

# Notes

## 1,1'-Bis(tri-*n*-butylstannyl)ferrocene: Selective Transmetalation Applied to the Synthesis of New Ferrocenyl Ligands

Michael E. Wright

Department of Chemistry and Biochemistry  
Utah State University, Logan, Utah 84322-0300

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**Summary:** Selective transmetalation of one tri-*n*-butylstannyl group of  $[\eta^5\text{-(Bu}_3\text{Sn)C}_5\text{H}_4]_2\text{Fe}$  (**1**) with 1 molar equiv of *n*-BuLi, followed by treatment with  $\text{Ph}_2\text{PCl}$  or *N,N*-dimethylformamide, produced 1-(tri-*n*-butylstannyl)-1'-(diphenylphosphino)ferrocene (**3**) and 1'-(tri-*n*-butylstannyl)-1-ferrocenecarboxaldehyde (**8**), respectively. Compound **8** was converted to 1'-(tri-*n*-butylstannyl)-1-[(dimethylamino)methyl]ferrocene (**9**) by reductive amination with dimethylamine and sodium cyanoborohydride. Subsequent treatment of **3** or **9** with 1 molar equiv of *n*-BuLi resulted in selective transmetalation of the tri-*n*-butylstannyl group. The selective transmetalation was utilized to prepare new ferrocenylphosphine ligands.

Since the discovery of ferrocene nearly four decades ago the compound has displayed a variety of intriguing and useful forms of chemical reactivity.<sup>1</sup> Lithiation of the cyclopentadienyl (Cp) ring has provided key intermediates for the elaboration of the ferrocene unit.<sup>2</sup> Similar methodology has been extended to other Cp transition-metal systems<sup>3</sup> and  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  compounds.<sup>4</sup>

Selected examples of lithiated ferrocenes are shown in Chart I.<sup>2k,5-7</sup> Treatment of the lithiated ferrocenes with  $\text{R}_2\text{PCl}$  has produced phosphine and bis(phosphino) ligands that have proved valuable in a number of transition-metal-catalyzed reactions.<sup>8</sup> In addition, Cullen and Butler have recently carried out an interesting study on the lithiation of phosphinoferrocene systems.<sup>9</sup>

The transmetalation reaction of the tri-*n*-butylstannyl group, originally developed by Seyferth and co-workers, is a very clean and efficient method for the preparation of vinyl- and allyllithium compounds.<sup>10</sup> This methodology was recently extended to the synthesis of  $(\eta^6\text{-1,3-dilithiobenzene})$ - and  $(\eta^6\text{-1,4-dilithiobenzene})\text{Cr}(\text{CO})_3$  complexes.<sup>11</sup> The present study demonstrates that *selective transmetalation* of the title compound permits the stepwise functionalization of the Cp rings of ferrocene, which ultimately leads to new ferrocenyl ligands.

## Results and Discussion

Treatment of **1**<sup>12</sup> with 1 molar equiv of *n*-BuLi in THF solution for 30 min, followed by reaction with diphenylchlorophosphine, produced complex **3**. Subsequent treatment of **3** with *n*-BuLi (1.0 molar equiv), followed by reaction with dimethylformamide, afforded compound **5** in 90% isolated yield (Scheme I). The lithio complex **4** was first prepared by Seyferth and Withers through nucleophilic ring opening of (1,1'-ferrocenediyl)phenylphosphine with phenyllithium (~10-fold excess).<sup>5</sup>

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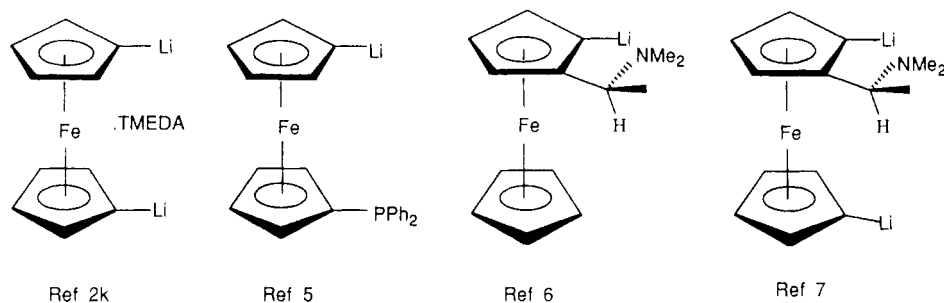
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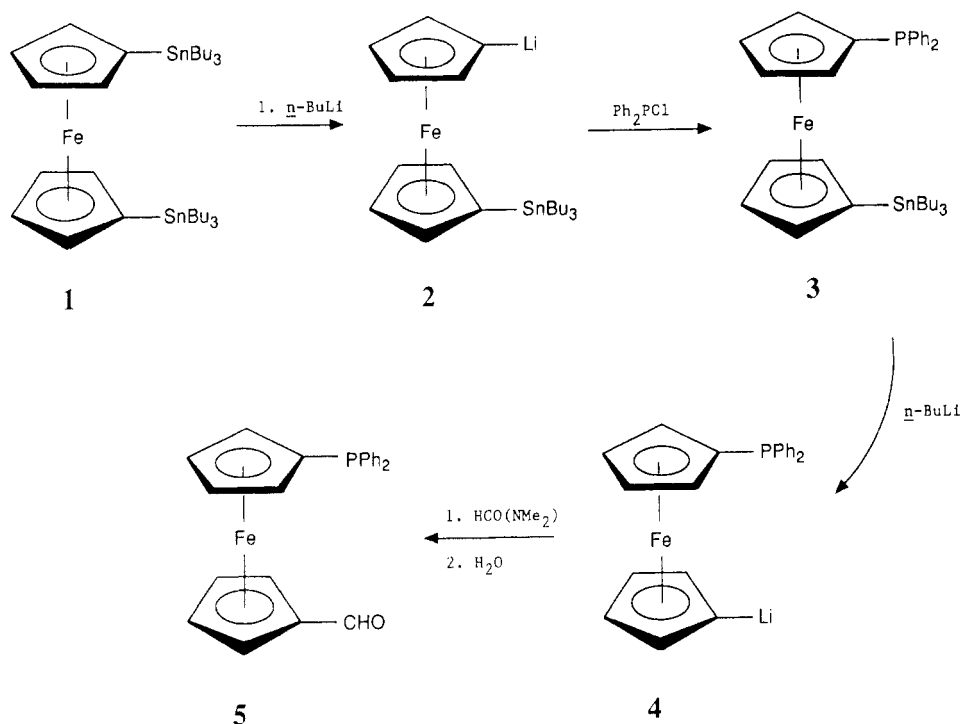
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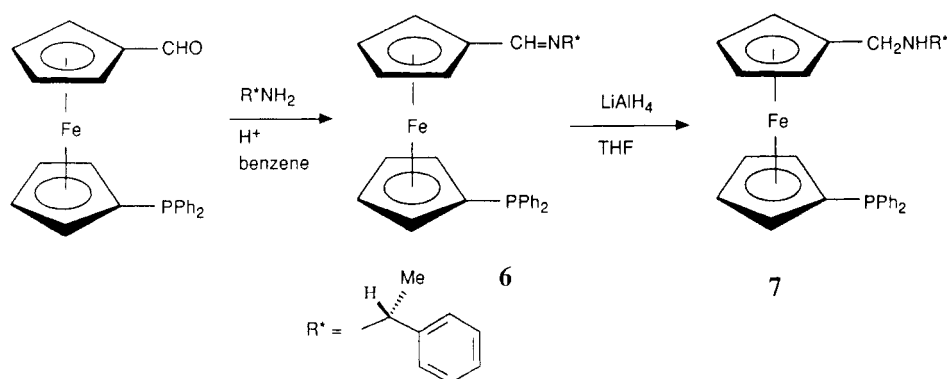
Chart I



Scheme I



Scheme II



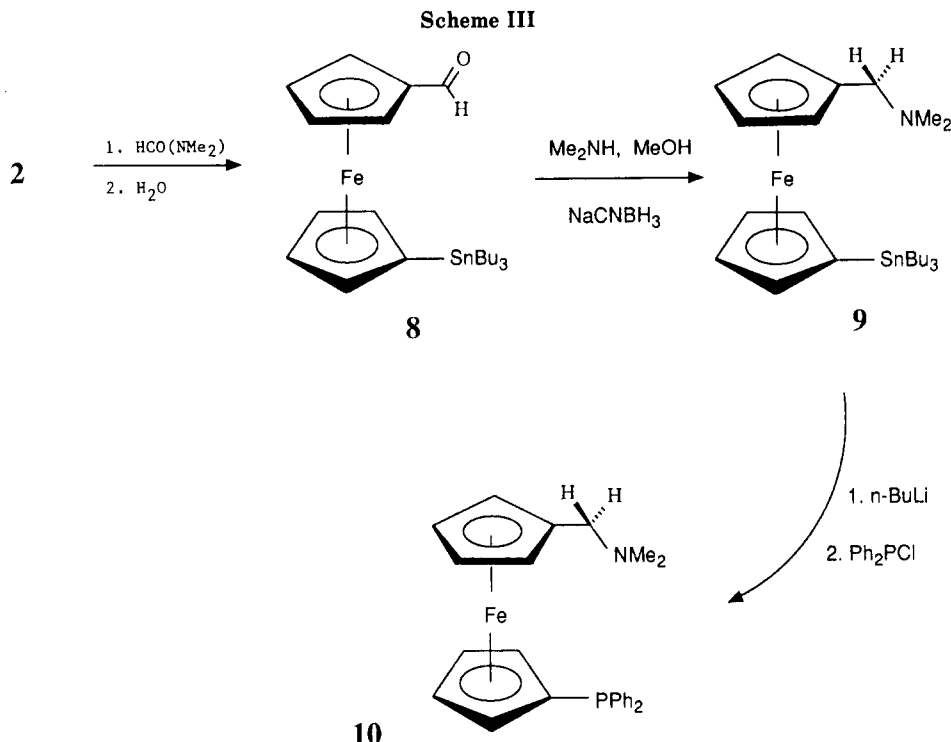
Treatment of 5 with (*R*)-methylbenzylamine produced the imine 6, which was isolated as a red oil. The imine could not be crystallized and decomposed on chromatographic supports. The compound was characterized spectroscopically and determined to be of sufficient purity for subsequent reaction. Treatment of 6 with LiAlH<sub>4</sub> afforded the new chiral complex 7 in over 80% isolated yield (Scheme II).

The further utility of the selective transmetalation is shown by the synthesis of 8, which is easily converted to the dimethylamino complex 9 by reductive amination (Scheme III).<sup>13</sup> The reaction sequence demonstrates the

ability of the tri-*n*-butylstannyl moiety to withstand fairly acidic reaction conditions. Treatment of 9 with 1 molar equiv of *n*-BuLi gave regioselective transmetalation of the tri-*n*-butylstannyl group, thus permitting selective functionalization.

We briefly explored the possibility of utilizing 1 as a precursor for the 1,1'-dilithioferrocene. Treatment of 1 with 2.2–3.0 molar equiv of *n*-BuLi followed by a quench with methanol produced a mixture of ferrocene and 1-

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(tri-*n*-butylstannyl)ferrocene in a 3:1 molar ratio, respectively. The addition of *N,N,N',N'*-tetramethylethylenediamine did not affect the product distribution. Although excess *n*-BuLi could conceivably produce the dilithio complex in better yield, this was not explored due to the diminished synthetic value.

In conclusion, the selective transmetalation achieved in this work permits the stepwise functionalization of the ferrocene system in a manner that complements existing methodology or represents a simplified alternative to lower yield synthetic pathways. We have also established the ability of the tri-*n*-butylstannyl moiety to undergo selective transmetalation even in the presence of the dimethylamino group, which is a strongly ortho-directing group in metalation reactions.

### Experimental Section

**General Considerations.** All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.<sup>14</sup> Spectroscopic measurements utilized the following instrumentation: <sup>1</sup>H NMR, Varian XL 300; <sup>13</sup>C NMR, Varian XL 300 (at 75.4 MHz); infrared, Perkin-Elmer 1750 FT-IR spectrometer. NMR chemical shifts are reported in  $\delta$  vs Me<sub>4</sub>Si (<sup>1</sup>H), the CDCl<sub>3</sub> resonance (<sup>13</sup>C, 77.00 ppm), or external H<sub>3</sub>PO<sub>4</sub> (85%, <sup>31</sup>P, 0.0 ppm). Ferrocene, tri-*n*-butylchlorostannane, chlorodiphenylphosphine, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), (*R*)-methylbenzylamine, and *n*-BuLi (2.5 M in hexane) were purchased from Aldrich Chemical Co. and used as received. Spectroscopic grade dimethylformamide was dried over 3A sieves prior to use. Anhydrous dimethylamine was purchased from the Matheson Gas Co. and used as received. TMEDA was freshly distilled from CaH<sub>2</sub> prior to use and stored under nitrogen. 1,1'-Bis(tri-*n*-butylstannyl)ferrocene<sup>12</sup> was prepared by a modified literature procedure. Column chromatography utilized nonactivated neutral alumina (32-63) purchased from Universal Scientific. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

[ $\eta^5$ -(Bu<sub>3</sub>Sn)C<sub>5</sub>H<sub>4</sub>]<sub>2</sub>Fe (1). An ether slurry of (C<sub>5</sub>H<sub>4</sub>Li)<sub>2</sub>Fe-TMEDA<sup>2k</sup> (27 mmol) at 0 °C was treated with Bu<sub>3</sub>SnCl (18.8 g,

57 mmol) and then warmed to ambient temperature over a 6-h period. The ether layer was washed with water and brine and then dried over K<sub>2</sub>CO<sub>3</sub>. The solvent was removed to afford a crude product, which contained varying amounts of ferrocene, 1-(tri-*n*-butylstannyl)ferrocene, and 1. Compound 1 was obtained by column chromatography (the crude product, ~20 g, was divided into four samples to avoid overloading the column) on alumina (5 × 30 cm) with pentane as eluant. The first orange band (from each sample) was collected and the solvent removed to afford sufficiently pure 1 (14 g, 68% yield, ~95% purity) for the chemistry outlined below.

**1-(Tri-*n*-butylstannyl)-1'-(diphenylphosphino)ferrocene (3).** A THF (30 mL) solution containing 1 (2.5 g, 3.3 mmol) chilled to -78 °C was treated with *n*-BuLi (1.3 mL, 3.3 mmol) and stirred for an additional 30 min. The mixture was treated with Ph<sub>2</sub>PCl (0.73 g) and the cooling bath removed. The mixture was diluted with ether (100 mL) and washed with water and then brine. The organic layer was dried, and the solvents were removed under reduced pressure. The crude product was column chromatographed with hexane as eluant. The first yellow band was collected, and the solvents were removed to afford pure 3 (2.00 g, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.43–7.25 (m, 10 H), 4.28 (t, *J* = 1.7 Hz, 2 H), 4.21 (t, *J* = 1.6 Hz, 2 H), 4.04 (q, *J* = 1.8 Hz, 2 H), 3.92 (t, *J* = 1.6 Hz, 2 H), 1.62–1.40 (m, 6 H), 1.40–1.20 (m, 6 H), 0.99–0.93 (m, 6 H), 0.90 (t, *J* = 7 Hz, 9 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  139.2 (d, *J* = 20 Hz, ipso PPh<sub>2</sub>), 133.5 (d, *J* = 19 Hz), 128.4, 128.1 (d, *J* = 7 Hz), 75.4 (CpSn), 72.7 (d, *J* = 15 Hz, CpPPh<sub>2</sub>), 72.0 (CpSn), 70.8 (d, *J* = 4 Hz, CpPPh<sub>2</sub>), 29.2, 27.4, 13.8, 10.2 (butyl carbons). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  11.6. Anal. Calcd for C<sub>34</sub>H<sub>48</sub>FePSn: C, 61.95; H, 6.88. Found: C, 61.77; H, 6.80.

**1'-(Diphenylphosphino)-1-ferrocenecarboxaldehyde (5).** A THF (20 mL) solution containing 3 (1.90 g, 2.8 mmol) was treated with *n*-BuLi (1.2 mL, 3.0 mmol) and allowed to react for an additional 30 min. DMF (0.29 g, 4.0 mmol) was added to the mixture and the cooling bath removed. When the reaction mixture reached ambient temperature, it was diluted with ether (100 mL), washed with water (2 × 100 mL) and brine, and then dried over K<sub>2</sub>CO<sub>3</sub>. The solvents were removed under reduced pressure, and the crude product was recrystallized from ether/hexane to afford 5 as orange crystals (mp 146–147 °C, 1.00 g, 90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.67 (s, 1 H, CHO), 7.42–7.26 (m, 10 H, phenyl H's), 4.70 (t, *J* = 2 H, Cp), 4.48 (q, *J* = 2 Hz, 4 H, Cp), 4.20 (q, *J* = 1.8 Hz, 2 H, Cp). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  193.5 (C=O), 138.2 (d, *J* = 10 Hz, ipso Ph), 133.6 (d, *J* = 20 Hz, Ph), 128.9 (Ph), 128.3 (d, *J* = 7 Hz, Ph), 79.7 (ipso Cp), 74.4 (Cp), 74.2 (d, *J* = 14 Hz,

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$\text{CpPPh}_2$ , 72.4 (d,  $J = 3$  Hz,  $\text{CpPPh}_2$ ), 70.6 (Cp).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  12.8. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{C=O}}$  1682  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{19}\text{FeOP}$ : C, 69.37; H, 4.81. Found: C, 69.30; H, 4.86.

***N*-(1*R*)-(+)-1-Phenylethyl][1'-(diphenylphosphino)-1-ferrocenyl]methylamine (6).** A benzene (20 mL) solution containing **5** (0.50 g, 1.3 mmol), (*R*)-methylbenzylamine (0.16 g, 1.3 mmol), and camphorsulfonic acid (5 mg) was heated at 40 °C for 2 h. The solvent was removed under reduced pressure to afford crude **6** as an orange oil. This product was used in the preparation of **7** below.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.88 (s, 1 H,  $\text{CH}=\text{N}$ ), 7.42–7.26 (m, 15 H, phenyls), 4.63 (q,  $J = 1.6$  Hz, 1 H, Cp), 4.57 (q,  $J = 1.7$  Hz, 1 H, Cp), 4.32–4.24 (m, 5 H, Cp and  $\text{CHMe}$ ), 4.06–4.02 (m, 2 H, Cp), 1.50 (d,  $J = 6.6$  Hz, 3 H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  159.2 ( $\text{CH}=\text{N}$ ), 145.2 (ipso phenyl from amine), 138.8 (d,  $J = 8$  Hz, doubled due to chiral environment, ipso carbon of *PPh*), 133.4 (d,  $J = 19$  Hz), 128.8 (Ph), 128.2 (Ph), 128.2 (d,  $J = 13$  Hz, *PPh*), 126.6 (Ph), 126.5 (Ph), 81.2 (ipso Cp carbon), 73.8 (d,  $J = 15$  Hz,  $\text{CpPPh}_2$ ), 73.7 (d,  $J = 15$  Hz,  $\text{CpPPh}_2$ ), 71.9 (apparent triplet,  $J = 3$  Hz, Cp), 71.6 ( $\text{CHCH}_3$ ), 69.9 (Cp), 69.3 (d,  $J = 9$  Hz), 24.2 ( $\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  12.0.

**1'-(Diphenylphosphino)-1-[(*R*)-methylbenzylamino]-methylferrocene (7).** To a THF solution (10 mL) chilled to 0 °C containing  $\text{LiAlH}_4$  (0.10 g, 2.6 mmol) was added a THF solution (5 mL) containing **6** (0.48 g, 0.96 mmol) in one portion. The cooling bath was removed and the mixture allowed to react for 2 h. The mixture was quenched (0.1 g of  $\text{H}_2\text{O}$ , 0.1 g of 10% NaOH, 0.3 g of  $\text{H}_2\text{O}$ ), dried over  $\text{K}_2\text{CO}_3$ , and filtered, and the solvent removed under reduced pressure. The crude product was subjected to column chromatography with use of gradient elution (0% to 5% MeOH in  $\text{CH}_2\text{Cl}_2$ ). The major yellow band was collected and the solvent removed to afford **7** as an orange oil (0.40 g, 83%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.32–7.25 (m, 15 H, phenyls), 4.26 (t,  $J = 1.8$  Hz, 2 H, Cp), 4.06 (t,  $J = 1.8$  Hz, 2 H, Cp), 4.04–3.96 (m, 4 H, Cp), 3.73 (q,  $J = 6.6$  Hz, 1 H,  $\text{CHCH}_3$ ), 3.20 (d,  $J = 13$  Hz, 1 H,  $\text{CH}_2$ ), 3.15 (d,  $J = 13$  Hz, 1 H,  $\text{CH}_2$ ), 1.53–1.42 (br s, 1 H, NH), 1.31 (d,  $J = 6.6$  Hz, 3 H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  145.9 (ipso phenyl, amine), 139.1, 139.0 (d's,  $J = 10$  Hz, ipso *PPh*), 133.4 (d's,  $J = 20$  Hz, 0.01 ppm difference for d's), 128.5 (doubling observed), 128.1 (d's,  $J = 7$  Hz, doubling observed), 126.9, 126.7 (phenyl C's of amine), 87.8 (ipso of  $\text{CpCH}_2\text{NHR}^*$ ), 75.9 (ipso of  $\text{CpPPh}_2$ ), 73.2 (d,  $J = 14$  Hz,  $\text{CpPPh}_2$ ), 71.3 (d,  $J = 4$  Hz,  $\text{CpPPh}_2$ ), 69.5, 69.2, 69.0, 68.9 ( $\text{CpCH}_2\text{NHR}^*$ ), 57.6 (benzylic CH), 46.2 ( $\text{CH}_2$ ), 24.6 ( $\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.6. Anal. Calcd for  $\text{C}_{31}\text{H}_{30}\text{FeNP}$ : C, 73.97; H, 6.01. Found: C, 74.20; H, 6.18.

**1'-(Tri-*n*-butylstannyl)-1-ferrocenecarboxaldehyde (8).** Compound **8** was prepared from **1** (2.07 g, 2.71 mmol) in a manner similar to that above (i.e. **5**). Purification was achieved by using column chromatography with gradient elution (0% to 5% ethyl acetate in hexane) to afford **8** as a red oil (1.10 g, 82%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  9.95 (s, 1 H, CHO), 4.74 (t,  $J = 1.8$  Hz, 2 H, Cp), 4.53 (t,  $J = 1.8$  Hz, 2 H, Cp), 4.48 (t,  $J = 1.6$  Hz, 2 H, Cp), 4.10 (t,  $J = 1.6$  Hz, 2 H, Cp), 1.60–1.51 (m, 6 H,  $\text{CH}_2$ ), 1.39–1.32 (m, 6 H,  $\text{CH}_2$ ), 1.06–1.01 (m, 6 H,  $\text{CH}_2$ ), 0.92 (t,  $J = 7.2$  Hz, 9 H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  193.4 ( $\text{C}=\text{O}$ ), 75.9 (Cp), 73.2 (Cp), 72.1 (Cp), 69.5 (Cp), 29.1 ( $\text{CH}_2$ ), 27.4 ( $\text{CH}_2$ ), 13.7 ( $\text{CH}_2$ ), 10.2 ( $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{23}\text{H}_{36}\text{FeOSn}$ : C, 54.91; H, 7.21. Found: C, 54.98; H, 7.24.

**1'-(Tri-*n*-butylstannyl)-1-[(dimethylamino)methyl]-ferrocene (9).** A methanol solution (20 mL) containing camphorsulfonic acid (0.45 g, 1.9 mmol) was saturated with dimethylamine while being chilled in an ice bath. A methanol solution containing **8** (1.07 g, 2.13 mmol) was transferred to the amine/methanol mixture and stirred for 2 min; then  $\text{NaBH}_3\text{CN}$  (0.50 g, 7.6 mmol) was added in one portion. The cooling bath was removed and the mixture stirred for an additional 30 min. The mixture was diluted with ether (100 mL) and washed with water (3  $\times$  100 mL), brine (100 mL), and then dried over  $\text{K}_2\text{CO}_3$ . The solvent was removed and the crude product purified by chromatography employing gradient elution (0 to 15% ethyl acetate in hexane). The third yellow band was collected to afford pure **9** (0.70 g, 62%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.27 (t,  $J = 1.7$  Hz, 2 H, Cp), 4.11 (t,  $J = 1.8$  Hz, 2 H, Cp), 4.04 (t,  $J = 1.8$  Hz, 2 H, Cp), 3.95 (t,  $J = 1.7$  Hz, 2 H, Cp), 3.27 (s, 2 H,  $\text{CH}_2$ ), 2.16 (s, 6 H,  $\text{NCH}_3$ ), 1.60–1.51 (m, 6 H,  $\text{CH}_2$ ), 1.39–1.32 (m, 6 H,  $\text{CH}_2$ ), 1.05–1.01 (m, 6 H,  $\text{CH}_2$ ), 0.92 (t,  $J = 7.2$  Hz, 9 H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR

( $\text{CDCl}_3$ ):  $\delta$  83.1 (ipso  $\text{CpCH}_2$ ), 74.9 (Cp), 71.0 (w satellites,  $\text{CpSn}$ ), 70.0 ( $\text{CpCH}_2$ ), 68.9 (ipso  $\text{CpSn}$ ), 68.0 ( $\text{CpCH}_2$ ), 59.4 ( $\text{CpCH}_2$ ), 44.8 ( $\text{NCH}_3$ ), 29.2 ( $\text{CH}_2$ ), 27.4 ( $\text{CH}_2$ ), 13.7 ( $\text{CH}_2$ ), 10.3 ( $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{43}\text{FeNSn}$ : C, 56.43; H, 8.15. Found: C, 56.37; H, 8.25.

**1'-(Diphenylphosphino)-1-[(dimethylamino)methyl]-ferrocene (10).** A THF solution (10 mL) of **9** (0.50 g) maintained at  $-78$  °C was treated with *n*-BuLi and allowed to react for an additional 30 min.  $\text{Ph}_2\text{PCl}$  was added to the mixture and the cooling bath removed. The mixture was diluted with ether and an aqueous workup applied. Final purification was achieved by column chromatography on alumina with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  as eluant (gradient elution) to afford analytically pure **10** as an orange solid (0.35 g, 86%, mp 106–108 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.40–7.27 (m, 10 H, phenyls), 4.32 (t,  $J = 1.7$  Hz, 2 H, Cp), 4.10 (t,  $J = 1.7$  Hz, 2 H, Cp), 4.05 (q,  $J = 1.8$  Hz, 2 H, Cp), 4.02 (t,  $J = 1.8$  Hz, 2 H, Cp), 2.98 (s, 2 H,  $\text{CH}_2\text{NMe}_2$ ), 2.10 (s, 6 H,  $\text{NCH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  139.2 (d,  $J = 10$  Hz, ipso *PPh*), 133.4 (d,  $J = 20$  Hz, phenyl), 128.5 (phenyl), 128.1 (d,  $J = 7$  Hz), 84.0 (ipso  $\text{CpCH}_2$ ), 73.3 (d,  $J = 15$  Hz,  $\text{CpPPh}_2$ ), 71.3 (d,  $J = 4$  Hz,  $\text{CpPPh}_2$ ), 71.2 ( $\text{CpCH}_2$ ), 69.3 ( $\text{CpCH}_2$ ), 58.5 ( $\text{CH}_2$ ), 44.7 ( $\text{CH}_3$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.8. Anal. Calcd for  $\text{C}_{25}\text{H}_{26}\text{FeNP}$ : C, 70.27; H, 6.13. Found: C, 70.00; H, 6.21.

**Transmetalation Study of 1,1'-Bis(tri-*n*-butylstannyl)-ferrocene with More Than 1 Equiv of *n*-BuLi.** A THF solution (20 mL) of **1** (0.98 g, 1.3 mmol) was treated with *n*-BuLi (3.9 mmol) and allowed to react at  $-78$  °C for 1 h. The mixture was quenched with an excess of methanol (20 molar equiv), and solvents were removed under reduced pressure. The product ratio (ferrocene/1-(tri-*n*-butylstannyl)ferrocene<sup>12</sup>) was determined by NMR spectroscopy.

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## Evidence for the Formation of $\text{Mn}_2(\text{CO})_9(\text{CS})$

Wolfgang Petz<sup>\*1a</sup> and Dieter Rehder<sup>1b</sup>

GMELIN-Institut für Anorganische Chemie der

Max-Planck-Gesellschaft, D-6000 Frankfurt am Main 90

Federal Republic of Germany

and Institut für Anorganische und Angewandte Chemie der

Universität Hamburg, D-2000 Hamburg 13

Federal Republic of Germany

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**Summary:** The reaction of  $[\text{Mn}(\text{CO})_5]^-$  with  $\text{SCCl}_2$  in pentane at room temperature produces minor amounts of a mixture of  $\text{Mn}_2(\text{CO})_9\text{CS}$  and  $\text{Mn}_2(\text{CO})_{10}$ , isolated from the solution. The main reaction product, which is insoluble in pentane, consists of a CO- and Cl-containing ionic material. In the presence of 18-crown-6,  $[\text{K}(18\text{-crown-6})][\text{Mn}(\text{CO})_4\text{Cl}_2]$  is formed exclusively. The thiocarbonyl derivative, which could not be separated from  $\text{Mn}_2(\text{CO})_{10}$ , was identified and characterized by mass, IR, and  $^{55}\text{Mn}$  NMR spectroscopic methods, which also showed that

(1) (a) Gmelin Institute Frankfurt. (b) Universität Hamburg.