Lithiation and derivatization of Group IVA bent-sandwich molecules

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α-[(2,2-dimethylpropanoyl)oxy]stilbene, 86846-74-4; (*Z*)-α-[(2,2-dimethylpropanoyl)oxy]stilbene, 86846-75-5; (*E*)-α-(benzoyloxy)stilbene, 86846-76-6; (*Z*)-α-(benzoyloxy)stilbene, 86846-77-7; 1-(benzoyloxy)-2,2-diphenylethylene, 86123-17-3; (*E*)-α-[(*p*-fluorobenzoyl)oxy]stilbene, 86846-78-8; (*Z*)-α-[(*p*-fluorobenzoyl)oxy]stilbene, 86846-79-9; 1-[(*p*-fluorobenzoyl)oxy]-2,2-diphenylethylene, 86846-80-2; (*E*)-α-[(*p*-methylbenzoyl)oxy]stilbene, 86846-81-3; (*Z*)-α-[(*p*-methylbenzoyl)oxy]stilbene, 86846-82-4; 1-[(*p*-methylbenzoyl)oxy]-2,2-diphenylethylene, 86846-83-5; (*E*)-β-(benzoyloxy)styrene, 86846-84-6; (*Z*)-β-(benzoyloxy)styrene, 84262-78-2; α-(benzoyloxy)styrene, 838-58-4; (*E*)-4-acetoxy-4-octene, 86846-85-7; dimethyl 2-acetoxy-2-butenedioate, 78704-24-2.

Lithiation and Derivatization of Group 4A Bent-Sandwich Molecules

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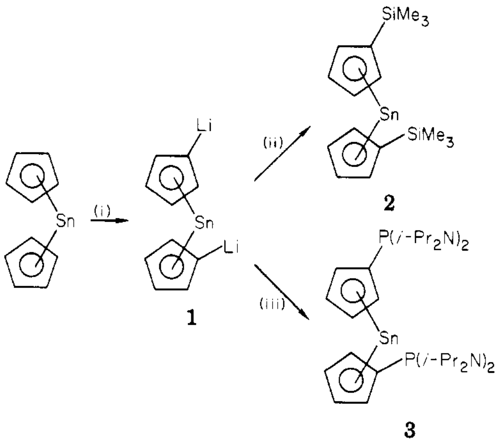
Summary: Dilithiation of stannocene, $(\eta^5\text{-}C_5H_5)_2Sn$, produces the synthetically useful 1,1′-dilithiostannocene, **1**. Treatment of **1** with 2 equiv of Me_3SiCl or $(i\text{-}Pr_2N)_2PCl$ affords the disubstituted derivatives $(Me_3SiC_5H_4)_2Sn$ (**2**) and $((i\text{-}Pr_2N)_2PC_5H_4)_2Sn$ (**3**), respectively. The structure of **3** has been determined by X-ray diffraction.

Interest in the reactivity of annulene complexes of the main-group elements has focused principally on ligative behavior, protolytic cleavage, oxidative addition, and ligand exchange reactions.[1] However Xα-SW calculations on bent-sandwich[2] and open-faced-sandwich[3] $\eta^5\text{-}C_5H_5$ compounds indicate that the HOMO is primarily ring localized. Thus, main-group annulene complexes should exhibit a ring substitution chemistry. To the best of our knowledge only two ring substitution reactions of bent-sandwich molecules have been documented, viz., the reaction of $(\eta^5\text{-}C_5H_5)_2Sn$ with Me_3SnNEt_2[4] and $[(i\text{-}Pr_2N)_2P][AlCl_4]$.[5] We now report that, like ferrocene,[6] $(\eta^5\text{-}C_5H_5)_2Sn$ readily forms a synthetically useful, 1,1′-dilithio derivative.

A THF solution of $(\eta^5\text{-}C_5H_5)_2Sn$ was treated with 2 equiv. of *n*-BuLi at −78 °C. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the resulting dark red solution comprised singlets at δ 5.6 and 102.9, respectively, indicating that 1,1′-dilithiostannocene (1) is fluxional at 30 °C (see later).

The dilithium compound 1 is reactive toward main-group organometallic chlorides. Treatment of 1 with 2 equiv of Me_3SiCl in THF at −78 °C caused an immediate discharge of the red color. After the solution was warmed to room temperature and the THF removed, the light yellow residue was extracted with *n*-hexane. Distillation of the resulting yellow oil (bp 115 °C at 5 × 10^{-3} torr) afforded 30–40% yields of 1,1′-bis(trimethylsilyl)stannocene, **2**.[7] Compound **2** can also be prepared via the reaction of $Me_3SiC_5H_4Li$ with $SnCl_2$ in THF solution at 0 °C, thus supporting the above formulation.

Scheme I[a]



[a] (i) 2*n*-BuLi; (ii) $2Me_3SiCl$; (iii) $2(i\text{-}Pr_2N)_2PCl$.

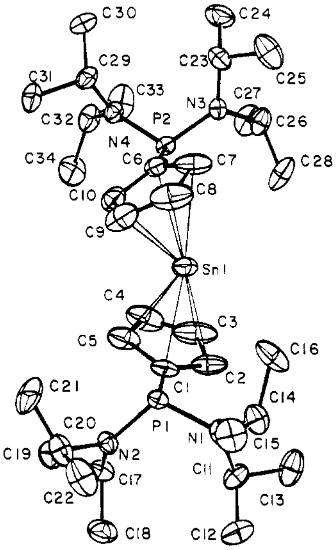


Figure 1. Structure of $[(i\text{-}Pr_2N)_2PC_5H_4]_2Sn$ (3) showing the atom numbering scheme. The hydrogen atoms are omitted. Important parameters include Sn(1)–C = 2.527 (8) − 2.807 (8) Å, C(1)–P(1) = 1.822 (7) Å, C(6)–P(2) = 1.824 (8) Å, P(1)–N(1) = 1.681 (8) Å, P(1)–N(2) = 1.686 (5) Å, P(2)–N(3) = 1.687 (6) Å, and P(2)–N(4) = 1.679 (5) Å.

Treatment of 1 with 2 equiv of $(i\text{-}Pr_2N)_2PCl$ in THF at −78 °C followed by removal of solvent and recrystallization from *n*-hexane afforded 30–40% yields of yellow crystalline 1,1′-bis((diisopropylamino)phosphido)stannocene, **3**, mp 162–164 °C (see Scheme I).[8] The structure of **3** was es-

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[1] For a review of the reactivity of bent-sandwich molecules see: (a) Connolly, J. W.; Hoff, C. *Adv. Organomet. Chem.* **1981**, *19*, 123. For examples of the reactivity of open-faced sandwich molecules see: (b) Habeeb, J. J.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1815. (c) Conteras, J. G.; Tuck, D. G. *Inorg. Chem.* **1973**, *12*, 2596.

[2] Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064.

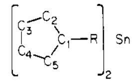
[3] Lattman, M.; Cowley, A. H. *Inorg. Chem.*, in press.

[4] Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1978**, *157*, C3.

[5] Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239.

[6] See, for example: Benkeser, R. A.; Goggin, D.; Scholl, G. *J. Am. Chem. Soc.* **1954**, *76*, 4025. Nesmeyanov, A. N.; Perevalova, E. G.; Golovinya, E. G.; Nesmayanova, D. A. *Dokl. Akad. Nauk SSSR* **1954**, *97*, 659. Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.

[7] Anal. Calcd for $C_{16}H_{26}Si_2Sn$: C, 48.7; H, 6.6. Found: C, 48.6; H, 6.8. ^1H NMR (200 MHz): δ 0.30 (s, 18 H, $SiMe_3$), 6.05 (m, 4 H, $H_{2,5}$ or $H_{3,4}$), 6.15 (m, 4 H, $H_{2,5}$ or $H_{3,4}$). $^{13}C\{^1H\}$ NMR (20 MHz): δ 1.4 ($SiMe_3$), 114.3 ($C_{2,5}$ or $C_{3,4}$), 117.5 ($C_{2,5}$ or $C_{3,4}$), 121.9 (C_1).



[8] 3: ^1H NMR (90 MHz) δ 1.05 (d, 12 H, Me (*i*-Pr group), $^3J_{HH}$ = 6.9 Hz), 1.20 (d, 12 H, Me′, $^3J_{HH}$ = 6.9 Hz), 3.40 (m, 4 H, Me_2CH), 5.90 (m, 4 H, $H_{2,5}$ or $H_{3,4}$), 6.10 (m, 4 H, $H_{2,5}$ or $H_{3,4}$); $^{13}C\{^1H\}$ NMR (20 MHz) δ 24.4 (d, Me, $^3J_{PC}$ = 10.3 Hz), 24.7 (d, Me′, $^3J_{PC}$ = 9.7 Hz), 47.5 (d, Me_2CH, $^2J_{PC}$ = 11.4 Hz), 110.4 (d, $C_{2,5}$ or $C_{3,4}$, J_{PC} = 6.0 Hz), 115.0 (d, $C_{2,5}$ or $C_{3,4}$, J_{PC} = 15.9 Hz), 132.6 (d, C_1, $^1J_{PC}$ = 6.4 Hz); $^{31}P\{^1H\}$ NMR (36.4 MHz) δ (relative to 85% H_3PO_4) 46.6.

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tablished by a single-crystal X-ray diffraction study (Figure 1). The structure consists of isolated neutral molecules of **3** in which the Sn atom is η^5 bonded to two $(i\text{-}Pr_2N)_2PC_5H_4$ ligands. The range of Sn–C bond lengths is typically large (2.53–2.81 Å), cf. in stannocene itself[11] (2.56 (2)–2.85 (3) Å), a situation often observed in bent-sandwich molecules.[12] The ring centroid–metal–ring centroid angle is 150.2° and thus slightly larger than that in stannocene (148.0° (molecule A) and 143.7° (molecule B)). The two $(i\text{-}Pr_2N)_2P$ moities adopt a mutually trans arrangement, and each nitrogen center is trigonal planar within experimental error.

Finally we note two aspects of the reaction of stannocene with 1 equiv of *n*-BuLi. First, the ^1H and ^{13}C NMR spectra show only single resonances, implying a time-averaged spectrum as a result of a fluxional process. Second, treatment of this solution with 1 equiv of Me_3SiCl affords **2** as the only isolable product. This result and others will be discussed in detail in a future paper.

Acknowledgment is made to the donors of the Petroleum Fund, administered by the American Chemical Society, for the support of this research.

Registry No. 1, 87050-55-3; 2, 87050-56-4; 3, 87050-57-5; $(\eta^5\text{-}C_5H_5)_2Sn$, 1294-75-3; $Me_3SiC_5H_4Li$, 76514-39-1; $(i\text{-}Pr_2N)_2PCl$, 56183-63-2.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond lengths, and bond angles and a listing of structure factor amplitudes for **3** (29 pages). Ordering information is given on any current masthead page.

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[9] Crystal data for 3: $C_{34}H_{64}N_4P_2Sn$; M_r = 708.36, triclinic, space group $P\bar{1}$ (No. 2)(by refinement), a = 9.209 (2) Å, b = 14.325 (3) Å, c = 14.726 (4) Å, α = 92.80 (2)°, β = 96.60 (2)°, γ = 92.62 (2)°, U = 1924.9 Å^3, D_{calcd} = 1.225 g cm^{-3}, Z = 2, λ(Mo Kα) (graphite monochromator) = 0.71069 Å, μ(Mo Kα) = 7.7 cm^{-1}. From a total of 6738 unique reflections, measured on an Enraf-Nonius CAD-4 diffractometer, 3382 ($I > 2.0\sigma(I)$) reflections were used to solve (Patterson and difference Fourier) and refine (full-matrix least-squares) the structure of 3. All non-hydrogen atoms were located and refined by using anisotropic thermal parameters although some carbon atoms showed a high degree of thermal motion. All unique hydrogen atoms were either located or calculated and allowed to refine positionally with a fixed isotropic temperature factor. Methyl hydrogens were neither located nor refined. This was the result of a low percentage of observed data as a result of poor crystal quality. Refinement with a weighting scheme[10] converged to give final residuals R = 0.0540, R_w = 0.0695, and GOF = 1.575.

[10] The weighting scheme used was of the form $w = (4F^2/\sigma^2(F^2) + P^2F^4)$ with P = 0.06.

[11] Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* **1981,** 925.

[12] See, for example: Lappert, M. F.; Riley, P. I.; Yarrow, P. I. W.; Atwood, J. L.; Hunter, W. E.; Zaworotko, M. J. *J. Chem. Soc., Dalton Trans.* **1981,** 814.

Preparation of a Carbon-Rich Metallacarborane from a Metallacycle

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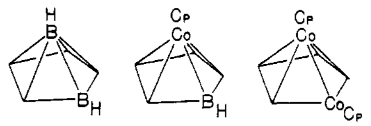
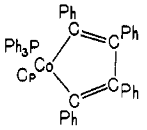
Summary: The reaction of $BH_3\cdot THF$ with the cobaltacycle $(\eta^5\text{-}C_5H_5)[P(C_6H_5)_3]CoC_4(C_6H_5)_4$ produces the *nido*-cobaltacarborane 3,4,5,6-$(C_6H_5)_4$-1,3,4,5,6-$(\eta^5\text{-}C_5H_5)CoC_4BH$ in 20% yield. This result demonstrates a new route to carbon-rich metallacarboranes, i.e., organometallic compounds with polyhapto heterocyclic rings.

Chart I



In a general sense, there are three, pair-wise routes to metallacarboranes, i.e., clusters containing a transition metal, carbon, and boron. The first involves reaction of a suitable carborane ligand with a metal fragment. The second is the reaction of a metallaborane with a source of carbon fragments. The final alternative is the reaction of a transition-metal hydrocarbon complex with a source of borane fragments. The first constitutes the major existing route to metallacarboranes and is well illustrated by the work of Hawthorne[1] and Grimes.[2] Examples of the second approach exist, but it has yet to be demonstrated that this is also a viable route to these systems.[3] Although there are notable exceptions[4] these two methods lead to compounds with cages containing high atom percents of boron whereas the third route leads naturally to carbon-rich cages. Indeed, the original synthesis of $(\eta^5\text{-}C_5H_5)Co(\eta^6\text{-}C_5H_5BC_6H_5)$ resulted from the insertion of a borane fragment into a C_5H_5 ring of cobaltacene.[5] We report here another example of the third route to metallacarboranes in which metallacycles are used as the metal–carbon source.

Some years ago we demonstrated the photochemical insertion of a borane fragment into $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ to yield the six-atom, nido cage $(CO)_3FeBC_4H_5$.[6] Although providing a demonstration of the third approach (above), yields were tiny and we have since sought other routes. As a nido cage can be viewed as a cyclic ligand bound to a capping BH,[4,7] we thought the reaction of a suitable metallacycle with a source of borane would provide a viable method. As many metallacycles contain metal-bound Lewis bases,[8] the use of $BH_3\cdot THF$ provides for both a source of the borane fragment as well as a means of removing the free ligand, generated in activating the metallacycle, from the reaction. The thermolysis of (triphenylphosphine)cyclopentadienylcobalta-2,3,4,5-tetraphenylcyclopentadiene, **1**,[9] has already been shown to yield the cyclobutadiene complex **2**.[10] Presumably an unsaturated metallacycle intermediate is produced, and, thus, we chose this system to investigate initially.



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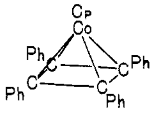

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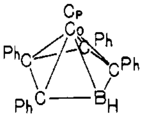

3

Reflux of 0.1 mmol of 1 in toluene with 0.2 mmol of $BH_3\cdot THF$ for 6 h, followed by hexane extraction and chromatography on silica gel, permitted the identification

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[1] Hawthorne, M. F. *J. Organomet. Chem.* **1975,** *100,* 97.

[2] Grimes, R. N. *Acc. Chem. Research* **1978,** *11,* 420.

[3] See for example: Weiss, R.; Bowser, J. R.; Grimes, R. N. *Inorg. Chem.* **1978,** *17,* 1522. Fehlner, T. P. *J. Am. Chem. Soc.* **1980,** *102,* 3424.

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[8] Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982,** *1,* 739.

[9] Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977,** *139,* 157.

[10] Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1967,** *7,* 22.

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