,\ 4h,\ 130^{\circ}C}]{hexane} \underset{M=Zn\ ,(\textbf{14})\ ;\ Hg\ ,(\textbf{15})}{(dmpe)Pt(MSiR_3)(SiR_3)} \quad (5)$$

*t*BuMe$_2$Si) compared to **14** and **15** (R$_3$Si = *t*Bu$_2$MeSi) reflects the different stability of the Pt^{III} and Pt^{I} radical species which result from cleavage of one of their Pt–MSiR$_3$ bonds. Thus, DFT calculations (at ZORA B3LYP-D3[20]/TZVP, data at 298.15 K) show that cleavage of the Pt–MSiR$_3$ bond (for model compounds in which the SiR$_3$ and dmpe groups were substituted by SiH$_3$ and PH$_3$ groups, respectively) of a Pt^{IV} complex to form a Pt^{III} paramagnetic species (Scheme 1, reaction a) require 6.0 kcal mol^{-1} (M = Zn) and 4.4 kcal mol^{-1} (M = Hg) less energy than cleavage of the Pt–MSiR$_3$ bond in a Pt^{II} complex to form a Pt^{I} paramagnetic species (Scheme 1, reaction b).



Scheme 1.

In conclusion, the Si–M (M = Zn, Hg) bonds in [(R$_3$Si)$_2$M], with the relatively non-bulky *t*BuMe$_2$Si substituents, are thermally activated by Pt^0 complex **1** to generate under mild conditions, *t*BuMe$_2$Si radicals. In contrast, the bulkier [(*t*Bu$_2$MeSi)$_2$M], (M = Zn, Hg) do not undergo Si–M bond activation. The enhancing effect of **1** on the homolytic cleavage of the M–Si bonds in [(*t*BuMe$_2$Si)$_2$M] is mediated by formation of octahedral hexacoordinate Pt–M bimetallic complexes **2** (for Zn) and **3** (for Hg) which dissociate under mild warming or under photolysis to yield R$_3$Si$^{\bullet}$ radicals and novel square-pyramidal paramagnetic Pt^{III} species, characterized by EPR spectroscopy and DFT calculations. The reported activation of the Si–M bonds in [(*t*BuMe$_2$Si)$_2$M] (M = Zn, Hg) occurs in the presence of stoichiometric amounts of [(dmpe)Pt(PEt$_3$)$_2$] (**1**). We are now searching for Pt^0 complexes and metallosilanes for the creation of a catalytic system based on Pt-mediated homolytic (radical) activation of R$_3$Si–M bonds which may be an interesting alternative to classic Pt-catalyzed or radical initiated reactions such as those used in hydrosilylation.[21]

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[6] A possible explanation for the different **9**:**10** ratio in photolysis and thermolysis is the presence of the alkyl phosphine ligands on **1** which act as an effective hydrogen source for the produced silyl radicals, thus, inverting the **9**:**10** ratio in Equation (4) compared to Equation (3). Another explanation, suggested by a referee, is that in photolysis (Equation (3)) two silyl radicals may be produced nearly simultaneously in a solvent cage, enhancing the relative amount of the disilane.

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[8] The denoted oxidation states are formal and do not indicate the actual charge on the Pt atom, in particular as the Pauling electronegativity of Zn (1.65), Hg (1.9), and Si (1.90) are lower than those of Pt (2.2).

[9] The supplementary crystallographic data for **2a** is given in CCDC 1023697 and for **3b** in CCDC-1023671. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[10] a) According to DFT calculations at ZORA B3LYP-D3/TZVP (for details see Supporting Information) of model systems in which the *t*BuMe$_2$Si-groups are substituted by Me$_3$Si groups, a possible explanation for the almost inverse product regioselectivity obtained from bis(silyl)zinc and bis(silyl)mercury lies in the relative stability of the isomers. Thus, **2a** is by 1.2 kcal mol^{-1} lower in energy than **2b** and **3a** is by 1.5 kcal mol^{-1} higher in energy than **3b**; b) The stereoisomer of **2** with two silylzinc groups *trans* to each other is not detected by NMR spectroscopy probably because it is 5.8 kcal mol^{-1} higher in energy than **2a**. Also for the mercury species **3** this isomer is not detected by NMR (see Supporting Information for more details) even though, it is only 0.9 kcal mol^{-1} higher in energy than **3b**.

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[14] a) The simulations were performed using the SimFonia software; b) Additional details of the calculations including the optimized calculated geometries and the simulated spectra are given in the Supporting Information; c) The calculations were carried out using the ORCA 2.9 software. F. Neese, *ORCA*, version 2.9, an ab initio, density functional and semi-empirical program package (Max Planck Institute for Bioinorganic Chemistry: Mülheim an der Ruhr, Germany, 2012).

[15] a) In principle, radicals **5** and **6** can also exist having the two SiR$_3$ groups in the equatorial positions and the MSiR$_3$ group in the axial position. According to the DFT calculations these two isomers are close in energy, within 1.2 kcal mol^{-1}, and can easily interconvert by a Berry pseudo-rotation. However, the observed EPR spectra fit only the calculated spectra of **5** and **6**; other isomers of **5** and **6** have significantly different calculated spectra; b) Isomers of **5** and **6** with a triangular-bipyramid structure having the spin pointing to an equatorial position are not observed and according to the DFT calculations these isomers are not in a local minimum on the potential-energy surface collapsing to isomers with the spin pointing to the axial position as in **5** and **6**.

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[18] Detailed information about the kinetic measurements for **5** and **6** is given in the Supporting Information.

[19] Compounds **14** and **15** were isolated and their X-ray crystallography structures are given in the Supporting Information; for **14** in CCDC 1023684 and for **15** in CCDC-1023698. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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