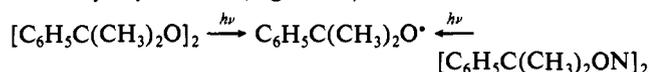


Figure 1. Absorption spectra of (A) *tert*-butoxyl (O) and benzyloxyl (●); (B) cumyloxyl (O) and *p*-methoxycumyloxyl (●). The spectra were obtained by 266-nm LFP of di-*tert*-butyl peroxide, dibenzyl hyponitrite, dicumyl peroxide, and bis(4-methoxycumyl) hyponitrite in CH₃CN, 56, 70, 63, and 61 ns, respectively, after the laser flash. Spectra were recorded under similar, but not standardized, conditions.

of decay of the visible and UV absorptions were equal (within experimental error), which demonstrates that they arise from a common transient (or, less probably, from two species in rapid equilibrium). The ratios of the 485-nm to 320-nm absorption intensities were found to be slightly dependent on the solvent, varying from a high of 1.35 in CCl₄ to a low of 0.72 in CH₃CN.¹² The absolute intensities immediately after LFP of both absorptions showed a linear dependence on laser flux, which implies that the transient(s) responsible for the two absorptions is formed by a monophotonic process. The intensities and decay rates of the visible and UV absorptions were unaffected by oxygen, as would be expected for an oxygen-centered radical but not for a carbon-centered radical or excited triplet.^{13,14} For all of these reasons, we confidently assign both the UV and the visible absorptions to the cumyloxyl radical (Figure 1B).



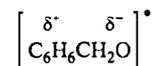
Similar experiments involving the direct LFP and the xanthone photosensitized LFP of dibenzyl hyponitrite⁹ "instantaneously" gave transient visible ($\lambda_{\text{max}} = 460$ nm) and UV absorptions (see Figure 1A). Application of all of the tests described above indicated that both absorptions were due to a single oxygen-centered radical, viz., to the benzyloxyl radical.

In a preliminary exploration of potential substituent effects on these "new" absorption bands, we subjected bis(4-methoxycumyl) hyponitrite^{9,15} to 266-nm LFP in CH₃CN. A transient having a UV and visible absorption was produced "instantaneously" (Figure 1B). The 4-methoxy substituent shifts the unsubstituted cumyloxyl radical's absorption maximum by a dramatic 105 nm into the red, i.e., λ_{max} shifts from 485 to 590 nm.

The arylcarbinoyloxyl radicals' visible absorptions are obviously fairly strong (Figure 1). The extinction coefficient of the visible cumyloxyl absorption was determined in a pair of carefully matched experiments involving the 308-nm LFP of 0.126 M

dicumyl peroxide in CH₃CN. In one experiment, diphenylmethanol was added at a concentration of 1.0 M (which was found to be sufficient to react with ca. 92% of the cumyloxyl radicals and generate benzophenone ketyl radicals, $\epsilon_{545} = 3220 \text{ M}^{-1} \text{ cm}^{-1}$,⁶ within 110 ns). From the ratio of the absorption intensities at 485 nm in the absence and 545 nm in the presence of the diphenylmethanol (appropriately corrected for the small absorption of the alcohol at the excitation wavelength), we estimate that $\epsilon_{485} \approx 1300 \text{ M}^{-1} \text{ cm}^{-1}$ for cumyloxyl.

The intriguing difference between the absorption spectra of alkoxyl and arylcarbinoyloxyl radicals suggests that there may be some internal charge transfer in the latter radicals:¹⁶



In reference to this, it is worth noting that, in a pair of carefully matched experiments involving 308-nm LFP of dicumyl peroxide in CCl₄ and CH₃CN, there was no measurable difference in either the intensity of the visible absorption immediately after the laser pulse or in the position of λ_{max} .

In conclusion, we note that the intensity and band width (e.g., ca. 120 nm at half-height for cumyloxyl) imply that arylcarbinoyloxyl radicals should be visible to the naked eye under certain conditions. In such a case, benzyloxyl and cumyloxyl will be a rose pink in color and 4-methoxycumyloxyl will be a beautiful dark blue.

Acknowledgment. We thank Dr. L. J. Johnston for her friendly advice with the LFP experiments.

(16) The possibility of homoconjunction in (incipient) arylcarbinoyloxyl radicals (produced by the thermal decomposition of hyponitrites) has been raised.¹⁷

(17) Quinga, E. M. Y.; Mendenhall, G. D. *J. Org. Chem.* **1985**, *50*, 2836-2840.

Lithium-Tin Exchange Reaction.¹ Stereochemistry at Tin

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Received December 27, 1991

The lithium-tin transmetalation reaction proceeds with retention of configuration at carbon.^{2,3} This observation provides important mechanistic information, but even more important in this context is the stereochemistry at tin, which has been examined in only one rather unusual case.⁴ In that case, exchange proceeded with

(12) It was not possible to determine the UV λ_{max} for any of these radicals. Measurements at 320 nm correspond to ΔOD on the (steep) "side" of the UV absorption. The change in the 485-nm/320-nm absorption intensity ratios may therefore be due either to solvent effects on the relative intensities of the two absorption bands or to a shift in the λ_{max} of the UV absorbance.

(13) Chateaufort, J.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877-2885.

(14) Chateaufort, J.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2886-2893.

(15) Dulog, L.; Klein, P. *Chem. Ber.* **1971**, *104*, 895-901.

(1) (a) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102. Reich, H. J.; Phillips, N. H. *Pure Appl. Chem.* **1987**, *59*, 1021. Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101. (b) Reich, H. J.; Bowe, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 8994. (c) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414. (d) Reich, H. J.; Green, D. P. Unpublished results. Green, D. P. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1989.

(2) Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883. Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1984**, *25*, 2415. Newman-Evans, R. H.; Carpenter, B. K. *Tetrahedron Lett.* **1985**, *26*, 1141. McDougal, P. G.; Condon, B. D.; Laffosse, M. D., Jr.; Lauro, A. M.; VanDerveer, D. *Tetrahedron Lett.* **1988**, *21*, 2547. Matteson, D. S.; Tripathy, P. B.; Sarkar, A.; Sadhu, K. M. *J. Am. Chem. Soc.* **1989**, *111*, 4399. Hoffmann, R. W.; Julius, M.; Oltmann, K. *Tetrahedron Lett.* **1990**, *31*, 7419. Pearson, W. H.; Lindbeck, A. C. *J. Am. Chem. Soc.* **1991**, *113*, 8546.

(3) The Li/Br,^{3a} Li/I,^{3b} and Li/Se^{1b} exchanges occur with retention of configuration at carbon as well: (a) Applequist, D. E.; Peterson, A. H. *J. Am. Chem. Soc.* **1961**, *83*, 862. Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3283. Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785. (b) Letsinger, R. J. *J. Am. Chem. Soc.* **1950**, *72*, 4842.

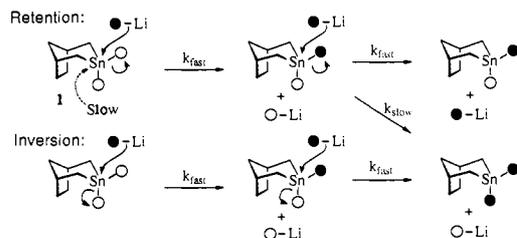


Figure 1. Kinetic procedure for determination of the stereochemistry of substitution at tin.

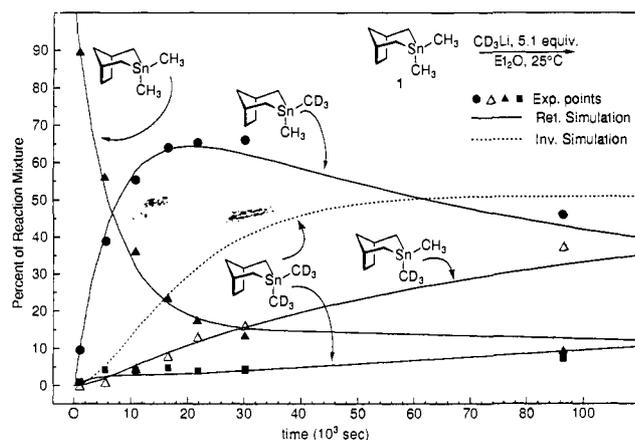


Figure 2. Isotopic exchange of **1** with methyl lithium- d_3 in ether at 25 °C. The lines are the best fit assuming second-order kinetics (rate = $k[\text{CD}_3\text{Li}][\text{1}]$) using two parameters: $k_{\text{fast}} = 8.1 \times 10^{-5} \text{ s}^{-1} \text{ M}^{-1}$ and $k_{\text{fast}}/k_{\text{slow}} = 12.5$. The average difference between calculated and experimental percentages was 1.1.

racemization, a result that has been interpreted in terms of a retention mechanism.⁵ We report here a stereochemical study that distinguishes among the several mechanisms that have been proposed for the Li/Sn exchange.^{1a,6}

We have developed a new procedure for determining the stereochemistry of substitution at an atomic center. The method can be carried out with an achiral compound and requires no configurational assignments, thus avoiding the difficulties of resolving chiral compounds and assigning absolute configurations to starting materials and products.⁴ The process, schematically illustrated in Figure 1, has been tested with the 3-stanna-3,3-dimethylbicyclo[3.2.1]octane system **1** first prepared by Cremer and Borsub.^{7a} Similar compounds have been used for stereochemical studies at germanium,^{7b} silicon,^{7c} and phosphorus.^{7d}

Consider a situation in which the exo substituent on tin exchanges significantly faster than does the endo. For a retention mechanism, the initially formed exo product will undergo subsequent substitutions, but these will be invisible. In the limit of $k_{\text{slow}} = 0$, only the exo substituents can be exchanged. The sit-

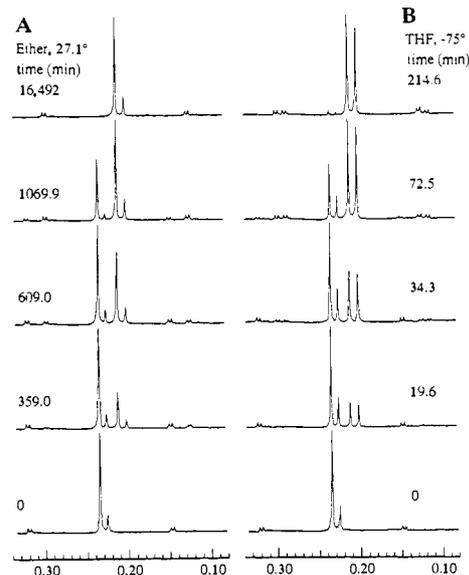


Figure 3. Sample 270-MHz ^1H NMR spectra of the Sn-methyl region of **2** and **3** during the reaction of **2** with 100 equiv of *p*-tolyllithium in ether (27.1 °C) (A) and 20 equiv of *p*-tolyllithium in THF (−75 °C) (B).

uation is quite different for an inversion mechanism. Here subsequent exchanges will result in rapid isotopic substitution of both groups even if $k_{\text{slow}} = 0$.

The results of such an experiment using methyl lithium- d_3 in ether are presented in Figure 2. For this system at 25 °C, computer simulation gave fitted values for $k_{\text{fast}}/k_{\text{slow}}$ of 12.5, so that the system is amenable to the procedure of Figure 1. The presence of a CD_3 group caused a large enough isotope shift of the geminal CH_3 group (3 ppb upfield, 1.5 Hz at 500 MHz) so that all isotopomers could be accurately analyzed by a combination of ^1H and ^2H NMR spectroscopy. The tentative configurational assignments for the isotopomers in Figure 2 are based on NMR studies on **1** and related compounds ($^3J_{\text{CH}}$ and $^3J_{\text{CC}}$). However, the conclusions are independent of such assignments. The points in Figure 2 are experimental values; the lines are best fit calculated values for a retention mechanism.⁸ For a similar simulation using an inversion process, the calculated lines did not even resemble the experimental ones (for example, in Figure 2, the dotted line is the best fit for the appearance of $\text{R}_2\text{Sn}(\text{CD}_3)_2$). We conclude that the substitution proceeds with high retention of configuration in ether.

Although the above experiment unambiguously demonstrates that the Li/Sn exchange of compound **1** in ether proceeds with retention, it has two shortcomings. First, the experiment is inherently incapable of detecting small amounts of an inversion process (these are hidden by the k_{slow} process). Second, the tin is part of a six-membered ring, and it is well established that the stereochemistry of substitution at second row atoms (P, Si) is strongly perturbed in favor of retention pathways when the atom is part of a small ring.⁹ We have, therefore, examined an acyclic tin compound (**2**).

The two diastereomers of **2** and several other related compounds proved inseparable by all techniques tried, but we were able to produce enriched samples by taking advantage of the slightly faster reaction rate (1.2 \times) of one isomer with *p*-tolyllithium in ether to produce **3** (kinetic enrichment). At 95% conversion, the un-

(8) See supplementary material.

(9) (a) For substitution at phosphorus, a preference for retention is seen in five-membered and smaller rings, but usually six-membered rings give inversion: Marsi, K. L. *J. Org. Chem.* **1975**, *40*, 1779. We feared that the longer bonds to tin might result in a strained C–Sn–C bond angle and thus preferential retention, even for the six-membered ring of **1**. (b) Roark, D. N.; Sommer, L. H. *J. Am. Chem. Soc.* **1973**, *95*, 969. McKinnie, B. G.; Bhacca, N. S.; Cartledge, F. K.; Fayssoux, J. *J. Org. Chem.* **1976**, *41*, 1534. Theory: Anh, N. T.; Minot, C. *J. Am. Chem. Soc.* **1980**, *102*, 103. Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686. Review: Gallagher, M. J.; Jenkins, I. D. *Top. Stereochem.* **1968**, *3*, 70.

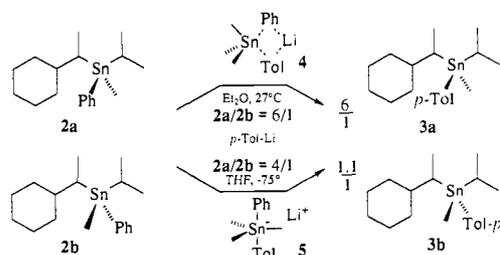
(4) (a) Gielen, M.; Vanden Eynde, I. *J. Organomet. Chem.* **1981**, *218*, 315. Gielen, M. *Top. Curr. Chem.* **1982**, *104*, 57. Gielen, M.; Mokhtar-Jamai, H. I. *Bull. Soc. Chim. Belg.* **1975**, *84*, 197. Vanden Eynde, I.; Gielen, M.; Stühler, G.; Mannschreck, A. *Polyhedron* **1982**, *1*, 1. (b) Configurational equilibration at tin in triorganohalostannanes has been detected by NMR coalescence. Peddle, G. J. D.; Redl, G. *J. Am. Chem. Soc.* **1970**, *92*, 365. Stynes, D. V.; Allred, A. L. *J. Am. Chem. Soc.* **1971**, *93*, 2666.

(5) The stereochemistry of substitution at phosphorus in an Li/P exchange was inversion: Kyba, E. P. *J. Am. Chem. Soc.* **1976**, *98*, 4805. Nucleophilic attack at bromine occurs from the back side: Beak, P.; Allen, D. J.; Lee, W. K. *J. Am. Chem. Soc.* **1990**, *112*, 1629.

(6) Seyferth, D.; Weiner, M. A.; Vaughan, L. G.; Raab, G.; Welch, D. E.; Cohen, H. M.; Alleston, D. L. *Bull. Soc. Chim. Fr.* **1963**, 1364.

(7) (a) Borsub, L. Ph.D. Dissertation, Marquette University, Milwaukee, WI, 1984. (b) Sommese, A. G.; Cremer, S. E.; Campbell, J. A.; Thompson, M. R. *Organometallics* **1990**, *9*, 1784. (c) Shen, Q.; Hilderbrandt, R. L.; Blankenship, C. S.; Cremer, S. E. *J. Organomet. Chem.* **1981**, *214*, 155. Haque, M.; Horne, W.; Cremer, S. E.; Blankenship, C. S. *J. Chem. Soc., Perkin Trans. 2* **1983**, 395. Cremer, S. E.; Blankenship, C. S. *Organometallics* **1986**, *5*, 1329. (d) Haque, N.; Horne, W.; Cremer, S. E.; Kremer, P. W.; Most, J. T. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1467.

reacted phenyl compounds were present in a 6:1 ratio. The tolyl products were separated from the mixture, and the phenyl compounds **2a** and **2b**¹⁰ were used for the stereochemical experiment in ether shown in Figure 3A. The 6:1 ratio of phenyl diastereomers



2 produced an almost identical ratio of tolyl diastereomers **3**. Although it is entirely reasonable that the sequence of NMR Sn-methyl signals is the same for phenyl and *p*-tolyl compounds (i.e., that the upfield methyl signal in each compound corresponds to the same diastereomer), the experiment itself proves that this is the case: the reaction must be going with very high retention of configuration to avoid isomer equilibration after each molecule has undergone numerous degenerate (tolyl–tolyl) exchanges. In fact, computer simulation of the data in Figure 3A shows that the reaction must proceed with greater than 99.7% retention (less than 0.3% inversion) to result in loss of less than 2% isomeric purity after 20 half-lives.¹¹ These data support a four-center intermediate (or transition state) **4** for this reaction. If **4** is an intermediate, no pseudorotations which place the SnClLiC four-membered ring spanning two equatorial positions of the trigonal bipyramidal structure can be traversed during its lifetime.¹²

An analogous experiment was carried out in THF, using a 4:1 mixture of the diastereomers of **2** (Figure 3B). The product appears as a 1:1.05 to 1:1.5 mixture throughout the experiment. Therefore, unlike the ether experiment, the THF reaction has occurred with epimerization of configuration at tin, which suggests that a pseudorotating pentacoordinate stannate complex (**5**)^{1a} is a likely intermediate. Furthermore, the tin configuration of the starting material is equilibrated at the rate predicted, assuming that the intermediate complex **5** returns to starting material with loss of configuration 26% of the time it is formed and produces stereochemically equilibrated tolyl product the rest of the time.¹⁴

Summary. We have shown that in ether the Li/Sn exchange of SnMe by methyl lithium in a tetraalkylstannane and SnPh by *p*-tolyl lithium in an aryltrialkylstannane proceeds with high retention of configuration, indicative of a tightly bound four-center transition state or intermediate (**4**). In THF a long-lived ate-complex intermediate (**5**) that can fully equilibrate isomers by multiple pseudorotations is probably involved.¹⁵

Acknowledgment. We thank the National Science Foundation for financial support of this work and Professor S. Cramer (Marquette University) for making unpublished information on

the synthesis of the [3.2.1]bicyclic silanes and stannanes available to us.

Supplementary Material Available: Listings of kinetic data, simulation equations, and plots of experimental and simulated percent composition for the lithium–tin exchange reactions of **1** and **2** (8 pages). Ordering information is given on any current masthead page.

Carbon Dioxide Complexes via Aerobic Oxidation of Transition Metal Carbonyls

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Received February 10, 1992

The oxidation of carbon monoxide by molecular oxygen over heterogeneous transition metal catalysts provides the basis for the operation of environmentally protective automobile and incinerator pollution control devices.^{1,2} Although a few homogeneous systems for catalytic oxidation of CO also have been reported,³ these have received little mechanistic attention.⁴ Carbon dioxide–metal complexes have been suggested as possible intermediates in these transition metal mediated oxidations of CO,^{2,4a,f,g} but heretofore, this hypothesis lacked direct experimental support. We report herein the first-time isolation of carbon dioxide complexes from the reaction of transition metal carbonyls with molecular oxygen.⁵

Admission of air or dioxygen into a green toluene solution of (η^5 -C₅H₄CH₃)₂Nb(CO)CH₂Ph (**1a**, 20 °C) results within minutes in decolorization accompanied by disappearance of the carbonyl absorption of **1a** at 1892 cm⁻¹ and the appearance of a new intense band at 1738 cm⁻¹ associated with **2a**. Solvent evaporation and recrystallization (hexane/toluene) provided nearly colorless crystals of the CO₂ complex (η^5 -C₅H₄CH₃)₂Nb(η^2 -CO₂)CH₂Ph (**2a**, 90%), whose structure was suggested by spectroscopic analysis⁸ and confirmed by X-ray crystallography (Figure 1).^{9,10}

(1) Kirk-Othmer Concise Encyclopedia of Chemical Technology; Wiley and Sons: New York, 1985; pp 442–5.

(2) Bielanski, A.; Haber, J. *Oxygen in Catalysis*; Marcel Dekker: New York, 1991; Chapter 6, pp 211–276. Engel, T.; Ertl, G. *Adv. Catal.* **1979**, *28*, 1.

(3) Mercer, G. D.; Shu, J. S.; Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 1967. Mercer, G. D.; Beaulieu, W. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 6551. Kiji, J.; Furukawa, J. *Chem. Commun.* **1970**, 977. Hayward, P. J.; Blake, D. M.; Wilkinson, G.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5873.

(4) For stoichiometric model reaction studies, see: (a) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235. (b) Atwood, J. D.; Lawson, H. J. *J. Am. Chem. Soc.* **1989**, *111*, 6223 and references therein. (c) Curtis, M. D.; Han, K. R. *Inorg. Chem.* **1985**, *24*, 378. (d) Kubota, M.; Rosenberg, F. S.; Sailor, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 4558. (e) Roundhill, D. M.; Allen, G. H.; Bechtold, R. A.; Beaulieu, W. B. *Inorg. Chim. Acta* **1981**, *54*, L99. (f) Huber, H.; McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 975. (g) Zecchina, A.; Spoto, G.; Coluccia, S.; Guglielminotti, E. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1975.

(5) An early claim⁶ of the formation of a rhodium–carbon dioxide complex by reaction of Rh₂(CO)₄(PPh₃)₄ with oxygen, based solely on infrared spectroscopy, was later reformulated as a bicarbonate complex.⁷

(6) Iwashita, Y.; Hayata, A. *J. Am. Chem. Soc.* **1969**, *91*, 2525.

(7) Flynn, B. R.; Vaska, L. *J. Am. Chem. Soc.* **1973**, *95*, 5081.

(8) The (η^5 -C₅H₄CH₃)₂Nb(CO)R complexes **1a–d** were prepared by Na/Hg reduction of (η^5 -C₅H₄CH₃)₂NbRCl (THF/20 °C) under a CO atmosphere. Spectroscopic data for **1a–d** and **2a,c,d** are given in the supplementary material.

(9) X-ray data for **2a** (data collected at –110 °C): C₂₀H₂₁NbO₂, *M*_r = 386.3; space group P1; *a* = 6.938 (2) Å, *b* = 10.234 (4) Å, *c* = 12.227 (5) Å, α = 94.46 (3)°, β = 92.80 (3)°, γ = 109.60 (3)°, *V* = 812.8 Å³, *Z* = 2, *D*_c = 1.578 g cm⁻³; *F*(000) = 396, λ (Mo K α) = 0.71069 Å, μ (Mo K α) = 6.8 cm⁻¹. Cell dimensions and intensities of 3338 reflections ($2\theta_{\max}$ = 53°) were measured. The structure was solved by the heavy atom method. All of the hydrogen atoms were located and refined isotropically; ρ_{\max} in final difference map = 0.39 e Å⁻³. For 2300 unique observed reflections [*I* > 2 σ (*I*)], final *R* = 0.030, *R*_w = 0.033, GOF = 1.1.

(10) The structural characteristics of **2a** are comparable to those of (η^5 -C₅H₄CH₃)₂Nb(η^2 -CO₂)CH₂Si(CH₃)₃ [**2b**, ref 11] except for the longer Nb–CH₂R bond of **2a** [2.337 (4) vs 2.282 (11) Å for **2b**].

(10) We have not attempted to determine the relative configurations of **2** or **3**.

(11) The simulation was done assuming that the degenerate tolyltin–tolyl lithium exchange rate (which we have not measured) was the same as the known phenyltin–tolyl lithium exchange rate.

(12) The kinetic order in *p*-tolyl lithium for the conversion of **2** to **3** in ether is 0.34. Phenyllithium is a mixture of dimer and tetramer in ether at –105 °C.^{14,2} If tolyllithium at 27 °C has a similar degree of aggregation, then the order is close to that expected if the kinetically active species is the monomer.

(13) Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. J. *J. Phys. Chem.* **1969**, *73*, 1624. Fraenkel, G.; Hsu, H.; Su, B. M. *Lithium: Current Applications in Science, Medicine and Technology*; Bach, R. O., Ed.; John Wiley & Sons, Inc.: New York, 1985; Chapter 19. Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1984**, *106*, 4627. Wehman, E.; Jastrzebski, J. T. B. H.; Ernsting, J.-M.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1988**, *353*, 133.

(14) At equilibrium the ratio of phenyllithium and tolyllithium is 65:35 in THF at –78 °C (PhSnEt₃ + TolLi = TolSnEt₃ + PhLi). It is reasonable that the ate-complex **5** collapses to the two aryllithium reagents in a similar ratio.

(15) We have previously shown that such ate-complex intermediates can be spectroscopically characterized in THF (for triarylstannanes) and THF/HMPA mixtures (for less highly arylated stannanes).^{1a}