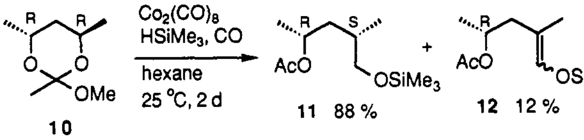
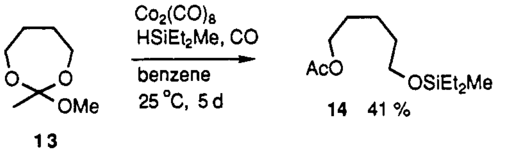
was added with use of a pressure syringe.[7] After 5 min, C_6H_6 (5 mL) and **1c** (2.5 mmol, 435 mg) were added and the mixture was stirred at 25 °C for 3 days under CO (1 atm). Analysis of the reaction mixture by GC showed it to contain a 94:6 mixture of **2c**[8] and **3c** in 72% yield. An analytical sample was obtained by Kugelrohr distillation followed by preparative GC (silicone OV-1). As mentioned above, the reaction of **1a** with $HSiEt_2Me$ and CO gave 1,3-propanediol derivative **2a** in high yield. A plausible reaction mechanism is shown in Scheme I.[9] Silylcobalt complex **4**[10] would be a key catalyst. Interaction of **4** with **1a** would give the alkylcobalt complex **6**, which is essential for CO insertion, via the silyloxonium ion **5**. The oxidative addition of $HSiR_3$, reductive elimination, and successive hydrosilylation give product **2a**. It is worthy of note that an orthoformate, an analogue of orthoacetate **1** but without the 2-methyl group, did not react at all. This suggests the importance of stabilizing the partial positive charge developing in **5**. In the case of substituted cyclic ortho esters such as **1b–e**, highly regioselective ring opening at the primary carbon center leading to **2** was observed. Reversed selectivity was obtained for the reaction of 2-methyl-2-methoxy-4-phenyl-1,3-dioxolane (**1f**).

Six-membered cyclic ortho esters **7** also reacted with a hydrosilane and carbon monoxide to afford the corresponding 1,4-diol derivatives **8** and **9** with high regioselectivities in fair to high yields, as shown in Table II.[6] The stereochemistry of the siloxymethylation process was examined by the use of (4*R*,6*R*)-2-methoxy-2,4,6-trimethyl-1,3-dioxolane (**10**), which was prepared from optically active (2*R*,4*R*)-2,4-pentanediol. The step of nucleophilic attack of $Co(CO)_4^-$ at **5** must be a stereodetermining step because CO insertion and subsequent processes occur with retention of configuration (see Scheme I). When **10** was subjected to the $Co_2(CO)_8$-catalyzed reaction with $HSiMe_3$ and CO, **11**[11] was obtained in 88% yield along with **12** in 12% yield (eq 2). It can be concluded that siloxymethylation occurred with inversion of configuration.[12]



(2)



(3)

The present reaction is also applicable to the seven-membered ortho ester **13**, providing 1,5-diol derivative **14** in 41% yield (eq 3).

In summary, the overall transformation is a novel siloxymethylative ring opening of cyclic ortho esters and provides a new method for homologation of 1,2-, 1,3-, and 1,4-diols to diols one carbon higher that are protected differently.

Acknowledgment. Partial support by grants from the Ministry of Education, Science, and Culture of Japan and encouragement by Professor Noboru Sonoda are greatly acknowledged.

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(7) We have designed a special apparatus for the handling of $HSiMe_3$, which has a low boiling point.[1b]

(8) **2c**: ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H, $SiCH_3$), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3), 1.22–1.37 (m, 4 H, CH_2), 1.51–1.56 (m, 2 H, CH_2), 1.77 (q, *J* = 6.8 Hz, CH_2), 2.02 (s, 3 H, CH_3CO), 3.60 (t, *J* = 6.8 Hz, 2 H, CH_2O), 4.97 (quint, *J* = 6.8 Hz, CHO); ^{13}C NMR ($CDCl_3$) δ –0.64, 13.93, 21.18, 22.54, 27.30, 34.05, 37.01, 59.02, 71.76, 170.67; IR (neat) 1743 cm^{-1} (C=O); MS *m/e* 246 (M^+, 0), 171 (8), 129 (14), 117 (100), 75 (48), 73 (47). Anal. Calcd for $C_{12}H_{26}O_3Si$: C, 58.49; H, 10.64. Found: C, 58.06; H, 10.66.

(9) For a detailed discussion on the mechanism of the $Co_2(CO)_8$-catalyzed reaction of epoxides with a hydrosilane and CO, see ref 1b.

(10) The reaction of $Co_2(CO)_8$ with $HSiR_3$ has been known to give $R_3SiCo(CO)_4$: Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. Baay, Y. L.; MacDiarmid, A. *Inorg. Chem.* **1969**, *8*, 986. Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 1019.

(11) The reaction of racemic **10** with $HSiMe_3$ and CO gave a 1:1 mixture of diastereoisomers, *R*S** and *R*R** isomers; these are easily separable by GLC. On the other hand, the chiral ortho ester **10** gave a single isomer that has the same retention time in GLC as the *R*S** isomer does. Furthermore, a carbon at which an acetoxy group attached in **11** is not a stereogenic center; therefore, **11** is the *RS* isomer. **11**: $[\alpha]_D^{19}$ = 11.7° (*c* = 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H, $SiCH_3$), 0.88 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.21 (d, *J* = 6.1 Hz, 3 H, CH_3), 1.58–1.72 (m, 3 H, CH_2, CH), 2.01 (s, 3 H, CH_3CO), 3.30–3.43 (m, 2 H, CH_2O), 4.99–5.06 (m, 1 H, CHO); IR (neat) 1742 cm^{-1} (C=O); MS *m/e* 232 (M^+, 0), 130 (43), 117 (89), 103 (47), 83 (66), 73 (100). Anal. Calcd for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41. Found: C, 56.80; H, 10.45.

(12) For **1f**, the reversed regiochemistry (Table I) suggests that a different mechanism (S_N1 type) is operating.

Synthesis and Structure of a Monomeric Diarylstannylene

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Summary: The novel diarylstannylene bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene **1** is synthesized conventionally from [2,4,6-(trifluoromethyl)phenyl]lithium and tin(II) chloride. It is a monomer in the solid state, as shown by an X-ray analysis, and is stabilized by intramolecular fluorine–tin contacts, which NMR data indicate also exist in solution. Compound **1** ($C_{18}H_4F_{18}Sn$) crystallizes in the monoclinic space group $P2_1/a$ (Z = 4) with a = 11.915 (6) Å, b = 13.801 (7) Å c = 12.961 (7) Å, β = 93.56 (4)°, and V = 2172.2 Å^3.

The existence of monomeric diarylstannylenes has been debated for a long time.[1] However, in the solid state these are polymeric with one exception. In 1981, Zuckerman et al. reported the synthesis of bis[2,6-bis(trifluoromethyl)phenyl]stannylene and postulated it to be monomeric on the basis of Mössbauer spectroscopy.[2] To date, no stannylene that is monomeric in the solid state and forms only σ bonds between the dicoordinated tin atom and carbon

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[†] Universität Heidelberg.

[‡] Universität Göttingen.

(1) Reviews: (a) Neumann, W. P. *Nachr. Chem., Tech. Lab.* **1982**, *30*, 190. (b) Connolly, J. W.; Hoff, C. *Adv. Organomet. Chem.* **1981**, *19*, 123. (c) Veith, M.; Recktenwald, O. *Top. Curr. Chem.* **1982**, *104*, 1.

(2) Bigwood, M. P.; Corvan, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643.

atoms has been structurally characterized.[3]

The 2,6-bis(trifluoromethyl)phenyl and 2,4,6-tris(trifluoromethyl)phenyl ligands permit the synthesis of surprisingly stable diphosphenes[4] and dimeric indium and thallium phenoxides,[5] which show unusual dicoordination at the metal atom. Sterically, the trifluoromethyl group probably lies between the methyl and the isopropyl group.[6] However, the mesityl ligand (the corresponding carbon–hydrogen analogue to the 2,4,6-tris(trifluoromethyl)phenyl group) does not allow the preparation of diphosphenes, nor does it prevent the polymerization of stannylenes. Even the 2,4,6-triisopropylphenyl ligand does not sufficiently hinder oligomerization, and a cyclotristannane is observed in the solid state.[7] Hence, a first explanation for the protection of the Lewis-acidic low-valent phosphorus or tin atoms might be the electrostatic repulsion by the high electron density of the trifluoromethyl groups (25 valence electrons in CF_3 compared to 7 in CH_3).[8] Here we describe the synthesis and solid-state structure of bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene (**1**), in which some interesting properties of the partially fluorinated ligand are revealed.

The synthesis of **1** proceeds in about 45% yield, when [2,4,6-tris(trifluoromethyl)phenyl]lithium is reacted with tin dichloride in diethyl ether at 0 °C. The compound is obtained as air- and moisture-sensitive yellow crystals[9] after recrystallization from *n*-hexane at −78 °C. The resonance in the ^{119}Sn NMR spectrum recorded in cyclohexane-d_{12} is split into 13 lines (9 of which can be observed) by coupling with the fluorine atoms of the trifluoromethyl groups in ortho positions ($J(^{119}SnF)$ = 239.5 Hz). Centered at 723 ppm (Me_4Sn as standard), it falls within the range of the distannene $\{[(Me_3Si)_2CH]_2Sn]\}_2$ (**2**; 725, 740 ppm, toluene[10]) and the monomeric amino-substituted stannylenes $[(Me_3Si)_2N]_2Sn$ (**3**; 787 ppm, cyclohexane-d_{12}) and $Me_2Si(^tBuN)_2Sn$ (**4**; 684 ppm, cyclohexane-d_{12}). The chemical shift of **1** in toluene (678 ppm) is almost temperature-independent. However, in diethyl ether-d_{10} the room-temperature signal at 660.8 ppm is shifted about 130 ppm upfield at −80 °C to 530.0 ppm.[11] These results are in line with a complexation of a monomeric stannylene in solution by ether molecules, rather than a monomer–dimer equilibrium.

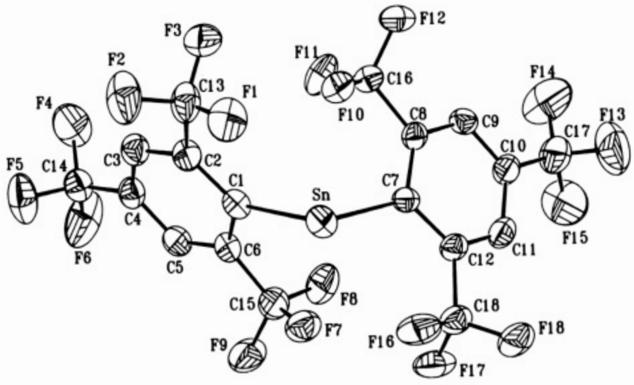

Figure 1. Molecular structure of **1** in the crystal form. Important bond lengths (Å) and angles (deg): C1–Sn = 2.278 (5), C2–Sn = 2.284 (5), F1–Sn = 2.807 (4), F7–Sn = 2.681 (4), F10–Sn = 2.663 (4), F16–Sn = 2.833 (4); C7–Sn–C1 = 98.3 (1).

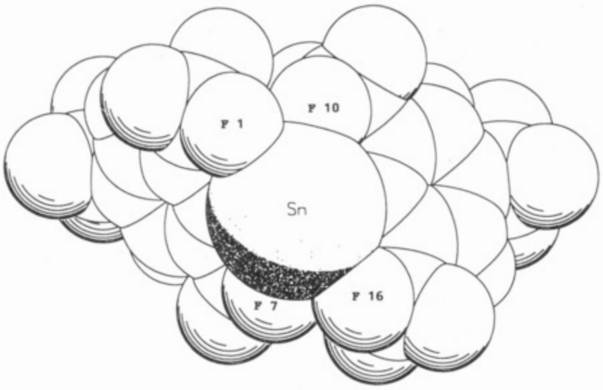

Figure 2. Space-filling model (Schakal plot[19]) of **1**.

Additionally, we have examined the temperature dependence of the ^{19}F NMR spectra of **1** in diethyl ether and toluene in the temperature range of −90 to +30 °C. No effect is observed in diethyl ether. On the other hand, in toluene, temperature-dependent couplings of the ^{19}F nuclei with ^{119}Sn and ^{117}Sn nuclei are detected. These couplings, 239.5 Hz (^{19}F–^{119}Sn) and 228.5 Hz (^{19}F–^{117}Sn), respectively, linearly increase about 1.4 Hz every 10 °C when the sample is cooled to −90 °C.

The above indication of fluorine–tin contacts was confirmed by an X-ray crystal structure determination. A suitable single crystal of **1** could be obtained from a concentrated cyclohexane solution at 10 °C. The result is shown in Figure 1 along with the atom-labeling scheme.[12] The diarylstannylene is a monomer in the solid state, and the shortest tin–tin contact is 6.31 Å. The carbon–tin bond length of 2.28 Å in **1** and the C7–Sn–C1 angle of 98.3° can be compared with the gas-phase structural data for the monomeric dialkylstannylene $[(Me_3Si)_2CH]_2Sn$ (**5**)[13] (Sn–C = 2.22 (2) Å; C–Sn–C = 97 (2)°) and the equilibrium structural parameters for Me_2Sn obtained by ab initio calculations[14] (Sn–C = 2.20 Å; C–Sn–C = 96°). Interest-

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[3] Compounds with additional intramolecular interactions to amino groups have been described: Angermund, K.; Jonas, K.; Krüger, C.; Latten, J. L.; Tsay, Yi-Hung. *J. Organomet. Chem.* **1988**, *353*, 17. Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 336.

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[5] Scholz, M.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem.* **1989**, *101*, 1419; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1383. Roesky, H. W.; Scholz, M.; Noltemeyer, M.; Edelmann, F. T. *Inorg. Chem.* **1989**, *28*, 3829.

[6] This assumption is based on an estimate of the corresponding van der Waals volumes: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[7] Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

[8] Grützmacher, H.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *Z. Naturforsch.* **1987**, *42B*, 1245.

[9] Physical and spectroscopic data for **1**: mp 73 °C; ^{19}F NMR (cyclohexane-d_{12}) δ −58.66 [s, 6 F, $J(^{119}SnF)$ = 239.5 Hz, $J(^{117}SnF)$ = 228.5 Hz), *o*-CF_3], −67.7 (s, 3 F, *p*-CF_3); ^1H NMR (cyclohexane-d_{12}) δ 7.985 (s, 2 H, aromat H); ^{13}C NMR (cyclohexane-d_{12}) δ 123.83 [q, $^1J(CF)$ = 306.9 Hz, *p*-CF_3], 126.88 [s, (broad), 3,5-CH], 127.96 [q, $^1J(CF)$ = 276.3 Hz, *o*-CF_3], 133.06 [q, $^2J(CF)$ = 34.0 Hz, 2,6-C], 138.12 [q, $^2J(CF)$ = 33.5 Hz, 4-C], 179.73 (s, 1-C); UV/vis (toluene): λ = 345 nm, ϵ = 1534 L mol^{-1} cm^{-1}; MS (EI, 70 eV) *m/z* 682 [M(^{118}Sn), 15%], 663 (M−F, 8), 401 (M−R_F, 100); MS (FI, 6 kV) *m/z* 682 [M(^{118}Sn), 100%], correct isotope distribution. Anal. Calcd for $C_{18}H_4F_{18}Sn$: C, 31.75; H, 0.59; F, 50.22; Sn, 17.43. Found: C, 31.22; H, 0.61; F, 50.41.

[10] Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. G. *J. Am. Chem. Soc.* **1987**, *109*, 7236. The authors suspect different isomers. Masamune et al. report a chemical shift for tetrakis(2,4,6-triisopropylphenyl)distannene of 427 ppm.[7]

[11] We thank Dipl.-Chem. A. Mix, Universität Bielefeld, for recording these ^{119}Sn spectra.

[12] X-ray structure determination of **1**: space group $P2_1/a$, a = 11.915 (6) Å, b = 13.801 (7) Å c = 12.961 (7) Å, β = 93.56 (4)°, V = 2172.2 Å^3, Z = 4. A total of 5283 reflections were collected on a four-circle diffractometer (Mo Kα, λ = 0.7107 Å, ω scan, $2\theta_{max}$ = 56°); 2841 of these with $I > 2\sigma_I$ were used in the refinement. R = 0.049, R_w = 0.052 (Sn, F, C refined anisotropically, H refined isotropically, 350 variables).

[13] Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

[14] Bleckmann, P.; Maly, H.; Minkwitz, R.; Neumann, W. P.; Watta, B.; Olbrich, G. *Tetrahedron Lett.* **1982**, *23*, 4655.

ingly, the C–Sn–C angles lie within a quite narrow range, while the carbon–tin bonds are elongated by 0.08 Å when the substituent is changed from methyl to 2,4,6-tris(trifluoromethyl)phenyl. Note that in the latter ligand an sp^2-hybridized carbon is attached to tin and a shorter carbon–tin bond is expected. Although X-ray and gas-phase electron diffraction parameters have to be compared carefully,[15] the data above indicate that possible electrostatic ligand–ligand repulsions lead to an elongation of bonds rather than a widening of angles. Additionally, reduced electron density on the tin-bonded carbon atoms by the electron-withdrawing trifluoromethyl groups will result in increasing repulsive interactions between the electropositive tin atom and the adjacent carbon atoms[16] and elongated bonds.

Although steric protection of the low-valent tin center certainly plays an important role in its stability, a space-filling model of 1 (Figure 2) shows that the trifluoromethyl groups of the ligands form *intra*molecular fluorine–tin contacts, leaving one side of the molecule sterically unprotected. The averaged fluorine–tin bond length F7–Sn/F10–Sn is 2.67 Å; the F2–Sn/F16–Sn bond distance is longer (2.82 Å) but still considerably shorter than the sum of the van der Waals radii (F, 1.47 Å; Sn, 2.17 Å[6]). The shortest *inter*molecular fluorine–tin distance is 3.51 Å and will not significantly contribute to the stability of 1. The position of the trifluoromethyl groups is not defined by steric congestions but by maximizing fluorine–tin interactions without interligand repulsions.

The stabilizing influence of the 2,4,6-tris(trifluoromethyl)phenyl ligand is only partly due to steric shielding. Despite the *electron-withdrawing* character of the trifluoromethyl group through the σ-bond framework and negative hyperconjugation,[17] the *electron-donating* ability via the lone pairs at the fluorine atoms is clearly established and is probably the most important factor preventing oligo- or polymerization of 1.[18] Obviously, these intramolecular contacts are observed in solution as well and might be responsible for the surprising high-field shift of the ^{119}Sn NMR signal.

Acknowledgment. This work was supported by Prof. W. Sundermeyer, Prof. G. Huttner, Prof. H. W. Roesky, the Deutsche Forschungsgemeinschaft (GR 955/1-2), and the Fonds der Chemischen Industrie.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles (3 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(15) The molecular structures of $[(Me_3Si)_2N]_2Sn$ determined by X-ray and GED methods differ by 8.7° in the N–Sn–N angle (104.7 vs 96°, respectively).

(16) Oberhammer, H. *J. Fluorine Chem.* **1983**, *23*, 147.

(17) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141.

(18) Zuckerman et al. already postulated fluorine–tin contacts in the closely related bis[2,6-bis(trifluoromethyl)phenyl]stannylene.[2] Escudié et al. found short phosphorus–fluorine contacts in a diphosphene bearing this ligand.[4] A good measure of the extent of these interactions is the ratio $r(M–F_{obsd})$:r(van der Waals), which equals 0.73 in 1.

(19) Keller, E. A Program for the Graphical Presentation of Molecular Models; Kristallographisches Institut der Universität Freiburg: Freiburg, FRG, 198.

Synthesis, Structure, and Reactivity of the First Stable Diaryllead(II) Compound

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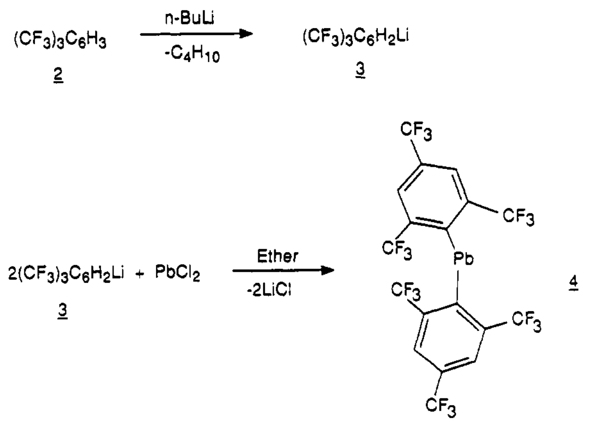
Summary: Reaction of $PbCl_2$ with $2,4,6\text{-}(CF_3)_3C_6H_2Li$ results in the formation of the first stable diaryllead(II) compound, $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Pb$ (**4**). X-ray structural analysis shows that in the solid state **4** is a bent monomer. **4** reacts with $2,4,6\text{-}(CF_3)_3C_6H_2SH$ (**5**) in hydrocarbon solutions to produce the solvent-free thiolate $[2,4,6\text{-}(CF_3)_3C_6H_2S]_2Pb$ (**6**).

Scheme I



Lead(II) compounds with σ-aryl substituents are unknown,[1] and the only authentic lead(II) alkyl is $[(Me_3Si)_2CH]_2Pb$ (1), which was obtained in minimal yield (3%) by Lappert et al. in 1976.[2] The synthesis of diphenyllead(II) was reported in 1922[3] but is not reproducible.[4] A difficulty in obtaining these compounds is their tendency to disproportionate. For example, the reaction of $PbCl_2$ with aryllithium or aryl Grignard reagents leads to organolead(IV) compounds and elemental lead.[4] Further complications result from the reactivity of these complexes as indicated by the extreme sensitivity of 1

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(1) See, for example: Elschenbroich, C.; Salzer, A. *Organometallchemie*; B. G. Teubner: Stuttgart, FRG, 1986; p 159.

(2) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

(3) Krause, E.; Reissaus, G. G. *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 888.

(4) Harrison, P. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; p 670.

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