# **ORGANOMETALLICS**

# Synthesis and Structure of New [3]Silametallocenophanes of Group 8 Metals

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**Supporting Information** 



**ABSTRACT:** The synthesis and characterization of new [3]silametallocenophanes of the group 8 metals via salt elimination is presented. Thereby, new [3]silaferrocenophanes as well as the first [3]silametallocenophanes of the heavier metals ruthenium and osmium could be synthesized and characterized. Also, the first solid-state structure of a [3]silaferrocenophane was determined by X-ray crystallographic analysis.

# 1. INTRODUCTION

Shortly after the report of the parent ferrocene as the archetypal sandwich complex,<sup>1</sup> a [3] carbaferrocenophane was presented in the literature as the first example of a bridged or ansa sandwich complex.<sup>2</sup> Over the past two decades, ferrocenophanes have been widely studied, in particular with respect to their propensity to undergo ring-opening polymerization with formation of well-defined organometallic polymers.<sup>3</sup> Recent years have brought about significant developments in the chemistry of non-iron metallocenophanes,<sup>3c</sup> extending the scope of this important class of compounds to transition metals such as Ti,<sup>4</sup> V,<sup>5</sup> Cr,<sup>6</sup> Mn,<sup>7</sup> Co,<sup>8</sup> and Ni.<sup>9</sup> However, as far as iron's higher homologues are concerned, ruthenocenophanes<sup>10</sup> are less prolific and only a few osmocenophanes<sup>11</sup> have been reported. Although the aforementioned [3]carbaferrocenophane may be considered the ancestor of ansa sandwich complexes, corresponding homonuclear [3]metallocenophanes of group 8 metals are rare. While [3]thiabridged representatives are known for the whole triad,<sup>11a</sup> [3] carba-bridged derivatives have been reported for ferro- and ruthenocenophanes<sup>2,12</sup>] and [3]sila bridges are exclusively known for iron (compounds 1 and 2, Figure 1).<sup>13,14</sup>

The latter compounds date back to an initial report by Kumada et al. in 1972, in which the 1,1'-dilithioferrocene– tmeda adduct 3 and dichlorohexamethyltrisilane were employed in a salt metathesis reaction to provide 1 as an orange oil.<sup>13</sup> An alternative protocol was reported by Marschner et al. in 2006,<sup>14</sup> involving treatment of the 1,1'-disilaferrocene 4 with potassium and Me<sub>2</sub>SiCl<sub>2</sub> to yield 2 as an orange powder. Scheme 1 shows the two different reaction pathways.



Figure 1. Known trisilaferrocenophanes 1 and 2.

Although [3]silaferrocenophanes 1 and 2 have been known in the literature since 1972, no single-crystal X-ray molecular structure has been reported. In this paper we report the synthesis of new [3]silaferrocenophanes as well as the first synthesis of [3]silaruthenocenophanes and [3]osmocenophanes.

# 2. RESULTS AND DISCUSSION

Using a modification of the synthetic route of Russell et al.,<sup>15</sup> three diphenyltrisilanes and the three corresponding dichlorotrisilanes were synthesized. The substituents at the central silicon atom were introduced by reacting lithiated phenyldimethylsilane with different dichlorodialkylsilanes. The known synthesis was improved by using lithium sand instead of lithium wire, furnishing the trisilanes 5-7 in yields up to 90%. The 1,3dichlorotrisilanes  $Et_2Si(SiMe_2Cl)_2$  (8),  $iPr_2Si(SiMe_2Cl)_2$  (9), and  $tBuMeSi(SiMe_2Cl)_2$  (10) were obtained in moderate to

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#### Scheme 1. Reaction Pathways to Trisila-Bridged Ferrocenophanes





PhMe <sub>2</sub> SiCl	1. 2 eq. Li 2. 0.5 eq. R <sup>1</sup> R <sup>2</sup> SiCl <sub>2</sub>	R <sup>1</sup> R <sup>2</sup> Si(SiMe <sub>2</sub> Ph) <sub>2</sub>		AcCI/AICI <sub>3</sub>	>	R <sup>1</sup> R <sup>2</sup> Si(SiMe <sub>2</sub> CI) <sub>2</sub>	2
		<b>5</b> $R^1 = R^2 = Et$ <b>6</b> $R^1 = R^2 = iPr$ <b>7</b> $R^1 = Me, R^2 = tBe$	72% 90% u 85%		8 9 10	$R^1, R^2 = Et$ $R^1, R^2 = iPr$ $R^1 = Me, R^2 = tBu$	90% 84% 51%

good yields by reacting the 1,3-diphenyltrisilanes with acetyl chloride and aluminum trichloride in hexane (Scheme 2).

The multinuclear NMR spectroscopic data of 6 and 9 agree with those previously reported for these compounds, while all data obtained for the new species 5, 7, 8, and 10 fulfill our expectations and require no further discussion.

In order to prepare ferrocenophanes, we reacted  $[Fe(\eta^5-C_5H_4Li)_2]$ ·tmeda (3; tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) with the 1,3-dichlorotrisilanes 8–10 in metathesis reactions. The novel compound 11 was obtained as a dark orange oil in 51% yield (Figure 2). The <sup>1</sup>H NMR spectrum in



 $C_6D_6$  shows two signals for the Cp protons at 4.18 and 4.06 ppm as well as a triplet signal at 1.16 ppm and a multiplet signal at 0.94 ppm for the ethyl protons and a singlet signal at 0.33 ppm for the methyl groups. The signals indicate an integration ratio of 4:4:6:4:12. The signals of the silicon atoms attached to the Cp rings can be detected in the <sup>29</sup>Si NMR signal at -21.24 ppm, while the signal for the central silicon nucleus appears at -19.13 ppm.

In contrast to the oily product **11**, the (*tert*-butyl)methyl- and diisopropyl-substituted compounds **12** and **13** were obtained as orange powders in 41% and 30% yields. Crystals suitable for a single-crystal X-ray crystallographic analysis of **13** were grown from pentane (Figure 3).

The two different substituents at the central silicon atom in **12** reduce the overall symmetry of the molecule, which leads to further splitting of the proton resonances of the Cp rings. In the <sup>1</sup>H NMR spectrum two signals appear at 4.18 and 4.16 ppm that integrate to two protons each and a third signal at 4.03 ppm that integrates to four protons. The former two resonances can presumably be ascribed to the protons in a position  $\alpha$  to the trisila bridge. Additionally, the nine *tert*-butyl protons result in a signal at 1.11 ppm, while the diastereotopic methyl groups of the SiMe<sub>2</sub> moieties display two independent



**Figure 3.** Two views of the molecular structure of **13** in the crystal (ellipsoids depicted at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 = 2.3581(7), Si2–Si3 = 2.3575(8), Si1–C<sub>ipso</sub> = 1.867(2), Si3–C'<sub>ipso</sub> = 1.872(2), Si1–C<sub>M</sub> = 1.877(2) and 1.886(2), Si3–C'<sub>M</sub> = 1.878(2) and 1.879(2), Si2–C<sub>iPr</sub> = 1.908(2) and 1.911(2); Si1–Si2–Si3 = 104.66(3), C<sub>ipso</sub>–Si1–Si2 = 113.37(5), C'<sub>ipso</sub>–Si3–Si2 = 113.49(6).

signals at 0.42 and 0.41 ppm, respectively. Finally, the signals of the three methyl protons at the central silicon atom were found at 0.30 ppm. The <sup>29</sup>Si NMR spectrum exhibits a pattern similar to that of **11**, showing a signal at -21.50 ppm for the dimethyl-substituted silicon atoms and at -23.05 ppm for the *tert*-butylmethyl-substituted silicon center.

The <sup>1</sup>H NMR of **13** shows two multiplet signals at 4.18 and 4.08 ppm for the cyclopentadienyl protons, as well as a septet signal at 1.20 and a doublet signal at 1.28 ppm for the isopropyl groups, respectively, and a singlet at 0.40 ppm for the methyl groups. The separation of the Cp proton resonances observed for these species is much smaller than in similar systems, for instance the highly distorted [1]boraferrocenophanes,<sup>17</sup> thus indicating significantly less strained molecular structures. Further proof for this assumption is provided by the results of the X-ray crystallographic analyses.

Complex 13 crystallizes in the orthorhombic space group  $Pna2_1$ . With a relatively small tilt angle  $\alpha$  of  $-4.9^\circ$ , the ipso carbon atoms are slightly bent away from the iron center and Cp rings deviate little from a mutually parallel orientation. In particular, the latter finding indicates that the [3]-silaferrocenophane 13 adopts the typical structure of a nonstrained ansa complex.<sup>2a</sup> The outer silicon atoms are slightly bent out of the plane of their corresponding cyclopentadienyl rings (5.3°). The ring-ring distance (3.297)

Å) and the silicon–silicon distances (2.357(1) and 2.358(1) Å) are similar to those of the tetramethyl[2]silaferrocenophane.<sup>16</sup>

Subsequently, this protocol was successfully extended to the heavier group 8 metals. In our studies we observed that the 1,1'-dilithio-substituted ruthenocene and osmocene can be prepared in higher yields when the lithiation is carried out in the presence of pmdta (pmdta =  $N_1N_1N'_1N'_1N'_2$ -pentamethyldiethylenetriamine) rather than the commonly employed tmeda (vide supra). Therefore, ruthenocene and osmocene were suspended in pentane, and pmdta was added subsequently. After a few minutes, n-butyllithium was added to the suspension and the mixture was stirred overnight to give off-white dilithium salts. The 1,1'-dilithioruthenocene 14 and the 1,1'-dilithioosmocene 15 are air- and moisture-sensitive solids but can be stored under an argon atmosphere at room temperature without signs of decomposition. These species were added to the trisilane 9, dissolved in an aromatic or aliphatic solvent, and the resulting suspension was stirred for 1 day at ambient temperature to give the first trisilaruthenocenophane and the first trisilaosmocenophane complexes after workup in yields of 42% (16) and 32% (17) as light brown oils (Figure 4).



Figure 4. Trisilaruthenocenophane 16 and trisilaosmocenophane 17.

While the oily consistency of the new [3]silametallocenophanes prevented their characterization by Xray crystallographic analyses, their structure in solution was unambiguously derived from multinuclear NMR spectroscopy. In the <sup>1</sup>H NMR spectrum, the trisilaruthenocenophane 16 shows two signals for the Cp protons at 4.62 and 4.47 ppm, a septet at 1.34 ppm and a multiplet at 1.22 ppm for the *i*Pr protons, and a singlet at 0.40 ppm for the methyl protons. The osmocenophane 17 shows signals at 4.62, 4.48, 1.36, 1.23, and 0.40 ppm which are similar to those of 16. The signals of both compounds integrate to 4:4:2:12:12. The rather small separation of the Cp signals by 0.15 ppm can be compared to the separation of the Cp protons in 13 (0.10 ppm) and indicates a rather small strain of the bridge. While the signals in the <sup>29</sup>Si NMR spectrum for the outer silicon atom (-20.8 ppm for 16 and -20.9 ppm for 17) are similar to the corresponding signals in 13 (-21.0 ppm), the signals for the central silicon atoms (-12.2 ppm (16) and -12.4 ppm (17)) show an upfield shift of more than 5 ppm with respect to that for the corresponding ferrocenophane 13 (-17.5 ppm).

#### 3. SUMMARY

In this paper we have reported the improved synthesis of 1,3diphenyltrisilanes 5-7 and their conversion to the 1,3dichlorotrisilanes 8-10. Their reaction with a 1,1'-dilithioferrocene-tmeda adduct (3) led to the trisila-bridged ferrocenophanes 11-13. Compound 13 was crystallographically characterized to give the first solid-state molecular structure of a trisilaferrocenophane. The pmdta adduct of 1,1'dilithioruthenocene-pmdta adduct 14 as well as the 1,1'- dilithioosmocene—pmdta adduct **15** have been synthesized and used as starting materials for synthesis of the first trisila-bridged ruthenocenophane **16** and osmocenophane **17**.

#### 4. EXPERIMENTAL SECTION

All experiments were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glovebox. Solvents were dried according to standard procedures, freshly distilled prior to use, degassed, and stored under argon over activated molecular sieves (4 Å). Deuterated solvents were degassed by three freeze-pumpthaw cycles and stored over molecular sieves. The starting material  $[Fe(\eta^5-C_5H_4Li)_2$ ·tmeda] (3) was prepared according to published methods;  $[Ru(\eta^5-C_5H_5)_2]$  and  $[Os(\eta^5-C_5H_5)_2]$  were purchased from ABCR and used without further purification. All other compounds were obtained commercially and used without further purification. NMR spectra were recorded on a Bruker AMX 400 or a Bruker Avance 500 NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to external TMS via the residual protio solvent (<sup>1</sup>H) or the solvent itself (13C). 29Si{1H} NMR spectra were referenced to external TMS. Assignments were made from the analysis of  ${}^{1}\text{H}, {}^{13}\text{C-HMQC}$ and <sup>1</sup>H, <sup>1</sup>H-COSY NMR spectroscopic experiments. All chemical shifts are reported in ppm. Elemental analyses were performed on a Vario Micro Cube (Elementar Analysensysteme GmbH) or a CHNS-932 (Leco) elemental analyzer.

**Et<sub>2</sub>Si(PhMe<sub>2</sub>Si)<sub>2</sub> (5).** Into a suspension of 0.907 g (13.2 mmol) of powdered lithium in 40 mL of thf at 0 °C, 10.87 g (63.7 mmol) of PhMe<sub>2</sub>SiCl was dropped over the course of 1 h. After 2 days at ambient temperature the unreacted lithium was removed over Celite, the remaining solution was cooled to 0 °C, and 5.00 g (31.8 mmol) of Et<sub>2</sub>SiCl<sub>2</sub> in 20 mL of thf was added at 0 °C. After 1 day at room temperature the solvent was removed, the residue was dissolved in 40 mL of hexane, and the salts were removed by filtration. After distillation at 115 °C under high vacuum, **5** was obtained as a colorless liquid in 72% yield (8.26 g, 23.2 mmol).

<sup>1</sup>H NMR (501 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 7.37 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.28 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 0.94 (m, 6H, Et), 0.75 (m, 4H, Et), 0.31 (s, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 140.72, 134.25, 128.60, 128.02, 10.18, 2.61, -1.77. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ -19.0, -37.4. Anal. Calcd for C<sub>20</sub>H<sub>32</sub>Si<sub>3</sub> (356.73): C, 67.34; H, 9.04. Found: C, 67.05; H, 8.65.

 $Et_2Si(Me_2SiCl)_2$  (8). A solution of 8.26 g (23.2 mmol) 5 in 75 mL of hexane was reacted with 4.54 g (57.9 mmol) of acetyl chloride at -78 °C. Afterward 7.72 g (57.9 mmol) of AlCl<sub>3</sub> was added and the reaction mixture was warmed to room temperature. After 16 h the solution was filtered and the hexane was removed. Distillation at 75 °C under high vacuum yielded 5.70 g (20.8 mmol, 90%) of 8 as a colorless liquid.

<sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>, 297 K): δ 1.10 (m, 6H, Et), 0.93 (m, 4H, Et), 0.59 (m, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 9.78, 4.55, 1.54. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ -25.6, -34.0. Anal. Calcd for C<sub>8</sub>H<sub>22</sub>Cl<sub>2</sub>Si<sub>3</sub> (273.42): C, 35.14; H, 8.11. Found: C, 34.90; H, 8.01.

*i*Pr<sub>2</sub>Si(PhMe<sub>2</sub>Si)<sub>2</sub> (6). A suspension of 0.850 g (12.5 mmol) of powdered lithium in 40 mL of thf at 0 °C was treated with 10.0 g (58.8 mmol) of Me<sub>2</sub>PhSiCl over the course of 1 h. After it was stirred for 16 h, the suspension was filtered over Celite and added dropwise to a solution of 5.43 g (29.4 mmol) of *i*Pr<sub>2</sub>SiCl<sub>2</sub> in 70 mL of thf. After another 16 h of stirring, all volatile components were removed under vacuum. The residue was suspended in 20 mL of hexane and filtered. Removal of the solvent and distillation at 160 °C resulted in 10.1 g (26.2 mmol, 90%) of 6 of a colorless oil.

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 7.34 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.22 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 1.16 (sept, <sup>3</sup>*J* = 7.7 Hz, 2H, *i*Pr), 0.93 (d, 12H, <sup>3</sup>*J* = 7.7 Hz, *i*Pr), 0.34 (s, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 140.96, 134.32, 128.42, 127.82, 21.06, 12.78, 0.04. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ -19.1, -27.8. Anal. Calcd for C<sub>22</sub>H<sub>36</sub>Si<sub>3</sub> (384.8): C, 68.67; H, 9.43. Found: C, 68.96; H, 9.57.

 $iPr_2Si(Me_2SiCl)_2$  (9). A 10.79 g amount (26.2 mmol) of 6 in 60 mL of hexane at -70 °C was first treated with 4.79 g (61.4 mmol) of acetyl

chloride and afterward with 9.07 g (68.0 mmol) of AlCl<sub>3</sub>. After 20 h of stirring at room temperature, the solid compounds were filtered off and the solvent was removed under vacuum at 0 °C. After distillation under high vacuum at 40 °C, 6.84 g (25.0 mmol, 84%) of the product was obtained as an oily colorless solid.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 297 K): δ 1.34 (sept, 2H, <sup>3</sup>*J* = 7.5 Hz, *i*Pr), 1.20 (d, 12H, <sup>3</sup>*J* = 7.5 Hz, *i*Pr), 0.65 (m, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 20.65, 11.96, 5.89. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K): δ 25.5, -25.5. Anal. Calcd for C<sub>8</sub>H<sub>22</sub>Cl<sub>2</sub>Si<sub>3</sub> (273.42): C, 35.14; H, 8.11. Found: C, 34.90; H, 8.01.

**tBuMeSi(PhMe<sub>2</sub>Si)**<sub>2</sub> (7). A suspension of 0.831 g (12.2 mmol) of powdered lithium in 40 mL of thf was added to 10.00 g (58.8 mmol) of Me<sub>2</sub>PhSiCl at 0 °C. After 16 h at room temperature, the suspension was filtered over Celite, cooled to 0 °C, and added dropwise to a solution of 5.00 g (27.2 mmol) of tBuMeSiCl<sub>2</sub> in 70 mL of thf. After 16 h the volatile compounds were removed under vacuum. Hexane (60 mL) was added, and the solids were removed by filtration. Kugelrohr distillation at 210 °C under high vacuum yielded 9.25 g (25.0 mmol, 85%) of the product as a colorless liquid.

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K) δ 7.392–7.422 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.322–7.283 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 0.81 (s, 9H, tBu), 0.37 (s, 6H, Me), 0.29 (s, 6H, Me), 0.20 (s, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CDCl<sub>3</sub>, 297 K): δ 140.68, 134.15, 128.44, 127.83, 29.73, 20.00, -1.31, -1.44, -8.79. <sup>29</sup>Si{<sup>1</sup>H} NMR (99.360 MHz, CDCl<sub>3</sub>, 297 K): δ -19.4, -31.5. Anal. Calcd for C<sub>21</sub>H<sub>34</sub>Si<sub>3</sub> (370.2): C, 68.03; H, 9.24; Si, 22.73. Found: C, 68.14; H, 9.38.

tBuMeSi(Me<sub>2</sub>SiCl)<sub>2</sub> (10). A solution of 7.83 g (21.2 mmol) of 7 in 60 mL of hexane was reacted first with 3.41 mL (3.75 g, 47.8 mmol) of acetyl chloride at -70 °C and then with 7.10 g (53.3 mmol) of AlCl<sub>3</sub>. After the mixture was warmed to room temperature and stirred for 40 h, the solution was filtered off and the solvent was removed at 0 °C. After distillation at 51 °C under high vacuum, 0.21 g (0.73 mmol, 20%) of 10 was obtained as a colorless liquid.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 297 K):  $\delta$  1.10 (s, 12H, *t*Bu), 0.61 (s, 12H, Me), 0.28 (s, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 297 K):  $\delta$  29.45, 19.66, 5.03, 4.94, -10.08. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>, 297 K):  $\delta$  . 25.3, -28.8. Anal. Calcd for C<sub>9</sub>H<sub>24</sub>Cl<sub>2</sub>Si<sub>3</sub> (287.4): C, 37.61; H, 8.42. Found: C, 38.01; H, 8.35.

 $[Fe(C_5H_4SiMe_2)_2SiEt_2]$  (11). To a solution of 0.50 g (1.6 mmol) of 3 in 20 mL of thf was slowly added 0.36 g (1.3 mmol) of Et<sub>2</sub>Si(Me<sub>2</sub>SiCl)<sub>2</sub> (8). After 16 h, the thf was removed under high vacuum, 20 mL of pentane was added, and the solid compounds were removed by filtration. The pentane was removed under high vacuum and the product purified by Kugelrohr distillation at 120 °C under high vacuum. A 0.31 g amount (0.80 mmol, 51%) of 11 as an orange-brown oil was obtained.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 4.18 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.06 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 1.17 (t, 6H, <sup>3</sup>J = 8.1 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.94 (q, 4H, <sup>3</sup>J = 8.1 Hz, CH<sub>2</sub>CH<sub>3</sub>), 0.33 (s, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 73.75, 72.34, 70.76, 10.68, 2.78, -0.94. <sup>29</sup>Si{<sup>1</sup>H} NMR (79 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ -19.1, -21.2. Anal. Calcd for C<sub>18</sub>H<sub>30</sub>FeSi<sub>3</sub> (386.53): C, 55.93; H, 7.82. Found: C, 56.80; H, 7.62.

[Fe( $C_5H_4SiMe_2$ )<sub>2</sub>SiMetBu] (12). A 0.25 g amount (0.73 mmol) of 3 was dissolved in 15 mL of thf and treated with 0.21 g (0.73 mmol) of tBuMeSi( $Me_2SiCl$ )<sub>2</sub> (10) over the course of 1 h. After 16 h, the solvent was removed under high vacuum, the residue was treated with 10 mL of hexane, and the solid compounds were removed by filtration. After removal of the solvent, the product was purified by column chromatography on silica using hexane to give 0.12 mg (0.30 mmol, 41%) of an orange powder.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 4.18 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.16 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.04 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 1.11 (s, 9H, fBu), 0.42 (s, 6H, Me), 0.41 (s, 3H, Me), 0.30 (s, 6H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 74.25, 73.31, 71.67, 71.38, 70.31, 30.12, 20.07, 0.03, -0.73, -8.58. <sup>29</sup>Si{<sup>1</sup>H} NMR (79 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ -21.5, -23.1. Anal. Calcd for C<sub>19</sub>H<sub>32</sub>FeSi<sub>3</sub> (400.60): C, 56.97; H, 8.05. Found: C, 57.29; H, 8.16.

 $[Fe(C_5H_4SiMe_2)_2Si/Pr_2]$  (13). A solution of 0.44 g (1.5 mmol)  $iPr_2Si(Me_2SiCl)_2$  in 5 mL of thf was added to a solution of 0.55 g (1.8 mmol) of 3 in 15 mL of thf at 0 °C. After 16 h the solvent was removed and the residue was extracted with 10 mL of hexane. The solvent was again removed, and the crude product was sublimed at 105  $^{\circ}$ C under high vacuum to yield 0.21 g (0.51 mmol, 30%) of an orange powder.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 4.18 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.08 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 1.28 (sept,, 2H, <sup>3</sup>J = 6.4 Hz, *i*Pr), 1.20 (d, 12H, <sup>3</sup>J = 6.4 Hz, *i*Pr), 0.401 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 73.95, 72.22, 70.89, 22.29, 13.12, 0.75. <sup>29</sup>Si{<sup>1</sup>H} NMR (79 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ -17.5, -21.0. Anal. Calcd for C<sub>20</sub>H<sub>34</sub>FeSi<sub>3</sub> (414.59): C, 57.94; H, 8.27. Found: C, 57.51; H, 8.31.

 $[Ru(C_5H_4Li)_2]$ -pmdta (14). A suspension of 1.00 g (4.33 mmol) of ruthenocene and 2.26 mL (10.8 mmol) of pmdta in 35 mL of pentane was stirred for 1 h. Afterward, 6.76 mL (10.8 mmol, 1.57 M in hexane) of *n*-butyllithium was added dropwise at 0 °C. After 12 h of stirring, the solid product was collected on a glass frit, washed with 3 × 7 mL of pentane, and dried under high vacuum. A 1.70 g amount (4.07 mmol, 94%) of a white powder was obtained.

Anal. Calcd for  $C_{19}H_{31}Li_2N_3Ru$  (417.2): C, 54.80; H, 7.50; N, 10.09. Found: C, 54.59; H, 7.44; N, 10.36.

 $[Ru(C_5H_4SiMe_2)_2SiiPr_2]$  (16). In a J. Young NMR tube, 77 mg (0.18 mmol) of 14 in 0.8 mL of  $C_6D_6$  was reacted with 70 mg of  $iPr_2Si(Me_2SiCl)_2$  (9; 0.18 mmol). After 1 day, all solid compounds were removed by filtration and the solvent was removed under high vacuum. After 3 h under high vacuum at 70 °C, 36 mg (0.078 mmol, 42%) of a light brown oil was obtained.

<sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 293 K):  $\delta$  4.62 (m, 4H,  $C_5H_4$ ), 4.47 (m, 4H,  $C_5H_4$ ), 1.34 (sept, 2H, <sup>3</sup>*J* = 6.8 Hz, *i*Pr), 1.22 (d, 12H, <sup>3</sup>*J* = 6.8 Hz, *i*Pr), 0.396 (s, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $C_6D_6$ , 293 K):  $\delta$  76.07, 75.04, 72.88, 22.40, 13.32, 0.99. <sup>29</sup>Si{<sup>1</sup>H} NMR (79 MHz,  $C_6D_6$ , 293 K):  $\delta$  –12.2, –20.8. Anal. Calcd for  $C_{20}H_{34}RuSi_3$  (459.80): C, 52.24; H, 7.45. Found: C, 51.55; H, 7.72.

 $[Os(C_5H_4Li)_2]$ -pmdta (15). A 0.57 g amount (1.8 mmol) of osmocene was stirred with 0.93 mL (4.5 mmol) of pmdta in 30 mL of pentane over the course of 1 h. Then, 2.60 mL (1.6 mmol, 1.57 M in hexane) of *n*-butyllithium was added at 0 °C. After 1 h in an ultrasound bath and 5 h of stirring, the solid compound was collected on a frit and washed with 3 × 5 mL of pentane. After drying under high vacuum, 0.86 g (1.7 mmol, 95%) of an off-white powder was obtained.

Anal. Calcd for  $C_{19}H_{31}Li_2N_3Os$  (507.2): C, 45.14; H, 6.18; N, 8.31. Found: C, 46.06; H, 6.46; N, 8.51.

 $[Os(C_5H_4SiMe_2)_2SiiPr_2]$  (17). A suspension of 0.10 g (0.29 mmol) of 15 in 10 mL of hexane was reacted with 70 mg (0.27 mmol) of  $iPr_2Si(Me_2SiCl)_2$  in 5 mL of hexane over the course of 1 h. After 28 h of stirring, the salts and the solvent were removed and the product was purified by sublimation of the osmocene at 100 °C under vacuum to yield 35 mg (0.063 mmol, 19%) of a slightly brown oil.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 4.62 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.47 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 1.35 (sept, 2H, <sup>3</sup>*J* = 6.4 Hz, *i*Pr), 1.23 (d, 12H, <sup>3</sup>*J* = 6.4 Hz, *i*Pr), 0.40 (s, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 75.03, 72.86, 70.43, 22.36, 13.30, 0.95. <sup>29</sup>Si{<sup>1</sup>H} NMR (79 MHz, C<sub>6</sub>D<sub>6</sub>): δ -12.4, -20.9. Anal. Calcd for C<sub>20</sub>H<sub>34</sub>OsSi<sub>3</sub> (549.0): C, 43.76; H, 6.24. Found: C, 43.81, H, 6.32.

**Crystal Structure Determination.** The crystal data of **13** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multilayer mirror monochromated Mo K $\alpha$  radiation. The structure was solved using direct methods, refined with the Shelx software package, and expanded using Fourier techniques.<sup>18</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystal data for 13:  $C_{20}H_{34}$ FeSi<sub>3</sub>,  $M_r = 414.59$ , yellow block, 0.496 × 0.407 × 0.222 mm<sup>3</sup>, orthorhombic, space group *Pna2*<sub>1</sub>, a = 18.704(5) Å, b = 13.274(4) Å, c = 8.821(4) Å, V = 2190.1(13) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.257$  g cm<sup>-3</sup>,  $\mu = 0.853$  mm<sup>-1</sup>, F(000) = 888, T = 100(2) K, R1 = 0.0169, wR2 = 0.0438, 4269 independent reflections ( $2\theta \le 5212^{\circ}$ ), 225 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-887330. These data can be obtained free of charge from

#### **Organometallics**

The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data request/cif.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

A CIF file giving X-ray diffraction data for **13** and figures giving <sup>1</sup>H NMR spectra of **11** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) (a) Kealy, T. J.; Pauson, P. L. Nature 1951, 168, 1039–1040.
(b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. J. Chem. Soc. 1952, 632–635.

(2) (a) Rinehart, K. L., Jr.; Curby, R. J., Jr. J. Am. Chem. Soc. 1957, 79, 3290–3291. (b) Jones, N. D.; Marsh, R. E.; Richards, J. H. Acta Crystallogr. 1965, 19, 330–336.

(3) (a) Foucher, D. A.; Tang, B.-Z.; Manners, I. J. Am. Chem. Soc.
1992, 114, 6246-6248. (b) Manners, I. Polyhedron 1996, 15, 4311-4329. (c) Nguyen, P.; Gómez-Elipe, P.; Manners, I. Chem. Rev. 1999, 99, 1515-1548. (d) Manners, I. Chem. Commun. 1999, 857-865. (e) Herbert, D. E.; Mayer, U. F. J.; Manners, I. Angew. Chem., Int. Ed. 2007, 46, 5060-5081.

(4) (a) Tamm, M. Chem. Commun. 2008, 3089–3100. (b) Braunschweig, H.; Fuß, M.; Mohapatra, S. K.; Kraft, K.; Kupfer, T.; Lang, M.; Radacki, K.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. Chem. Eur. J. 2010, 16, 11732–11743. (c) Braunschweig, H.; Fuß, M.; Kupfer, T.; Radacki, K. J. Am. Chem. Soc. 2011, 133, 5780–5783.

(5) (a) Elschenbroich, C.; Bretschneider-Hurley, A.; Hurley, J.; Behrendt, A.; Massa, W.; Wocadlo, S.; Reijerse, E. *Inorg. Chem.* **1995**, *34*, 743–745. (b) Braunschweig, H.; Lutz, M.; Radacki, K.; Schaumloeffel, A.; Seeler, F.; Unkelbach, C. *Organometallics* **2006**, *25*, 4433–4435. (c) Adams, C. J.; Braunschweig, H.; Fuß, M.; Kraft, K.; Kupfer, T.; Manners, I.; Radacki, K.; Whittell, G. R. *Chem. Eur. J.* **2011**, *17*, 10379–10387.

(6) (a) Elschenbroich, C.; Paganelli, F.; Nowotny, M.; Neumueller, B.; Burghaus, O. Z. Anorg. Allg. Chem. 2004, 630, 1599–1606.
(b) Braunschweig, H.; Lutz, M.; Radacki, K. Angew. Chem. 2005, 117, 5792–5796; Angew. Chem., Int. Ed. 2005, 44, 5647–5651.
(c) Braunschweig, H.; Kupfer, T.; Lutz, M.; Radacki, K. J. Am. Chem. Soc. 2007, 129, 8893–8906.

(7) Braunschweig, H.; Kupfer, T.; Radacki, K. Angew. Chem. 2007, 119, 1655–1658; Angew. Chem., Int. Ed. 2007, 46, 1630–1633.

(8) (a) Drewitt, M. J.; Barlow, S.; O'Hare, D.; Nelson, J. M.; Nguyen, P.; Manners, I. Chem. Commun. 1996, 2153–2154. (b) Fox, S.; Dunne, J. P.; Tacke, M.; Schmitz, D.; Dronskowski, R. Eur. J. Inorg. Chem. 2002, 3039–3046. (c) Cheng, A. Y.; Clendenning, S. B.; Manners, I. Macromol. Containing Met. Met.-Like Elem. 2006, 6, 49–58. (d) Braunschweig, H.; Breher, F.; Kaupp, M.; Gross, M.; Kupfer, T.; Nied, D.; Radacki, K.; Schinzel, S. Organometallics 2008, 27, 6427–6433.

(9) (a) Eilbracht, P. Chem. Ber. 1976, 109, 3136-3141.
(b) Buchowicz, W.; Jerzykiewicz, L. B.; Krasinska, A.; Losi, S.; Pietrzykowski, A.; Zanello, P. Organometallics 2006, 25, 5076-5082.
(c) Braunschweig, H.; Gross, M.; Radacki, K. Organometallics 2007, 26, 6688-6690.

(10) (a) Herberhold, M.; Baertl, T. Z. Naturforsch., B: Chem. Sci. **1995**, 50, 1692–1698. (b) Vogel, U.; Lough, A. J.; Manners, I. Angew. Chem., Int. Ed. **2004**, 43, 3321–3325. (c) Schachner, J. A.; Tockner, S.; Lund, C. L.; Quail, J. W.; Rehahn, M.; Müller, J. Organometallics **2007**, 26, 4658–4662. (d) Bagh, B.; Schatte, G.; Green, J. C.; Müller, J. J. Am. Chem. Soc. **2012**, 134, 7924–7936.

(11) (a) Abel, E. W.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Sik, V. J. Organomet. Chem. 1991, 419, 375–382. (b) Gusev, O. V.; Kalsin, A. M.; Petrovskii, P. V.; Lyssenko, K. A.; Oprunenko, Y. F.; Bianchini, C.; Meli, A.; Oberhauser, W. Organometallics 2003, 22, 913–915. (c) Bianchini, C.; Meli, A.; Oberhauser, W.; Parisel, S.; Gusev, O. V.; Kal'sin, A. M.; Vologdin, N. V.; Dolgushin, F. M. J. Mol. Catal. A: Chem. 2004, 224, 35–49. (d) Gusev, O. V.; Peganova, T.; Kal'sin, A. M.; Vologdin, N. V.; Lyssenko, K. A.; Tsvetkov, A. V.; Beletskaya, I. P. Organometallics 2006, 25, 2750–2760. (e) Martinak, S. L.; Sites, L. A.; Kolb, A. J.; Bocage, K. M.; McNamara, W. R.; Rheingold, A. L.; Golen, J. A.; Nataro, C. J. Organomet. Chem. 2006, 691, 3627–3632.

(12) (a) Kamiyama, S.; Suzuki, T. M.; Kimura, T.; Kasahara, A. Bull. Chem. Soc. Jpn. **1978**, *51*, 909–912. (b) Ohba, S.; Saito, Y.; Kamiyama, S.; Kasahara, A. Acta Crystallogr., Sect. C **1984**, *40*, 53–55.

(13) Kumada, M.; Kondo, T.; Mimura, K.; Ishikawa, M.; Yamamoto, K.; Ikeda, S.; Kondo, M. J. Organomet. Chem. **1972**, 43, 293–305.

(14) Wagner, H.; Baumgartner, J.; Marschner, C. Organometallics 2007, 26, 1762–1770.

(15) Russell, A. G.; Guveli, T.; Kariuki, B. M.; Snaith, J. S. J. Organomet. Chem. 2009, 694, 137–141.

(16) Finckh, W.; Tang, B. Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993**, *12*, 823–829.

(17) Braunschweig, H.; Dirk, R.; Müller, M.; Nguyen, P.; Resendes, R.; Gates; Manners, I. Angew. Chem. 1997, 109, 2433–2435; Angew. Chem., Int. Ed. 1997, 36, 2338–2340.

(18) Sheldrick, G. Acta Crystallogr. 2008, A64, 112-122.

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