by chloride ions in an Arbuzov-type dealkylation[17] leading to the formation of phosphonate-bridged dimers. Such a mechanism has also been reported to occur during the formation of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe\{P(CO)(NR_2)_n(OR')_{2-n}\}]$ (n = 1, 2).[18] The identification of ethyl chloride by GC-MS[19] as a volatile material generated in the course of the reaction, along with the structural characterization of 1, leads us to believe that the reaction mechanism involved in the present system is similar to those mentioned above. On the basis of experimental spectroscopic and crystallographic results, the overall reaction stoichiometry is proposed to proceed as illustrated in eq 3.

$$2YCl_3 + 4NaL_{OEt} \rightarrow \underset{1}{[L_{OEt}Y\{(C_5H_5)Co(P({=}O)(OEt)_2)_2(P({=}O)(OEt)(O))\}_2YL_{OEt}]} + 4NaCl + 2EtCl \quad (3)$$

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[17] For a review of the Arbuzov reaction see: Arbuzov, B. A. *Pure Appl. Chem.* 1964, 9, 307-335.

[18] Nakazawa, H.; Kadoi, Y.; Miyoshi, K. *Organometallics* 1989, 8, 2851-2856.

[19] Mass spectrometry results for EtCl (70 eV): m/e 64 ($Et^{35}Cl$), 66 ($Et^{37}Cl$), in the correct isotopic ratio.

Concluding Remarks

A straightforward synthetic route is used in the isolation of the unusual dimeric complex 1 containing a L_{OEt} ligand in a normal tripod chelating mode as well as in an unusual bridging fashion, accessible via phosphonate ethyl loss. To our knowledge, this is the first example of an Arbuzov-type dealkylation reaction involving an yttrium complex. Our current efforts are directed toward gauging the scope of this reaction type in lanthanide chemistry as well as investigating the reactivity of the present yttrium dimer.

Acknowledgment. S.P.N. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The LEQSF is also acknowledged for providing funds necessary to purchase the NMR instrument (Grant ENH-53, 1990-1991).

Supplementary Material Available: Tables of crystal intensity data, selected distances and angles, and anisotropic thermal parameters for 1 (15 pages). Ordering information is given on any current masthead page.

OM920146+

Regiospecific Mono-Transmetalation of 4-Stanna-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacenes

Ilya E. Nifant'ev,* Maxim V. Borzov, Pavel V. Ivchenko, Vassily L. Yarnykh, and Yu. A. Ustynyuk

Organic Division, Department of Chemistry, Moscow University, Moscow 119899, Russia

Received November 19, 1991

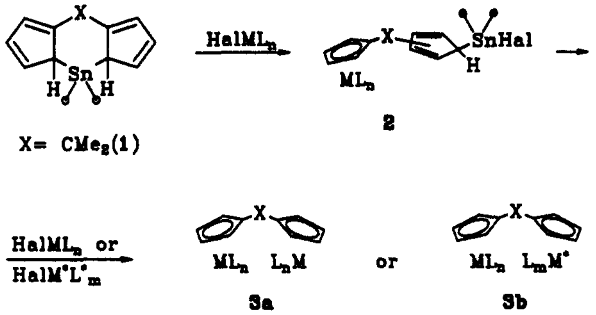
Summary: The reactivity of $BrMn(CO)_5$ toward two 4-stannatetrahydro-*s*-indacenes 1 and 7 is described. Only mono-transmetallation products were obtained. Regiospecific mono-transmetallation is found when compound 7 and $BrMn(CO)_5$ are reacted.

η^1-Cyclopentadienyl derivatives of group 4A elements are known to undergo a smooth substitution reaction with transition-metal halides to yield both sandwich and half-sandwich η^5 complexes. This reaction has been employed widely as a convenient method to obtain several η^5-Cp derivatives:[1,2]

El= Si, Ge, Sn

Recently we published the protocol for the synthesis of 4-stanna-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacene (1).[3] Compound 1 and its analogs can be successfully used for the synthesis of mono- and binuclear η^5-Cp derivatives of the types 2 and 3, which are currently the focus of interest (Scheme I).[4]

Scheme I



For the preparation of heterometallic compounds the synthetic procedure will be efficient only if the reactivity of a given $HalML_n$ species toward 1 or its analogs (X = CMe_2) is significantly higher than that toward 2. Given this condition, it is possible to isolate from the reaction mixture of 1 with $HalML_n$ the main product 2 in high yield and, subsequently, to introduce 2 in the reaction with any other active transition-metal halide complex to yield the heterometallic compound 3b. If this is not the case, generally a mixture of 2 and 3a would be the result.

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[1] (a) Bunker, M. J.; DeCian, A.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* 1977, 59. (b) Jutzi, P.; Kuhn, M. *J. Organomet. Chem.* 1979, 173, 221. (c) Sornay, C.; Meunier, P.; Gautheron, B.; O'Doherty, G. A.; Paquette, L. A. *Organometallics* 1991, 10, 2082. (d) Lund, E. C.; Livinghouse, T. *Organometallics* 1990, 9, 2426.

[2] Abel, E. W.; Moorhouse, S. *J. Organomet. Chem.* 1971, 29, 227.

[3] (a) Nifant'ev, I. E.; Yarnikh, V. L.; Borzov, M. V.; Mazurchik, B. A.; Rozniatovskii, V. A.; Mstislavskii, V. I.; Ustynyuk, Yu. A. *Organometallics* 1991, 10, 3739. (b) Nifant'ev, I. E.; Chestakova, A. K.; Lemenovskii, D. A.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *Metalloorg. Khim.* 1991, 10, 293.

[4] (a) Bitterwolf, T. E.; Gambaro, A.; Gottardi, F.; Valle, G. *Organometallics* 1991, 10, 1416. (b) Rausch, M. D.; Spink, W. C.; Conway, B. G.; Rogers, R. D.; Atwood, J. L. *J. Organomet. Chem.* 1990, 383, 227. (c) Reddy, K. P.; Petersen, J. L. *Organometallics* 1989, 8, 2107. (d) Buzinkai, J. F.; Schrock, R. R. *Inorg. Chem.* 1989, 28, 2837. (e) Lynch, T. J.; Helvenston, M. C.; Rheingold, A. L.; Staley, D. L. *Organometallics* 1989, 8, 1959 and references therein.

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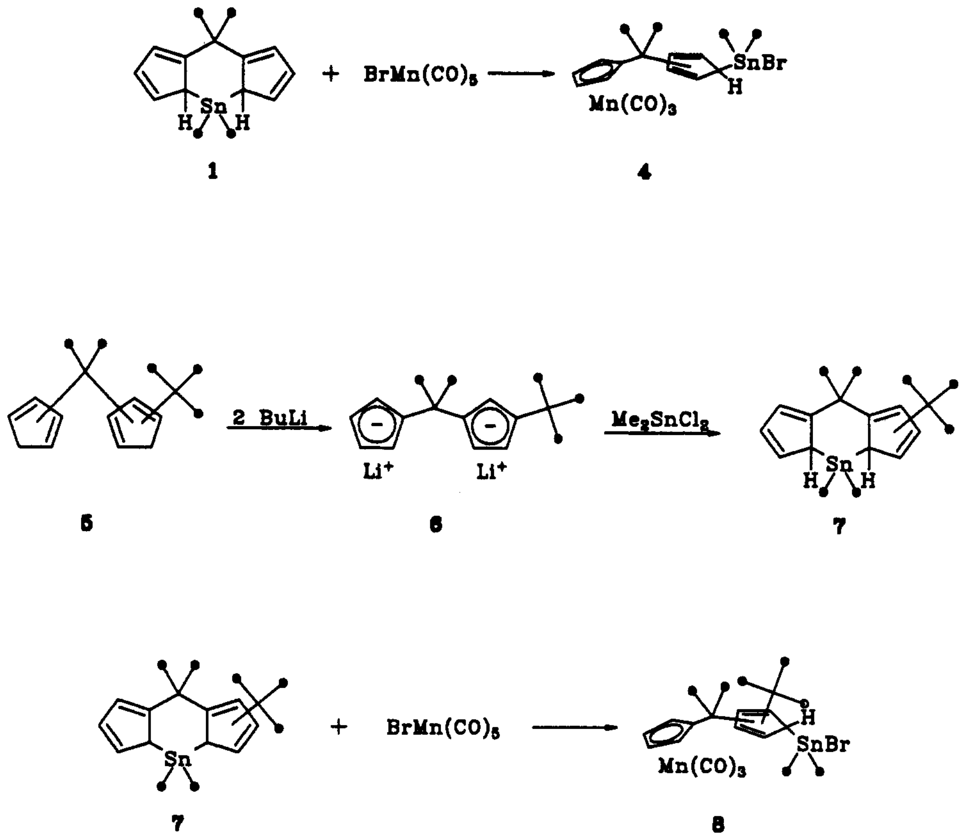
Scheme II



To check the real situation, we studied the reaction of two 4-stanna-3a,4,4a,8-tetrahydro-*s*-indacenes, 1 and 7, with BrMn(CO)$_5$. This choice is due to the availability of previous information concerning the reaction between BrMn(CO)$_5$ and some stannylcyclopentadienes.[2]

We found that compound 1 smoothly reacts with BrMn(CO)$_5$, in a 1:1 ratio, to give as the only isolable product the mononuclear complex 4, almost quantitatively. Unexpectedly the alkyl group in one of the Cp rings of 7 was discovered to determine which one of the two nonequivalent Sn–C bonds would be broken. 7 reacts with BrMn(CO)$_5$ to give in 91% yield only one of the two possible reaction products, the compound 8. Any other products were not detectable in the reaction mixture by the NMR technique (Scheme II).

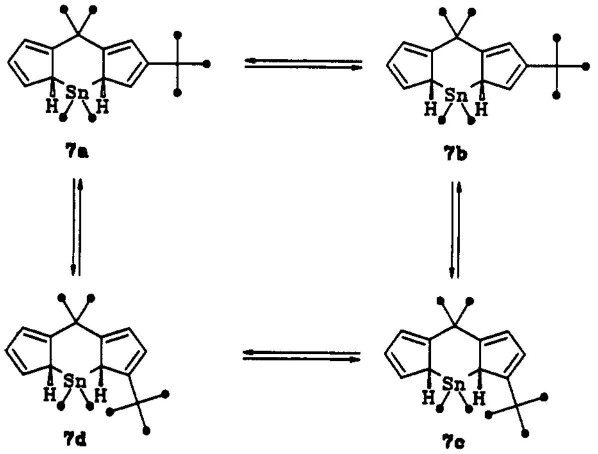
Therefore, 4-stanna-3a,4,4a,8-tetrahydro-*s*-indacenes were found to react selectively and regioselectively with at least some halides of transition metals, which may be used in the synthesis of various homo- and heterobimetallic complexes of the type 3.[5]

Compound 7 demonstrates fluxional behavior like that of 1[3] due to [1,5]-sigmatropic shifts. Therefore, 7 represents the equilibrium mixture of four isomers (7a–d) which rearrange quickly, one to another (Scheme III). The relative content of isomers 7a–d at −80 °C established by ^{119}Sn NMR spectroscopy is 7a:7b:7c:7d = 65:21:12:2. A detailed investigation of the dynamic behavior of 7 by means of the DNMR method will be published soon.

Experimental Section

All reactions with compounds 1 and 7 were performed in sealed glass evacuated vessels of the Schlenk type. The reactions with BrMn(CO)$_5$ were carried out in darkness. The solvents were dried and degassed as usual and stored in evacuated vessels. Compounds 1[3] and 5,[6] BrMn(CO)$_5$,[7] *tert*-butylcyclopentadiene,[8] and 6,6-dimethylfulvene[9] were prepared as described in the literature. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Varian VXR-400 spectrometer. Elemental analyses were performed on a Carlo-Erba analyzer.

Scheme III



***tert*-Butyl-4-stanna-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacene (7).** A solution of 6.29 g (27.55 mmol) of 5 in 200 mL of THF was treated with 31.67 mL of a 1.74 M hexane solution of *n*-BuLi (55.10 mmol) at −30 °C. The mixture was stirred for 0.5 h and was warmed to room temperature. This mixture was heated to 50 °C with stirring and then within 2 h cooled gradually to −50 to −60 °C, and a solution of 6.05 g (27.55 mmol) of dimethyldichlorostannane in 60 mL of THF was added over 3 h with vigorous stirring. When the resultant mixture was

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(9) Freiesleben, W. *Angew. Chem.* **1963**, *75*, 576.

Table I. ^{1}H NMR (400 MHz, Toluene-d_8, −90 °C) Data for Compound 7

	isomers			
	7a	**7b**	**7c**	**7d**
$(CH_3)_2Sn$				
δ^a	−0.94, −0.31	−0.25, −0.16	−0.96, 0.27	−0.02, 0.01
$^2J(^{119/117}Sn-^1H)$, Hz	53.5, 54.4	53.7, 53.1	52.8, 53.2	*b*
$(CH_3)_3C$				
δ^a	1.30	1.35	1.34	*b*
$(CH_3)_2C$				
δ^a	~1.59, 1.81	~1.80, 1.64	1.58, 1.47	*b*
H–C(3a), H–C(4a)				
δ^c	3.77, 3.93	3.49, 3.70	3.60, 3.88	*b*
$^2J(^{119/117}Sn-^1H)$, Hz	97.0, 92.5	97.4, 93.1	*b*	*b*
H (Cp)				
δ^d	5.65–6.65			

^{a} Singlet. ^{b} Cannot be measured. ^{c} Broadened multiplet. ^{d} Group of overlapping multiplets.

warmed to room temperature, the solution was decanted, THF and hexane were removed, and the resultant brownish red oil was extracted with pentane three times. On removal of pentane and distillation 6.25 g of a yellowish oil was obtained: bp 110 °C/5 × 10^{-2} mmHg; yield 60.5%. Anal. Calcd for $C_{19}H_{28}Sn$: C, 60.83; H, 7.52. Found: C, 60.57; H, 7.61. ^{1}H NMR (400 MHz, toluene-d_8, 26 °C): δ 6.29–6.23 (m, 3 H); 5.87–5.86 (m, 2 H); 5.40–4.70 and 4.15–3.85 (very br signals, 2 H); 1.58 (s, 3 H); 1.41 (s, 3 H); 1.19 (s, 9 H); 0.31, 0.06, −0.53, −0.54 (br s, 6 H). ^{1}H NMR at −90 °C: see Table I.

Compound 4. A solution of 1.44 g (4.51 mmol) of 1 and 1.24 g (4.51 mmol) of $BrMn(CO)_5$ in 20 mL of THF was mixed at room temperature over 12 h. The gaseous products were removed periodically. After THF was removed, the resultant oil was treated with pentane to give 4 as a crystalline precipitate: yield 2.25 g (93%). Anal. Calcd for $C_{18}H_{20}BrMnO_3Sn$: C, 40.19; H, 3.75. Found: C, 40.35; H, 3.63. ^{1}H NMR (400 MHz, THF-d_8, 27 °C): δ 6.43 (m, 2 H); 5.37 (m, $^2J_{H-Sn}$ = 56.5 Hz, 2 H); 4.98 (m, 2 H); 4.64 (m, 2 H); 1.49 (s, 6 H); 0.52 (s, 6 H). ^{13}C NMR (100 MHz, THF-d_8, 27 °C): δ 226.43; 153.78; 125.82; 116.42; 93.47 ($^1J_{C-Sn}$ = 59.2 Hz); 85.12; 80.82; 35.83; 29.96; −1.41.

Compound 8. The reaction was performed similarly to that described above. Above 0.73 g (1.95 mmol) of 7 and 0.54 g (1.95 mmol) of $BrMn(CO)_5$ 1.05 g of orange oil 8 was obtained (yield 91%). All attempts to crystallize the product failed. Anal. Calcd for $C_{22}H_{28}BrMnO_3Sn$: C, 44.49; H, 4.75. Found: C, 44.11; H, 4.69. ^{1}H NMR (400 MHz, THF-d_8, 27 °C): δ 6.55 (m, 1 H); 6.50 (m, 1 H); 5.03 (m, 1 H); 4.98 (m, 1 H); 4.78 (m, 1 H); 4.68 (m, 2 H); 1.51 (s, 3 H); 1.49 (s, 3 H); 1.21 (s, 9 H); 0.61 (br s, 3 H); 0.55 (br s, 3 H). ^{13}C NMR (100 MHz, THF-d_8, 27 °C): δ 226.38; 156.76; 153.37; 124.72; 116.51; 102.67; 85.25; 85.12; 80.82; 80.60; 36.11; 33.39; 31.67; 30.41; 29.75; 0.47; −0.31.

OM910717I

Reactions of 2-Lithio-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane with Benzaldehyde, Benzoyl Chloride, and Benzonitrile

Dietmar Seyferth* and Jennifer L. Robison

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

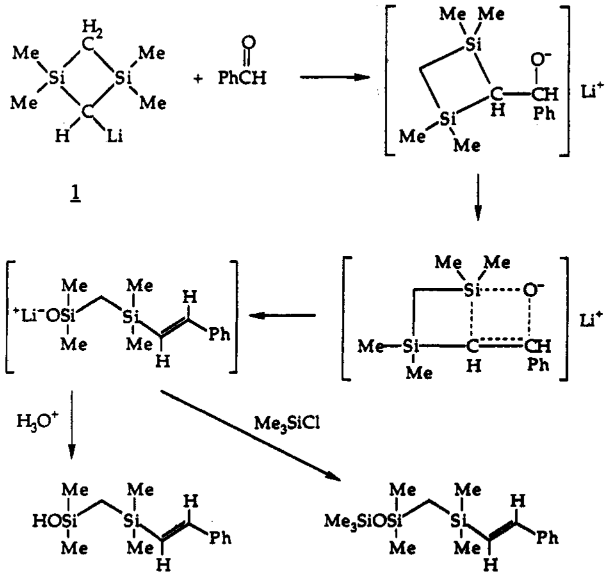
Received June 15, 1992

Summary: Reaction of the title cyclic organolithium compound with benzaldehyde gave a ring-opened product. With benzoyl chloride the expected ketone was produced (which underwent ring expansion rearrangement when heated to 140 °C). Reaction of the title organolithium compound with benzonitrile resulted in isolation of a ring-expanded product. The latter, when heated to 140 °C, underwent a ring contraction rearrangement.

Introduction

The reactions of 2-lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane (1) with benzaldehyde, benzoyl chloride, and benzonitrile, followed by hydrolytic workup (or methanolic workup in the case of PhCN), gave ring-opened or ring-expanded products.[1] In the case of the 1/PhCHO reaction a modified Peterson olefination process appears to be involved (Scheme I). The reaction of 1 with PhC(O)Cl most likely involved initial formation of the β-ketosilane which then underwent a modified Brook rearrangement to give the ring-expanded product (Scheme II). The course of the 1/PhCN reaction is believed to involve first addition to the C≡N bond. Anionic rearrangement, as shown in Scheme III, then gives the six-membered cyclic lithium

Scheme I



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[1] Seyferth, D.; Robison, J. L.; Mercer, J. *Organometallics* **1990**, *9*, 2677.

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